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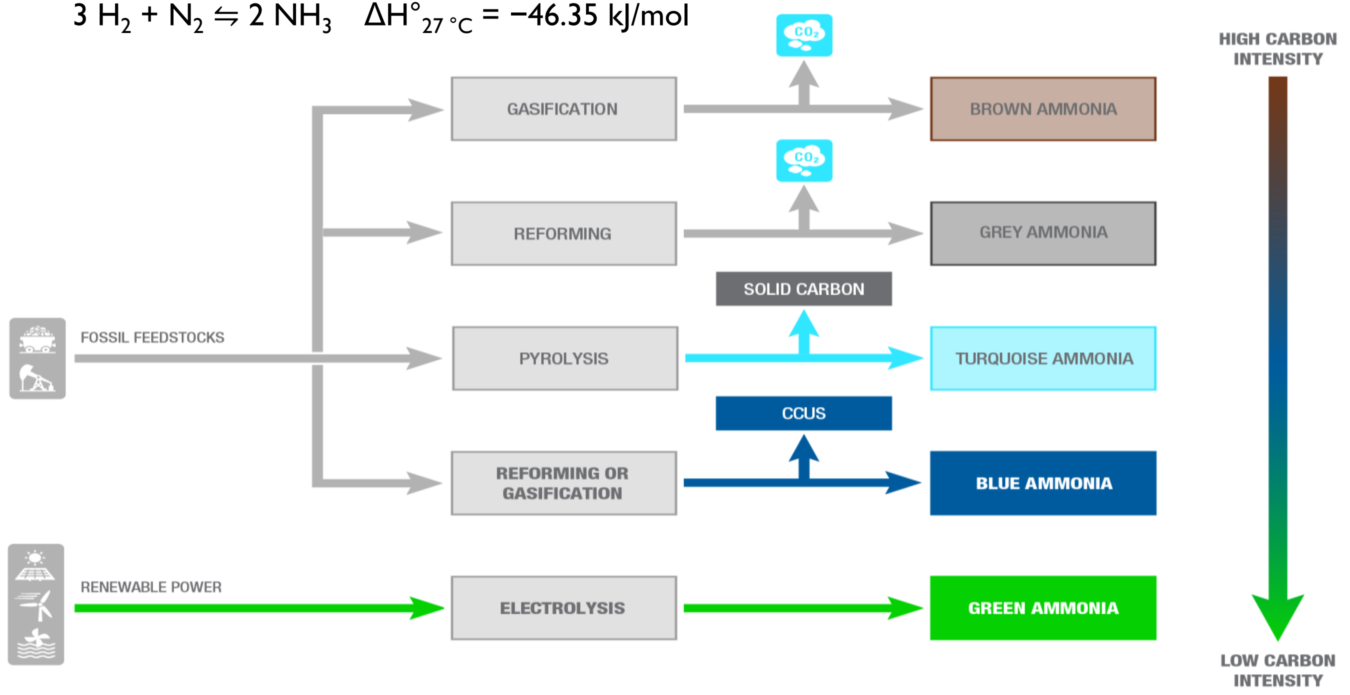
South Asia Regional Energy Partnership (SAREP)

Sizing Principle for a Typical Green Ammonia Plant

Ammonia Synthesis, Separation, and Storage

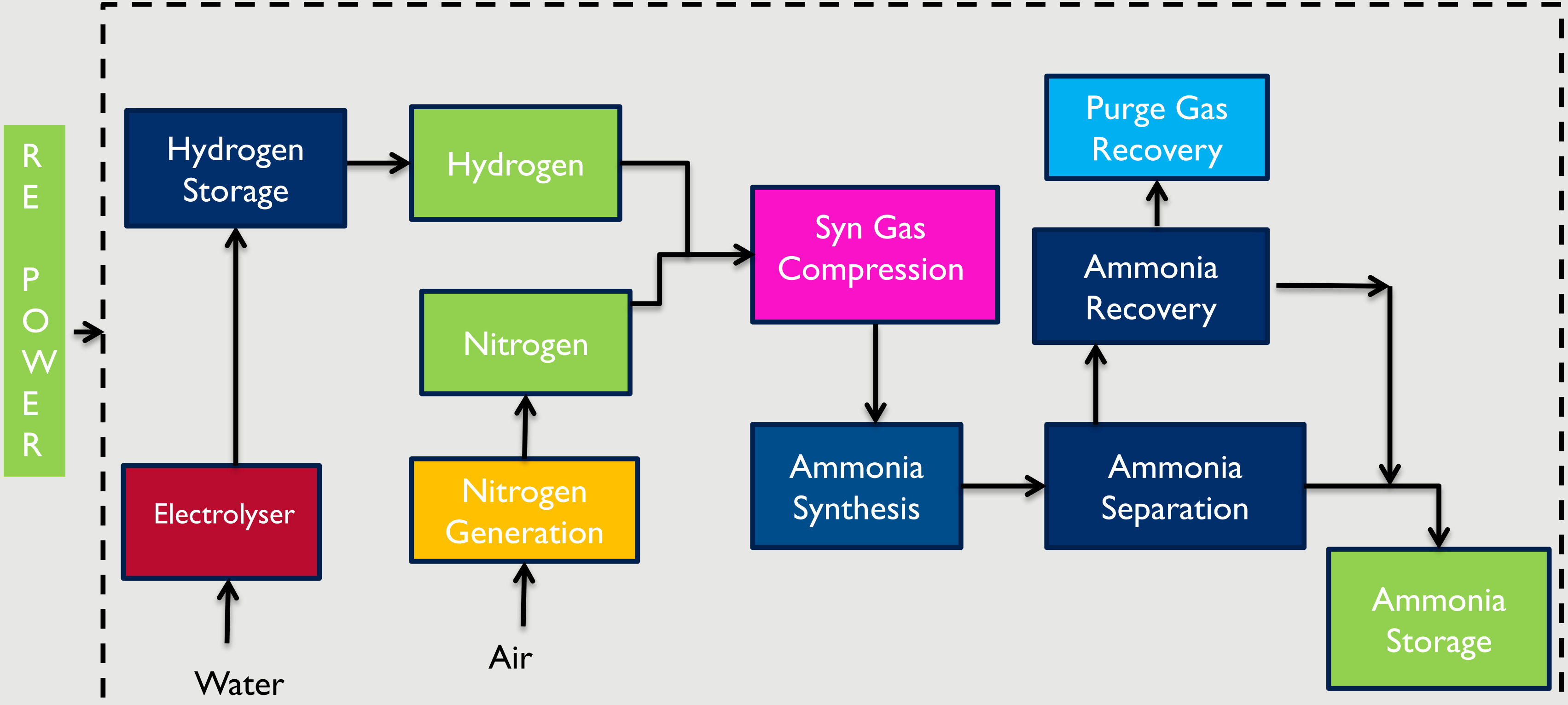
What is Green Ammonia ?

