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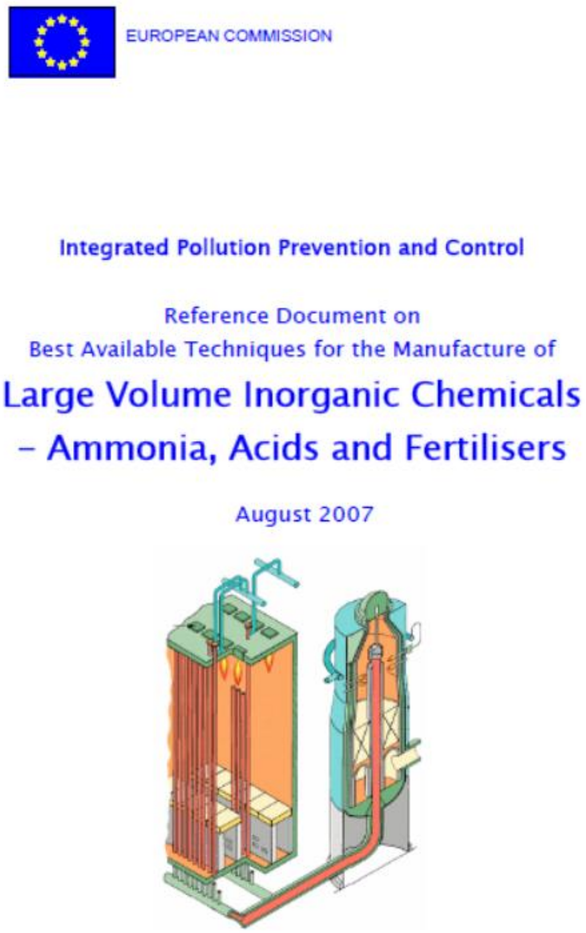
University of Zagreb



EUROPEAN COMMISSION

Integrated Pollution Prevention and Control

Reference Document on
Best Available Techniques for the Manufacture of

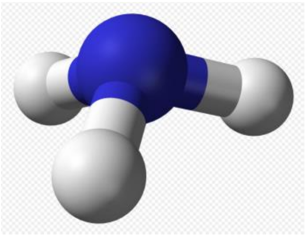
Large Volume Inorganic Chemicals
– Ammonia, Acids and Fertilisers

August 2007

BAT in Chemical Industry

Ammonia Production

Prof. dr. sc. Ante Jukić



AMMONIA

NH_3, $t_v = -33.3$ ºC.

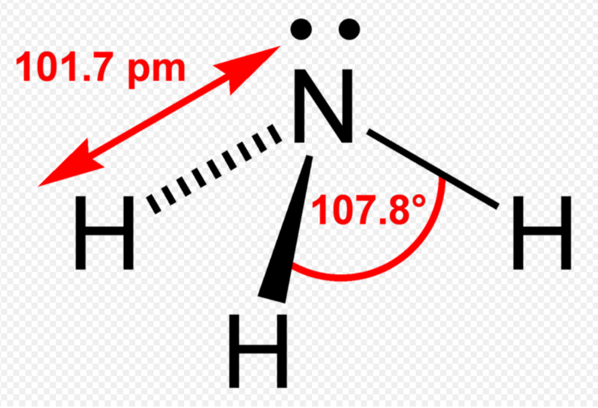
$N_2 + 3\,H_2 = 2\,NH_3$ (high pressure, Fe-based catalysts)

About 80 % of the ammonia is currently used as the nitrogen source in fertilisers, with the other 20 % being used in several industrial applications, such as the manufacture of plastics, fibres, explosives, hydrazine, amines, amides, nitriles and other organic nitrogen compounds which serve as intermediates in dyes and pharmaceuticals manufacturing.

Among the important inorganic products manufactured from ammonia are nitric acid, urea and sodium cyanide.