$3\ H_2 + N_2 \leftrightharpoons 2\ NH_3 \quad \Delta H^\circ_{27\,^\circ C} = -46.35\ \mathrm{kJ/mol}$



Source: CASALE

Green Ammonia Plant Configuration



Ammonia Reaction Stoichiometry

- Basic Equation

  $0.5\ N_2 + 1.5\ H_2 \leftrightharpoons 1\ NH_3 \quad \Delta H^{\circ}_{27\,^{\circ}C} = -46.35\ kJ/mol$

  $0.5 \times 28 + 1.5 \times 2 = 1 \times 17$

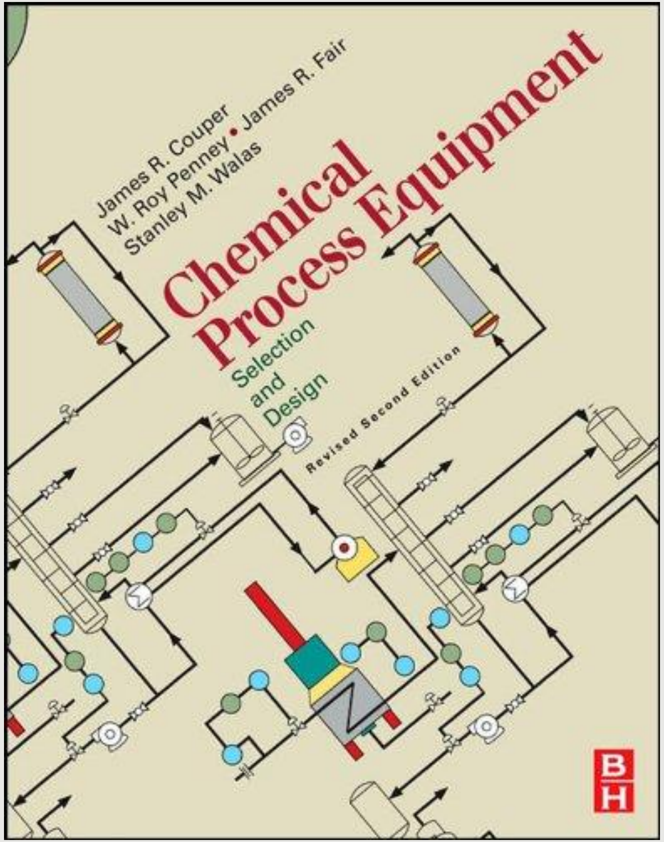
  $14 + 3 = 17$

  (Molecular weight of N_2=28, H_2=2 , NH_3=17)

  - From above , to produce say 17 kg of Ammonia, we need 14 kg of Nitrogen and 3 kg of Hydrogen on theoretical basis
  - Alternatively, to produce 1 kg of Ammonia, we need (14/17)= 0.824 kg of Nitrogen and (3/17)=0.176 kg of Hydrogen

Sizing Methodology

1. Define required Green Ammonia Plant capacity in MT/Day with capacity margin and Ammonia product specification (pressure, temperature, and purity)
2. Define Hydrogen specification (pressure, temperature, purity, flow rates – normal, minimum, and maximum) at the battery limit of Green Ammonia Plant
3. Calculate Hydrogen and Nitrogen requirement (t/d) based on the Plant capacity desired
4. Select the type of air separation process (Membrane/ PSA/Cryogenic) depending on the Nitrogen requirement and purity (minimum 99.99%)
5. Select the Ammonia synthesis loop pressure (140 to 300 bar) and type of equipment's applicable
6. Configure the flow sheet using a suitable simulation software/calculation methods by feeding in required process parameters (~~F~~low/ pressure/ temperature/ vapor fraction/ composition/ catalyst volume etc). Carry out the simulation by suitably adjusting required parameters till the required production capacity and specification is achieved after convergence.
7. Calculate Heat & Mass balance, Power and Utility consumptions
8. Carryout Major Equipment's sizing using software/ Design resources (books & literatures)
9. Based on the broad specification arrived, carryout equipment costing (vendor/ cost indices/ historical cost/ correlations etc.)
10. Arrive at the project cost including all other project components using total equipment cost and typical percentages of equipment cost for other components



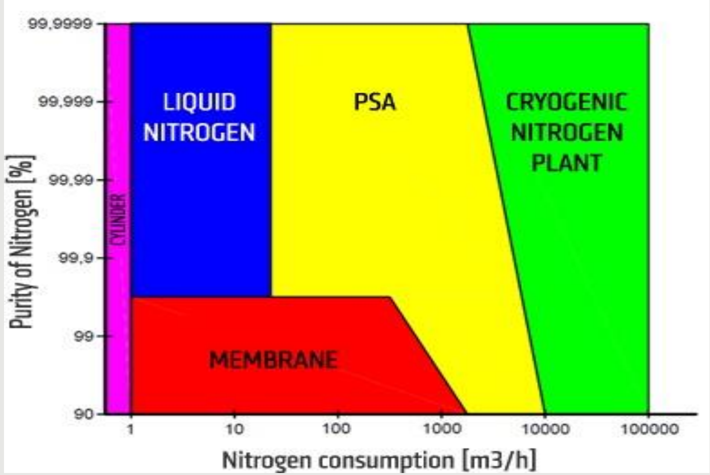
Source: Chemical Process Equipment - Selection and Design

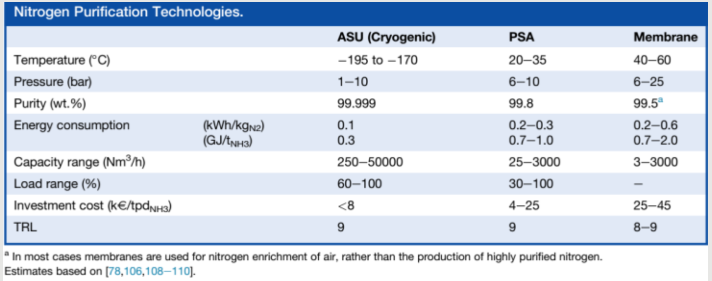
Basic Assumptions/ Thumb Rule for Green Ammonia Plant Sizing

- Hydrogen Required = 179.4 kg/t of NH_3 (minimum purity of 99.99%)
- Nitrogen required = 830.7 kg/t of NH_3 (minimum purity of 99.99%)
- Plant availability = 8000 hrs/year
- Plant Life = 25 to 30 years
- Overall conversion in syn loop = 97 to 99%
- Power required = 0.738 MW/t of NH_3(Synthesis section)
  = 0.13 to 0.38 MW/t of NH_3(Air separation)
  = 0.75 to 0.480 MW (for refrigerated Ammonia storage)
- Cooling water circulation rate = 170 to 240 m^3/t of NH_3
- Steam generation = 0.7 to 1 t/t of NH_3
- Raw water requirement = 1.62 t/t of NH_3

Source 1. M. Fasihi et al.
2. thyssenkrupp

Nitrogen Generation Options





Nitrogen Purification Technologies.

		ASU (Cryogenic)	PSA	Membrane
Temperature (°C)		−195 to −170	20–35	40–60
Pressure (bar)		1–10	6–10	6–25
Purity (wt.%)		99.999	99.8	99.5[a]
Energy consumption	(kWh/kg$_{N2}$) (GJ/t$_{NH3}$)	0.1 0.3	0.2–0.3 0.7–1.0	0.2–0.6 0.7–2.0
Capacity range (Nm^3/h)		250–50000	25–3000	3–3000
Load range (%)		60–100	30–100	–
Investment cost (k€/tpd$_{NH3}$)		<8	4–25	25–45
TRL		9	9	8–9

[a] In most cases membranes are used for nitrogen enrichment of air, rather than the production of highly purified nitrogen.
Estimates based on [78,106,108–110].

Source: omega-air

Parameter	Cryogenic	PSA	Membrane
Advantages	• Low amount of electricity per unit Nitrogen • Produces very high purity Nitrogen • Can generate liquid Nitrogen for storage on site	• Low to moderate capital cost • Cost-effective Nitrogen production of relatively high purities • Quick installation and start-up	• Low capital cost • Production output is very flexible • Quick installation and start-up • Easy to vary purity and flow rate
Disadvantages	• Large site space and utility requirements • High capital cost • Limited scalability in production • Long start-up and shutdown	• High maintenance equipment • Noisy operation • Limited scalability	• Uneconomical for high purity requirements • Uneconomical for large outputs • Requires relatively large amount of electricity per unit nitrogen

Selection aspects of Nitrogen generation Unit (PSA & CRYO)

Effects of Purity Selection on Energy Required

Generator Inlet 8.0 Bar

System Type	N_2 Purity	N_2 (m^3/min)	ANR	Air req (m^3/Min)	CCF	Min Comp m^3/Min	Compressor KW req
PSA	95%	1.5	1.94	2.91	1.15	3.34	18kw
PSA	99.50%	1.5	2.42	3.63	1.15	4.17	30kw
PSA	99.99%	1.5	4.24	6.36	1.15	7.31	45kw
PSA	100.00%	1.5	7.45	11.17	1.15	12.85	75kw

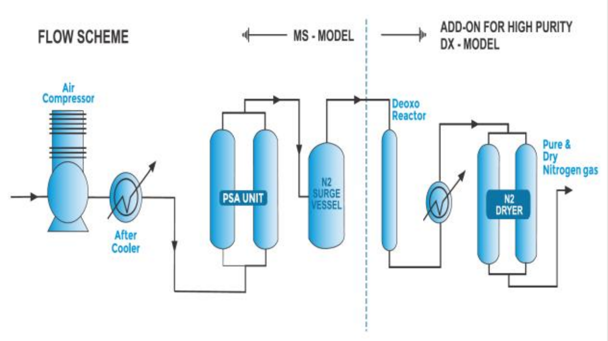
ANR= Air to Nitrogen ratio; CCF = Compressor correction factor

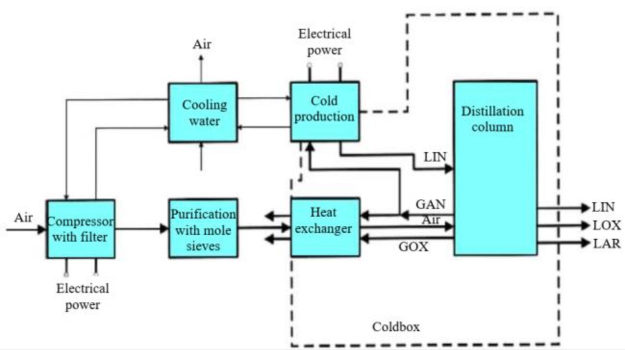
Source: oneillcompressedair.com

Cryogenic Air Separation Unit production details (N_2≥99.999)