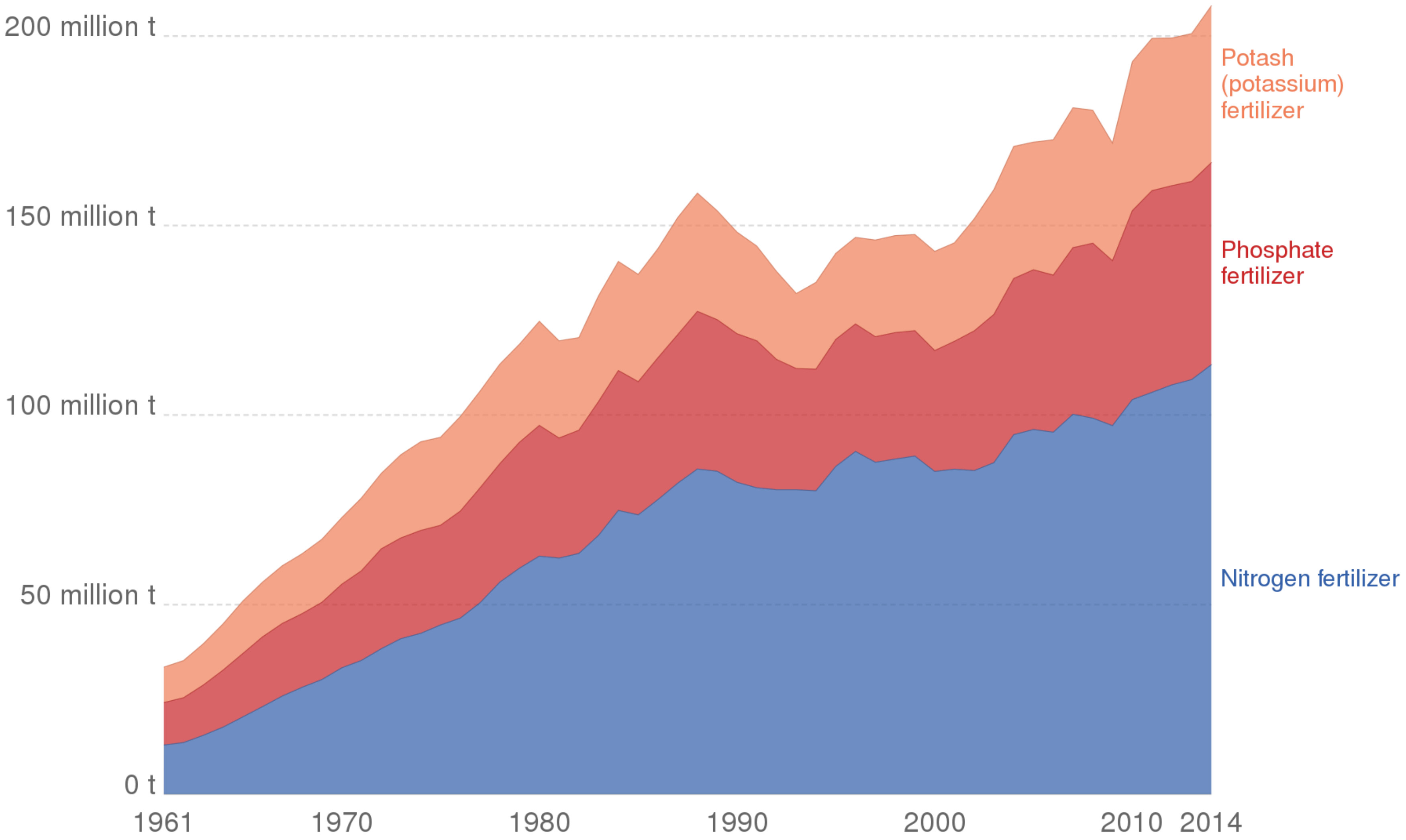
Ammonia is also used for environmental protection measures, e.g. in the removal of NO_x from flue-gases. Liquid ammonia is an important solvent and is also used as a refrigerant.

A modern ammonia plant has a typical capacity of 1000 – 2000 tonnes/day and new plants are commonly designed for up to 2200 tonnes/day.