Model	Unit	ZO-NZDN-200	ZO-NZDN-300	ZO-NZDN-400	ZO-NZDN-700	ZO-NZDN-1000	ZO-NZDN-1600	ZO-NZDN-3000
Nitrogen Production	Nm^3/h	200	300	400	700	1000	1600	3000
Liquid Nitrogen Production	L/H	/	10	10	20	40	60	150
Nitrogen Purity	$PPmO_2$	≤3	≤3	≤3	≤3	≤3	≤3	≤3
Nitrogen Pressure	Mpa.A	0.34~1	0.34~1	0.34~1	0.34~1	0.34~1	0.34~1	0.34~1
Plant Area	m^2	95	150	220	260	300	320	410

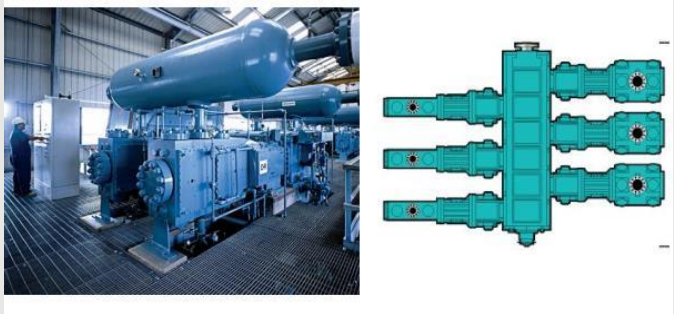
Source: z-oxygen





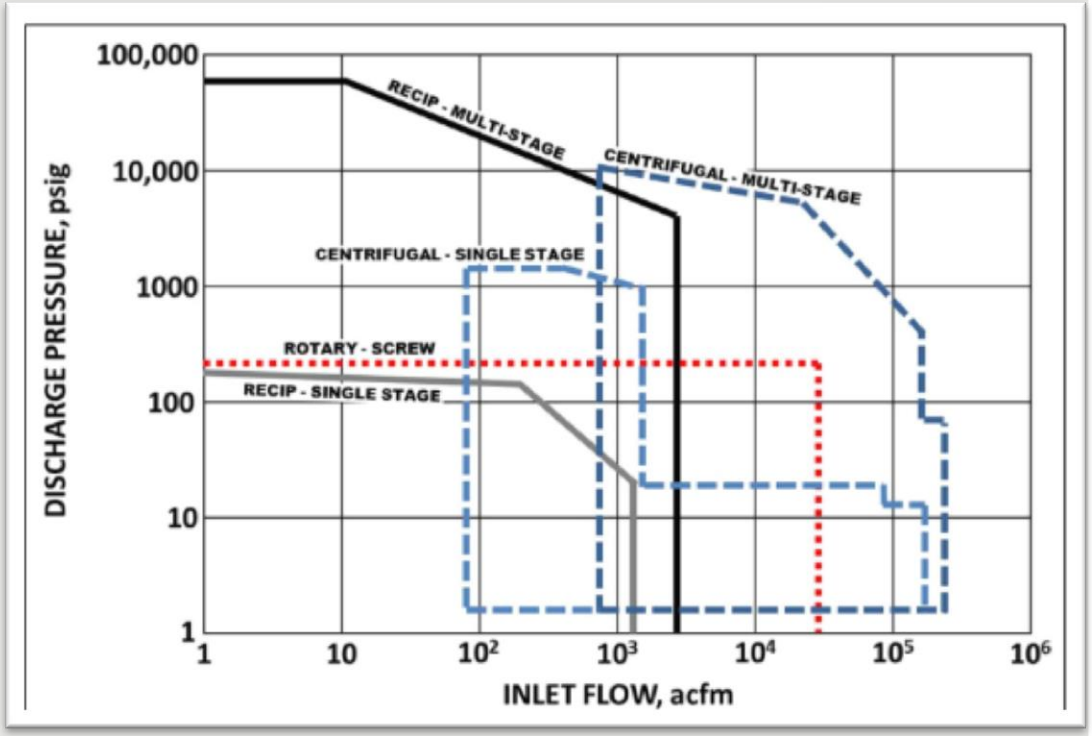
Source: mvsengg.com

Selection chart for compressor type based on discharge pressure and flow



Source: DresserRand

- Number of stages depends upon the compressor ratio R_C selected (~1.3 to 3.5)

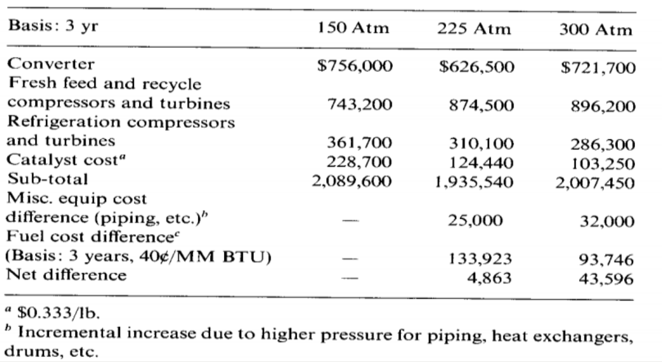


Source: Turbomachinery Laboratory, Texas A&M Engineering Experiment Station conference proceedings, 2016

Synthesis Loop pressure selection

Loop Pressure	Advantages	Disadvantage
Around 150 kg/cm2	• Lower compressor power • reduced number of stages, • lower vessel and pipe/accessories thickness	• Almost double the catalyst volume(for pressure 150 vs 220)- higher catalyst cost and inventory • Bigger equipment sizes • High refrigeration loads • Lower conversion per pass • Higher recycle load
Around 200 kg/cm2	• Higher conversion per pass • Reduced catalyst volume • Reduced refrigeration load • Reduced vessel sizes • Reduced recycle load	• More stages of compressor and operating cost • Higher thickness of pipes and vessels

Cost Impact analysis of Loop pressure



Basis: 3 yr	150 Atm	225 Atm	300 Atm
Converter	$756,000	$626,500	$721,700
Fresh feed and recycle compressors and turbines	743,200	874,500	896,200
Refrigeration compressors and turbines	361,700	310,100	286,300
Catalyst cost[a]	228,700	124,440	103,250
Sub-total	2,089,600	1,935,540	2,007,450
Misc. equip cost difference (piping, etc.)[b]	—	25,000	32,000
Fuel cost difference[c] (Basis: 3 years, 40¢/MM BTU)	—	133,923	93,746
Net difference	—	4,863	43,596

[a] $0.333/lb.