Total fertilizer production by nutrient, World

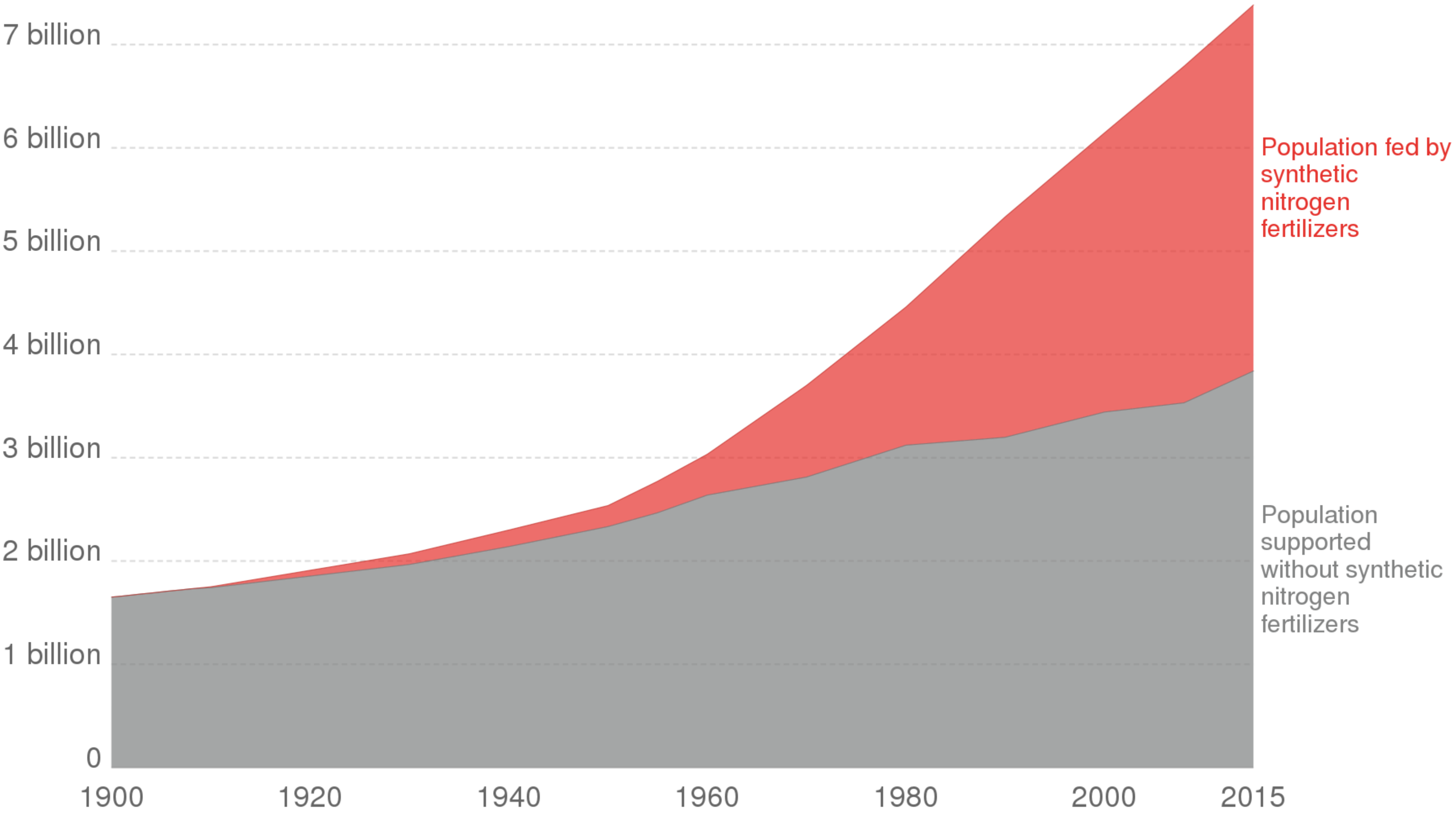
Total fertilizer production by nutrient type (nitrogen, phosphate and potash/potassium), measured in tonnes per year.



Source: UN Food and Agricultural Organization (FAO)

World population supported by synthetic nitrogen fertilizers

Estimates of the share of the global population which could be supported with and without the production of synthetic nitrogen fertilizers (via the Haber-Bosch process) for food production. Best estimates project that just over half of the global population could be sustained without reactive nitrogen fertilizer derived from the Haber-Bosch process.



Source: Erisman et al. (2008); Smil (2002); Stewart (2005)

Ammonia is synthesised from nitrogen and hydrogen by the following reaction:

$$N_2 + 3\,H_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\,NH_3$$

$\Delta H = -92 \text{ kJ mol}^{-1}$, $\Delta S = -198 \text{ kJ mol}^{-1}$, $\Delta G = -16{,}3 \text{ kJ mol}^{-1}$

$$K_p = \frac{p_{NH_3}^2}{p_{N_2} \cdot p_{H_2}^3}$$

The best available source of nitrogen is from atmospheric air.

The hydrogen required can be produced from various feedstocks but currently it is derived mostly from fossil fuels (natural gas).

Depending of the type of fossil fuel, two different methods are mainly applied to produce the hydrogen for ammonia production: **steam reforming** or **partial oxidation**.