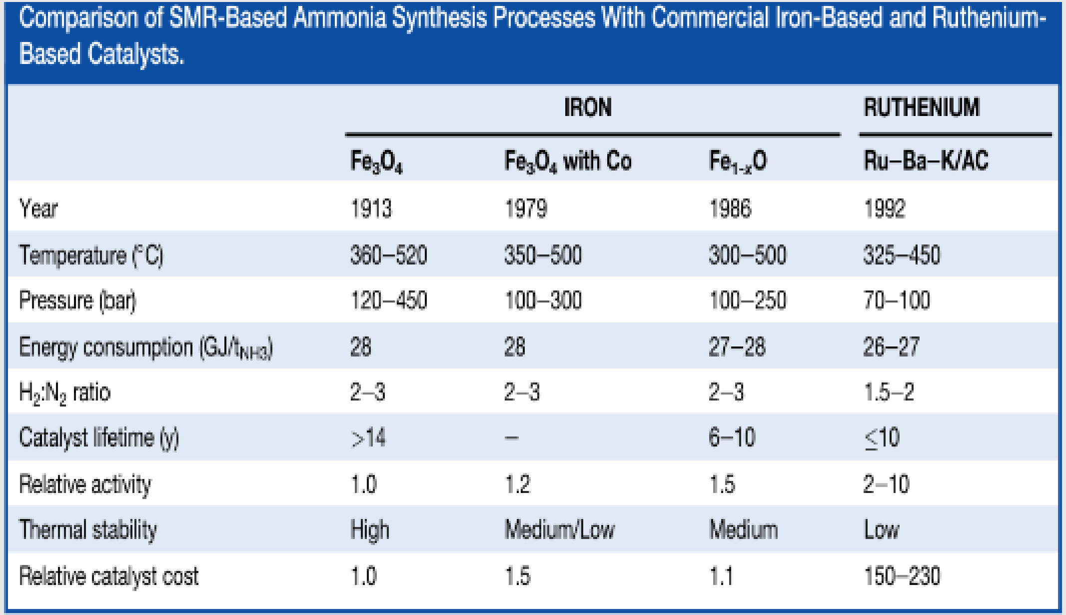
[b] Incremental increase due to higher pressure for piping, heat exchangers, drums, etc.

Source: Chemical Reactor Design for Process Plants

- Higher synthesis loop pressure (say 300 bar) may be preferred for plant capacity upto 100 tpd (mostly) modular, to take advantage of higher conversion per pass, lower number of equipment, reduced refrigeration requirement etc.
- Loop pressure around 200 to 220 bar may be preferred for capacities upto 2200 tpd (as seen in most of the running plants)
- Capacities beyond 3000 tpd (say upto 10000 tpd, presently heard) cost effectiveness may be analysed for loop pressure depending upon whether the equipment like compressor etc are available for such single stream capacity. It may call for parallel stream of some equipment.

Selection of Catalysts for Ammonia synthesis

- Looking at the table, **conventional promoted Iron catalyst seems to be cost effective with catalyst life of >10 yrs**.
- But for the **cost and stability issue, Ruthenium based catalyst is desirable with low impurity level in Green Ammonia plant**.
- KBR is already using this in one of their technologies.



Comparison of SMR-Based Ammonia Synthesis Processes With Commercial Iron-Based and Ruthenium-Based Catalysts.

	IRON			RUTHENIUM
	Fe_3O_4	Fe_3O_4 with Co	$Fe_{1-x}O$	Ru–Ba–K/AC
Year	1913	1979	1986	1992
Temperature (°C)	360–520	350–500	300–500	325–450
Pressure (bar)	120–450	100–300	100–250	70–100
Energy consumption (GJ/t_{NH3})	28	28	27–28	26–27
H_2:N_2 ratio	2–3	2–3	2–3	1.5–2
Catalyst lifetime (y)	>14	–	6–10	≤10
Relative activity	1.0	1.2	1.5	2–10
Thermal stability	High	Medium/Low	Medium	Low
Relative catalyst cost	1.0	1.5	1.1	150–230

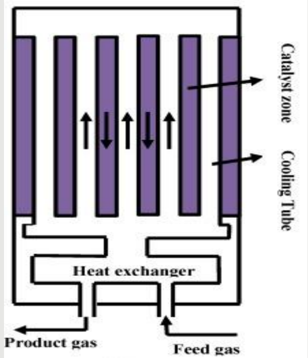
Source: Techno-Economic Challenges of Green Ammonia as an Energy Vector

Effect of Variables on Ammonia Synthesis Reactor

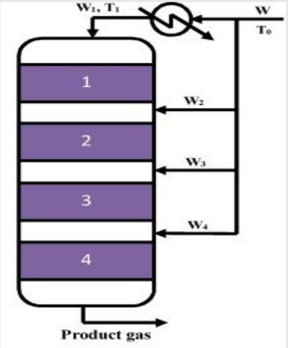
$$3\,H_2 + N_2 \leftrightharpoons 2\,NH_3 \quad \Delta H^\circ_{27\,^\circ C} = -46.35\ \mathrm{kJ/mol}$$

- **Pressure**: An increase in pressure will improve the conversion rate by increasing the reaction rate and improving the ammonia equilibrium.
- **Inlet temperature**: The temperature has conflicting effects since a higher temperature will increase the reaction rate while decreasing the equilibrium concentration.
- **Space velocity** (m^3 of gas per hour/ m^3 of catalyst): Increased space velocity increases the total ammonia production but decreases the outlet ammonia concentration.
- **Inert level**: Inert gases decrease the partial pressures of hydrogen and nitrogen forcing the equilibrium to change detrimentally.
- **Nitrogen/Hydrogen ratio**: The reaction rate exhibits a maximum at a particular nitrogen/hydrogen ratio while the maximum depends on space velocity. This ratio is generally between **2.0-3.0**.
- **Catalyst particle size**: Smaller particles have higher conversion rates due to lower diffusion restrictions and larger surface area.