Raw Materials

- N_2 (g) is taken from the air (1) via a process of fractional distillation (2, more importnat) by burning of oxygen from air with hydrogen (nitrogen from air remains).
- H_2 (g) comes from natural gas, CH_4 (g)

$$CH_4\,(g) + H_2O\,(g) \rightleftharpoons 3H_2\,(g) + CO\,(g)$$

- The carbon monoxide then reacts with more steam:

$$CO\,(g) + H_2O\,(g) \rightleftharpoons H_2\,(g) + CO_2\,(g)$$

The Haber Process

In the early 1900’s a German chemist called Fritz Haber came up with his chemical process to make ammonia using the “free” very unreactive nitrogen from the air:

$$\text{Nitrogen} + \text{Hydrogen} \rightleftharpoons \text{Ammonia}$$

$$N_2\,(g) \quad + \quad 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

1. *Influence of temperature*

The process is highly exothermic with a ΔH value of 92.2 kJ per mole.
As a result a compromise has to be made with regards to what temperature is used.
A high temperature favours a higher rate of reaction and so equilibrium is reached more quickly; a high temperature however favours the backward reaction since the process is exothermic.
However, at low temperatures the reaction rate is incredibly slow.

Compromise between rate and yield has to be reacted. (*kinetics vs. thermodynamics !*)

Haber process runs at about 450 ^{o}C.

(LeCheteliers principal states that any changes made to a reaction mixture will be compensated for by the reaction).
Therefore, since the process is exothermic, increasing the temperature promotes the backward reaction since this takes in heat from the surroundings, hence lowering the temperature. As a result, a compromise is made between the two.
This compromise temperature is 673-923 K.

2. *Influence of pressure*

- The reversible reaction to form ammonia:

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_2\ (g)$$

4 moles of gas — 2 moles of gas

96 litres (4 x 24) — 48 litres (2 x 24)

- If pressure is increased in reaction vessel, the reversible reaction favours ammonia production.
- Increase external pressure → favours side with least gas (ammonia).

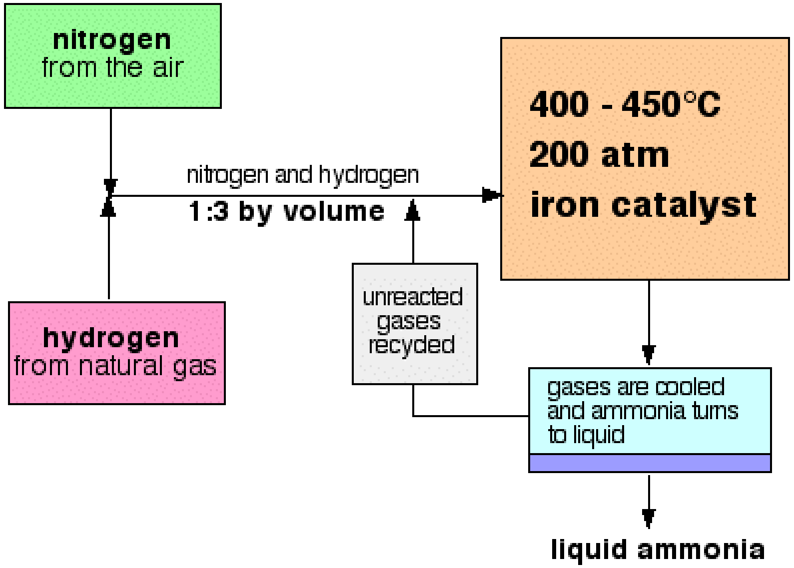
Haber process runs at about 200 atmospheres in order to maximise yield of ammonia.

Also due to LeCheteliers principle a high pressure is used.
The mol ratio of gases is 4:2, therefore if a high pressure is used the forward reaction is promoted, since at a higher pressure the products hold a smaller volume, hence decreasing the pressure.
The pressure used is 200 - 400 atmospheres, which is quite high.

3. *Use of catalyst*

Third condition present within the reaction vessel is an iron (Fe-based) catalyst (Fe, Ru, Re, Os); the catalyst provides an alternative pathway for the reaction to occur, which has lower activation energy E_a from 230 kJ mol^{-1} to 80 kJ mol^{-1}.

- The catalyst is a fine mesh designed to maximise surface area.
- Catalyst poisons: S-compounds ($S < 0,5$ mg kg^{-1}), CO, CO_2, H_2O, O_2



Catalyst - mechanism of action

N≡N / 945 kJ mol^{-1}
C–C / 347 kJ mol^{-1}
H–H / 436 kJ mol^{-1}
catalytically active center (*)

$$\left.\begin{array}{l} N_2 + 2^* \rightarrow 2\,N^* \\ H_2 + 2^* \rightarrow 2\,H^* \end{array}\right\} \text{kemisorpcija}$$

$$N^* + H^* \rightarrow NH^*$$

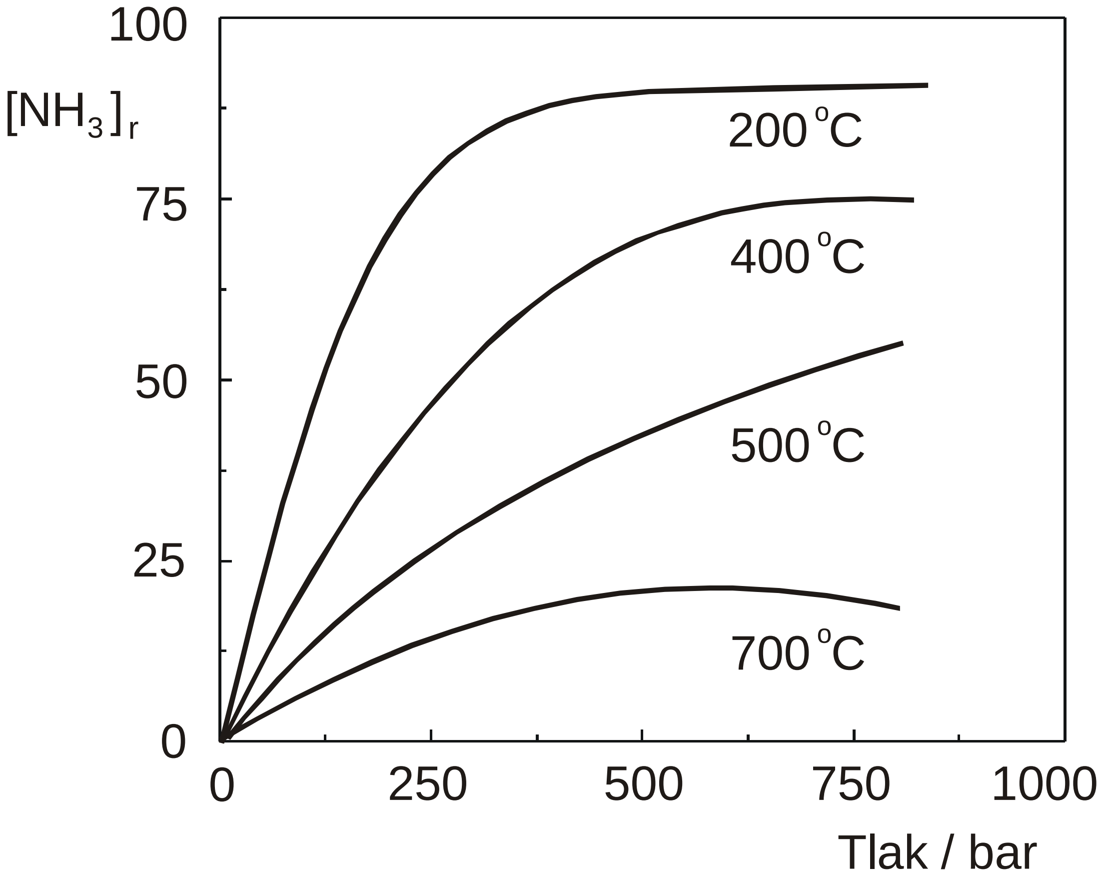
$$NH^* + H^* \rightarrow NH_2$$

$$NH_2^* + H^* \rightarrow NH_3 + 2^*$$

chemisorption = r.d.s.