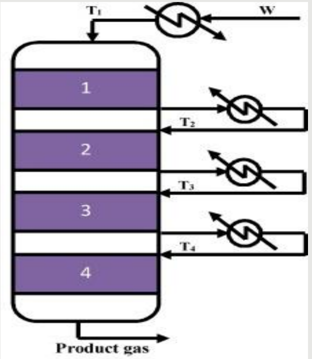
Typical converter arrangement with heat recovery



Internal Direct Cooling Reactor



Adiabatic Quench Cooling Reactor

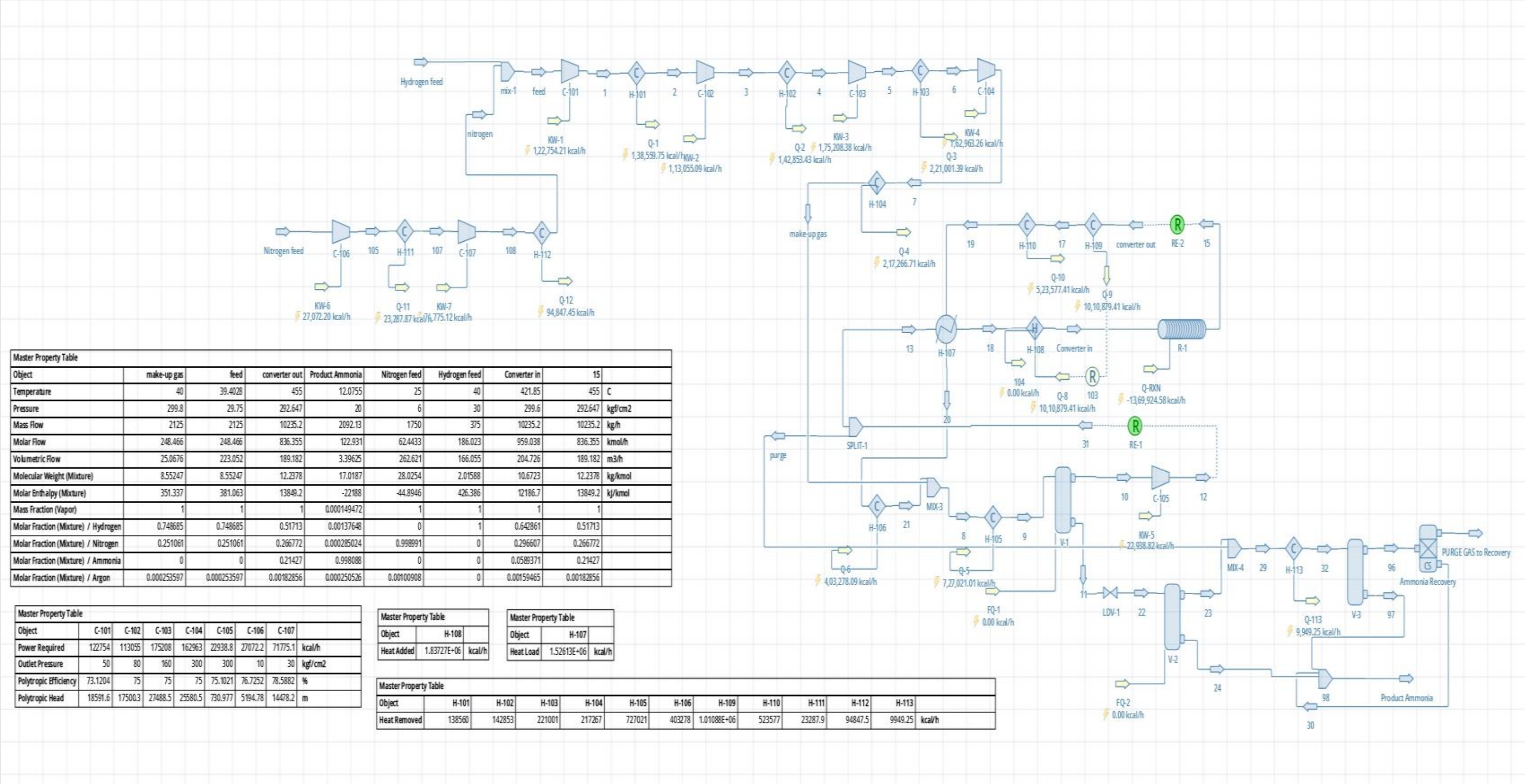


Adiabatic Indirect Cooling Reactor

Types	Internal Direct Cooling Reactor (TVA)	Adiabatic Quench Cooling Reactor (KBR	Adiabatic Indirect Cooling Reactor (Thyssun Krupp)
Advantages	Near to isothermal condition	a) Quench dilution favours NH3 equilibrium b) Higher Thermal efficiency	a) External heat exchangers, easy to maintain b) Uniform space velocity with entire flow
Disadvantages	Heat Transfer coefficient (to metal and catalyst) will be a limitation	Uniform temperature depends upon quench control and mixing	a) Comparatively lower thermal efficiency b) Increasing Ammonia content affects favourable equilibrium

Source: M.H. Khademi et al.