Overall reaction: $2\,N + 6\,H \rightarrow 2\,NH_3$

Influence of reaction pressure and temperature on ammonia conversion



t / °C	K_r	p (NH$_3$)		
		1 bar	10 bar	100 bar
25	5.27×10^{5}	0.937	9.80	99.3
100	0.275×10^{3}	0.660	8.76	95.9
200	0.382×10^{0}	0.172	5.37	81.9
300	0.452×10^{-2}	0.031	2.07	58.0
400	0.182×10^{-3}	0.00781	0.682	34.1
500	0.160×10^{-4}	0.00271	0.259	18.2

Process

Process of production of ammonia at industrial scale comprises of six main interconnected stages:

(1) Desulphurisation,

(2) Steam reforming of natural gas (methane),

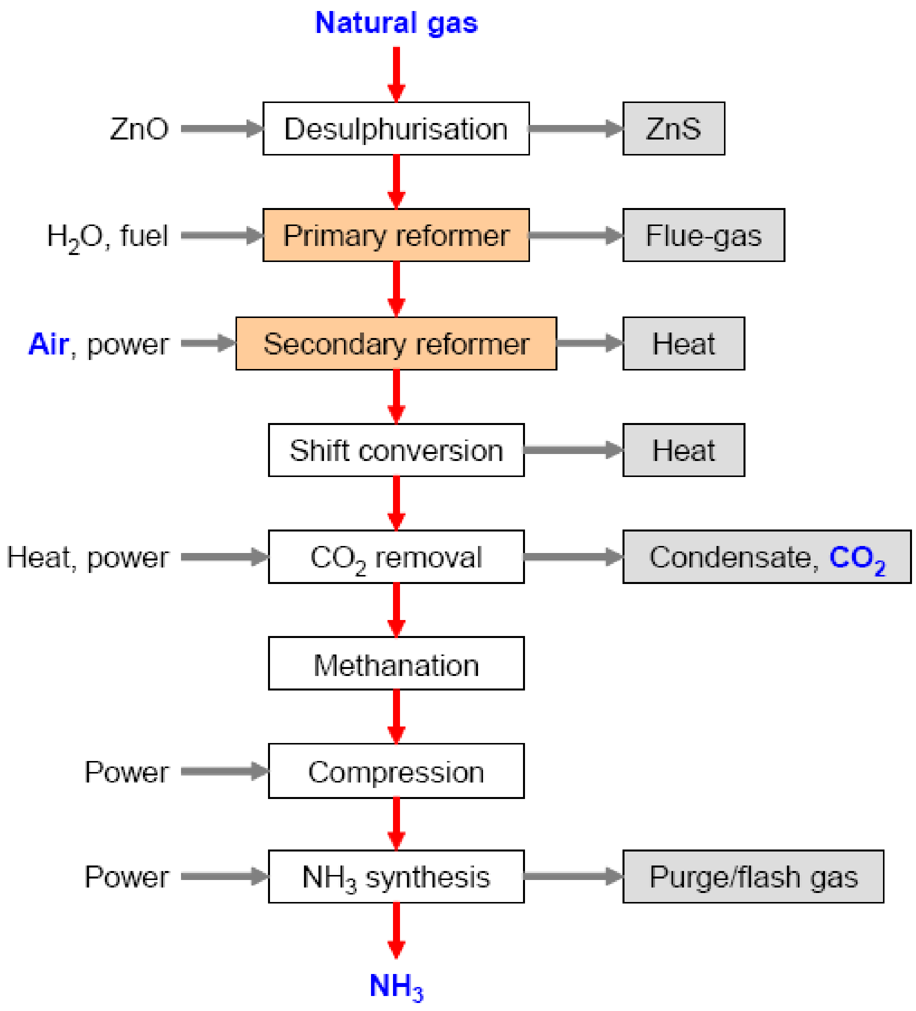
(3) Shift conversion (oxidation of carbon monoxide by water steam),

(4) CO_2 removal,

(5) Methanation of remaining CO and CO_2

(6) NH_3 synthesis

NH_3 production by conventional steam reforming



Natural gas

ZnO → Desulphurisation → ZnS

H_2O, fuel → Primary reformer → Flue-gas

Air, power → Secondary reformer → Heat

Shift conversion → Heat

Heat, power → CO_2 removal → Condensate, **CO_2**

Methanation

Power → Compression

Power → NH_3 synthesis → Purge/flash gas

NH_3

(1) Desulphurisation – removal of S-compounds (catalyst poisons) from natural gas

The catalyst used in the steam reforming process is highly sensitive to any sulphur compounds, therefore these compounds need to be reduced to a concentration of less than 0.15 mg S / Nm^3 feed gas.
To achieve this, the feed gas is preheated up to 350 – 400 °C.
Thereafter, the sulphur compounds are hydrogenated to H_2S,
typically using a cobalt molybdenum catalyst, and then finally adsorbed on pelletised zinc oxide (R = alkyl group):

1a) $$R\text{-}SH + H_2 \rightarrow H_2S + RH$$

1b) $$H_2S + ZnO \rightarrow ZnS + H_2O$$

(2) Steam reforming of methane (hydrogen production)

$$CH_4 + H_2O \longrightarrow CO + 3\ H_2$$

2.a. Primary reforming

The hydrocarbon conversion rate in the primary reformer in the conventional steam reforming plant is about 60 %. The overall reaction is highly endothermic:

$$CH_4 + H_2O = CO + 3H_2 \qquad \Delta H_o = 206\ \text{kJ/mol}$$

Gas from the desulphuriser is mixed with steam and the preheated mixture enters the primary reformer at a temperature in the range of 400 – 800 °C.

The primary reformer consists of a large number of catalyst (Ni) filled tubes. In some new or revamped plants, the preheated steam/gas mixture is passed through an adiabatic pre-reformer and then reheated in the convection section. The applied steam to carbon molar ratio (S/C ratio) is typically around 3.0; although the actual optimum ratio depends on several factors, such as the feedstock quality, purge gas recovery, primary reformer capacity, shift operation, and the plant steam balance. In new plants, the optimum S/C ratio may be lower than 3.0.

The heat for the primary reforming process is supplied by burning natural gas or other gaseous fuel, in the burners of a radiant box containing the catalyst filled tubes.

About half of the heat is utilised for the reforming reaction, the rest remains in the flue-gas and is utilised in the convection section of the reformer to preheat several process streams.

2.b. Secondary reforming

$H_2 + \text{air} (O_2 + N_2) \longrightarrow H_2O + N_2$

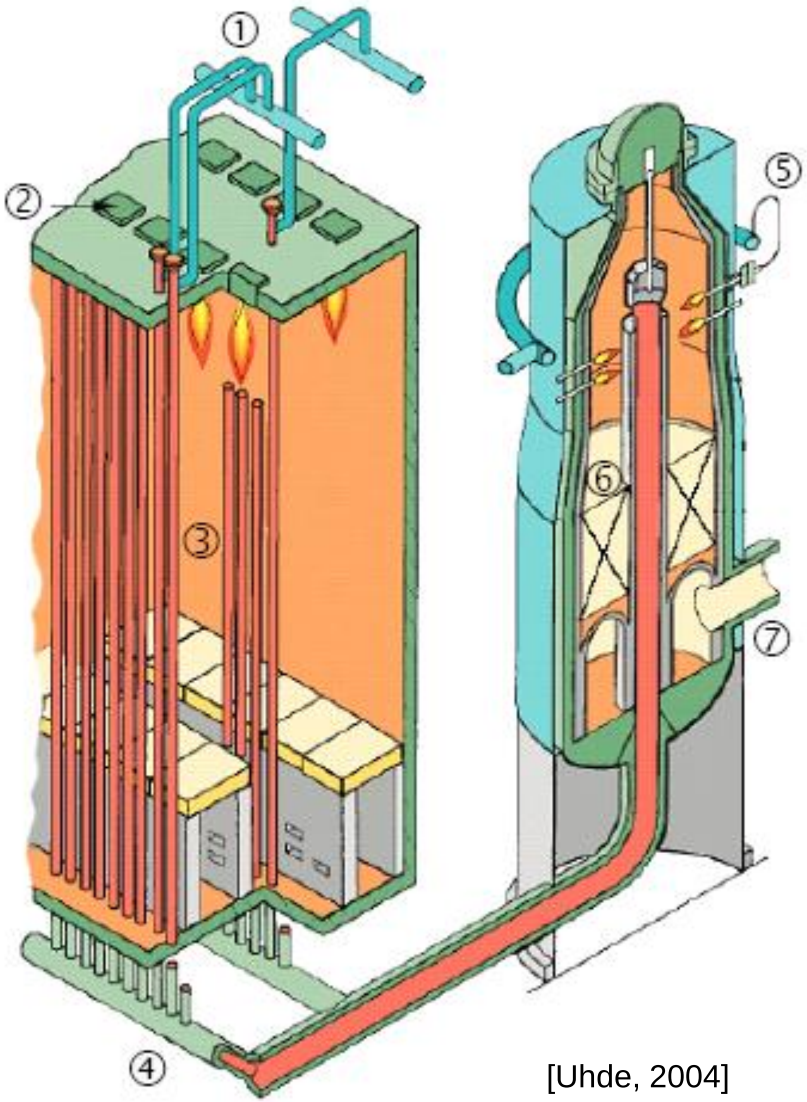
... together with complete conversion of CH_4 (>99.6 %).