Typical flow sheet configuration & output of a simulation study for Green Ammonia



Master Property Table

Object	make-up gas	feed	converter out	Product Ammonia	Nitrogen feed	Hydrogen feed	Converter in	15	
Temperature	40	39.4028	455	12.0755	25	40	421.85	455	C
Pressure	299.8	29.75	292.647	20	6	30	299.6	292.647	kgf/cm2
Mass Flow	2125	2125	10235.2	2092.13	1750	375	10235.2	10235.2	kg/h
Molar Flow	248.466	248.466	836.355	122.931	62.4433	186.023	959.038	836.355	kmol/h
Volumetric Flow	25.0676	223.052	189.182	3.39625	262.621	166.055	204.726	189.182	m3/h
Molecular Weight (Mixture)	8.55247	8.55247	12.2378	17.0187	28.0254	2.01588	10.6723	12.2378	kg/kmol
Molar Enthalpy (Mixture)	351.337	381.063	13849.2	-22188	-44.8946	426.386	12186.7	13849.2	kJ/kmol
Mass Fraction (Vapor)	1	1	1	0.000149472	1	1	1	1	
Molar Fraction (Mixture) / Hydrogen	0.748685	0.748685	0.51713	0.00137648	0	1	0.642861	0.51713	
Molar Fraction (Mixture) / Nitrogen	0.251061	0.251061	0.266772	0.000285024	0.998991	0	0.296607	0.266772	
Molar Fraction (Mixture) / Ammonia	0	0	0.21427	0.998088	0	0	0.0589371	0.21427	
Molar Fraction (Mixture) / Argon	0.000253597	0.000253597	0.00182856	0.000250526	0.00100908	0	0.00159465	0.00182856	

Master Property Table

Object	C-101	C-102	C-103	C-104	C-105	C-106	C-107	
Power Required	122754	113055	175208	162963	22938.8	27072.2	71775.1	kcal/h
Outlet Pressure	50	80	160	300	300	10	30	kgf/cm2
Polytropic Efficiency	73.1204	75	75	75	75.1021	76.7252	78.5882	%
Polytropic Head	18591.6	17500.3	27488.5	25580.5	730.977	5194.78	14478.2	m

Master Property Table

Object	H-108	
Heat Added	1.83727E+06	kcal/h

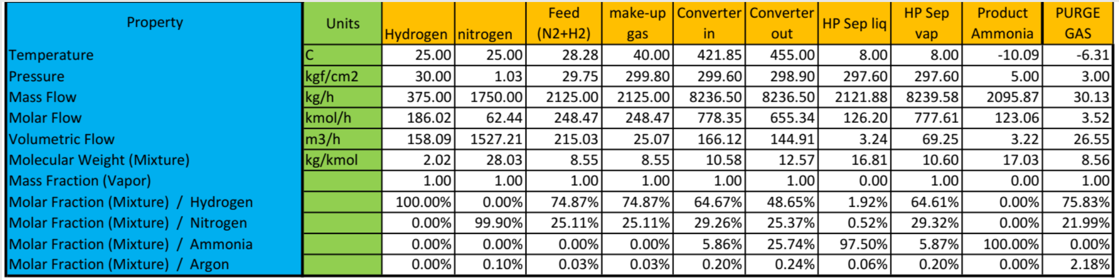
Master Property Table

Object	H-107	
Heat Load	1.52613E+06	kcal/h

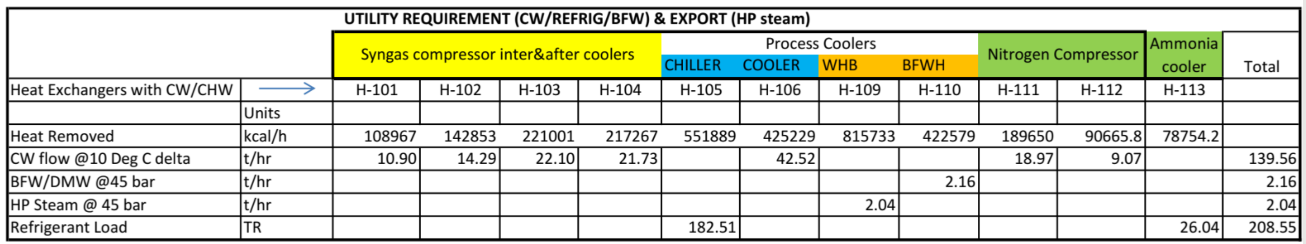
Master Property Table

Object	H-101	H-102	H-103	H-104	H-105	H-106	H-109	H-110	H-111	H-112	H-113	
Heat Removed	138560	142853	221001	217267	727021	403278	1.01088E+06	523577	23287.9	94847.5	9949.25	kcal/h

Mass balance, Power and Utility calculations-typical plant

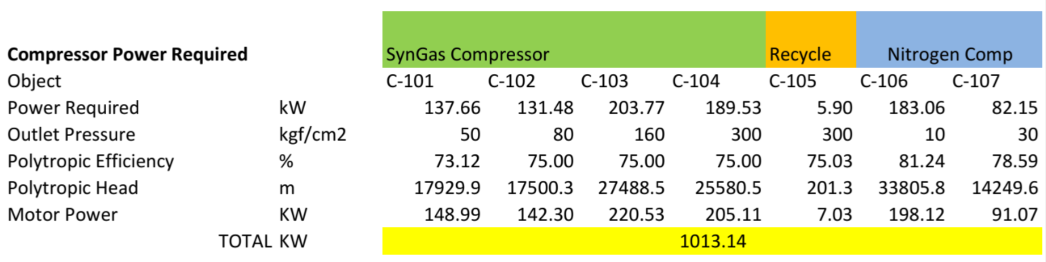


Property	Units	Hydrogen	nitrogen	Feed (N2+H2)	make-up gas	Converter in	Converter out	HP Sep liq	HP Sep vap	Product Ammonia	PURGE GAS
Temperature	C	25.00	25.00	28.28	40.00	421.85	455.00	8.00	8.00	-10.09	-6.31
Pressure	kgf/cm2	30.00	1.03	29.75	299.80	299.60	298.90	297.60	297.60	5.00	3.00
Mass Flow	kg/h	375.00	1750.00	2125.00	2125.00	8236.50	8236.50	2121.88	8239.58	2095.87	30.13
Molar Flow	kmol/h	186.02	62.44	248.47	248.47	778.35	655.34	126.20	777.61	123.06	3.52
Volumetric Flow	m3/h	158.09	1527.21	215.03	25.07	166.12	144.91	3.24	69.25	3.22	26.55
Molecular Weight (Mixture)	kg/kmol	2.02	28.03	8.55	8.55	10.58	12.57	16.81	10.60	17.03	8.56
Mass Fraction (Vapor)		1.00	1.00	1.00	1.00	1.00	1.00	0.00	1.00	0.00	1.00
Molar Fraction (Mixture) / Hydrogen		100.00%	0.00%	74.87%	74.87%	64.67%	48.65%	1.92%	64.61%	0.00%	75.83%
Molar Fraction (Mixture) / Nitrogen		0.00%	99.90%	25.11%	25.11%	29.26%	25.37%	0.52%	29.32%	0.00%	21.99%
Molar Fraction (Mixture) / Ammonia		0.00%	0.00%	0.00%	0.00%	5.86%	25.74%	97.50%	5.87%	100.00%	0.00%
Molar Fraction (Mixture) / Argon		0.00%	0.10%	0.03%	0.03%	0.20%	0.24%	0.06%	0.20%	0.00%	2.18%



UTILITY REQUIREMENT (CW/REFRIG/BFW) & EXPORT (HP steam)

		Syngas compressor inter&after coolers				Process Coolers				Nitrogen Compressor		Ammonia cooler	Total
						CHILLER	COOLER	WHB	BFWH				
Heat Exchangers with CW/CHW	→	H-101	H-102	H-103	H-104	H-105	H-106	H-109	H-110	H-111	H-112	H-113	
	Units												
Heat Removed	kcal/h	108967	142853	221001	217267	551889	425229	815733	422579	189650	90665.8	78754.2	
CW flow @10 Deg C delta	t/hr	10.90	14.29	22.10	21.73		42.52			18.97	9.07		139.56
BFW/DMW @45 bar	t/hr								2.16				2.16
HP Steam @ 45 bar	t/hr							2.04					2.04
Refrigerant Load	TR					182.51						26.04	208.55



Compressor Power Required		SynGas Compressor				Recycle	Nitrogen Comp	
Object		C-101	C-102	C-103	C-104	C-105	C-106	C-107
Power Required	kW	137.66	131.48	203.77	189.53	5.90	183.06	82.15
Outlet Pressure	kgf/cm2	50	80	160	300	300	10	30
Polytropic Efficiency	%	73.12	75.00	75.00	75.00	75.03	81.24	78.59
Polytropic Head	m	17929.9	17500.3	27488.5	25580.5	201.3	33805.8	14249.6
Motor Power	KW	148.99	142.30	220.53	205.11	7.03	198.12	91.07
TOTAL	KW	1013.14						

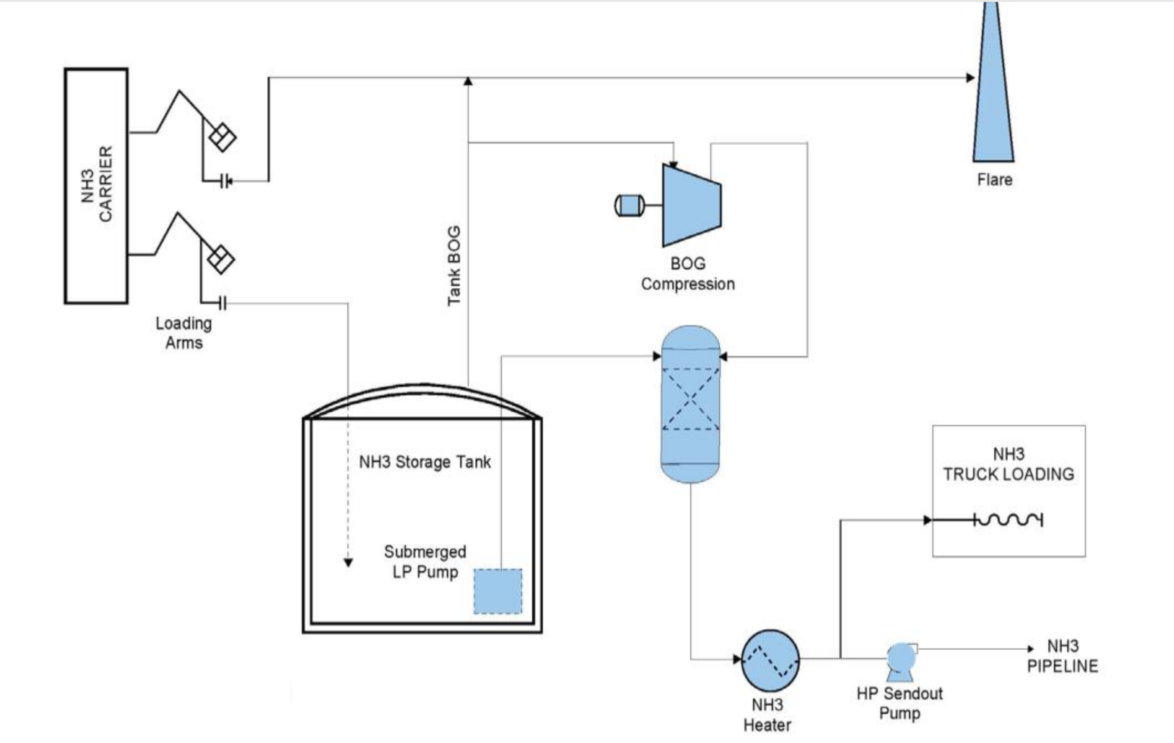
Ammonia Storage Tank Sizing and Selection

Type	Storage Pressure (bar)	Temp °C	Capacity range (Tons)	Ton of NH_3/t of steel	Refrigeration compressor
Non refrigerated	16 to 18	20 to25	Up to 270 tons	2.8	None
Semi refrigerated	3 to 5	5	450 to 2700	10	Single stage
Refrigerated	1.1 to 1.2	-33	5000 to 50000	41 to 45	Two stage

- Normal fill volume 85% (to allow for expansion/vaporization)
- Normal boil - off rate in refrigerated storage tank =0.04%/day of storage capacity
- Loading operation – Tanker/Wagon/Ship
- Unloading operation –Tanker/wagon/Ship

Source: fertilizerseurope.com

Schematic Diagram of Refrigerated Ammonia Storage



Source: Black & Veatch

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