The main objective of secondary reforming is to add the nitrogen required for the synthesis and to complete the conversion of the hydrocarbon feed.
For this purpose, the reaction heat and the required temperature are achieved by an internal combustion of part of the reaction gas before it is passed over the catalysts containing nickel.

The process air is compressed and heated in the primary reformer convection section to around 500 – 600 °C, with the result that the methane is converted down to a residual content of around 0.2 – 0.3 %. The reaction proceeds adiabatically, resulting in a gas outlet temperature of approximately 1000 °C.
Heat is removed in a waste heat steam boiler, a superheater/boiler or a boiler/preheater, cooling the gas to approximately 330 – 380 °C.

Example of a reformer radiant section and a secondary reformer

(1) inlet manifold, (2) burners, (3) reformer tubes, (4) outlet manifold, (5) process air inlet, (6) catalyst bed, (7) gas outlet



[Uhde, 2004]

The applied steam to carbon molar ratio (S/C ratio) is typically around 3.0; although the actual optimum ratio depends on several factors, such as the feedstock quality, purge gas recovery, primary reformer capacity, shift operation, and the plant steam balance.

In new plants, the optimum S/C ratio may be lower than 3.0.

(3) Shift conversion (oxidation of carbon monoxide by water steam)

The process gas from the secondary reformer contains 12 – 15 % CO (dry gas base). Most of this CO will be converted in the shift section to CO_2 and H_2 :

$$CO + H_2O \xrightarrow[\text{2. Cu, 225 °C}]{\text{1. Fe, 450 °C}} CO_2 + H_2 \qquad \Delta H = -41.2\ \text{kJ mol}^{-1}$$

3.a. High-temperature conversion

Reaction temperature 350-450 °C, Fe/Cr-catalyst, CO < 3 vol. %

3.b. Low-temperature conversion

Reaction temperature 200-225 °C, Cu/Zn-catalyst, CO < 0.2 vol. %

This reaction is carried out in two steps with intermediate heat removal.
Initially, the process gas is passed through a bed of iron oxide/chromium oxide catalyst at 350 – 380 °C and then over a copper oxide/zinc oxide catalyst at approximately 200 – 220 °C. The final residual CO content of the gas is 0.2 – 0.4 %.
New developments can enable an isothermal shift one-step conversion to take place, applying an internal cooling of the process gas with cooling tubes running through the catalyst layers.

Process condensates. The gas exiting the low temperature shift reactor is cooled and after most of the excess steam is condensed and removed it passes into the CO_2 removal system.
This is needed to prevent dilution of the CO_2 removal solvent and to maintain the correct equilibrium balance.
Condensates normally containing 1500 – 2000 ppm of ammonia and 800 – 1200 ppm of methanol can be recycled to the process in various ways. The heat released during cooling and condensation can be used for several purposes, e.g. to regenerate the CO_2 scrubbing solution, to drive an absorption refrigeration unit, or to preheat the boiler feed-water.

(4) CO_2 removal

This process step removes the CO_2 from the reaction gas and the quantity corresponds to nearly all the carbon introduced as feed gas into the overall process. The residual CO_2 content is usually in the range of 50 – 3000 ppmv.

The CO_2 is removed in a chemical or physical absorption process.
The solvents used in chemical absorption processes are mainly aqueous amine solutions, e.g. mono ethanolamine (MEA) activated methyl diethanolamine (aMDEA) or hot potassium carbonate solutions.
Two typically used physical absorption solvents are glycol dimethylethers (Selexol) and propylene carbonate. The MEA process requires a high regeneration energy.

Another emerging process is pressure swing adsorption (PSA).
This process has the potential to combine in one step both the classical CO_2 removal and the methanation (next process step).
This is valid for all cases where the CO_2 purity is unimportant.
However, if pure CO_2 is needed as a product, then a classical solvent scrubbing of the low pressure off-gas of the PSA can be used to recover CO_2.

A1. Absorption processes with chemically active solvents

A1-1. Benfield process

The process is described as reversible chemical reaction of acid gases with aqueous solution of potassium carbonate.
Regeneration of saturated solution is performed by desorbtion.
This method is commonly used when of CO_2 is present in natural gas in higher share.

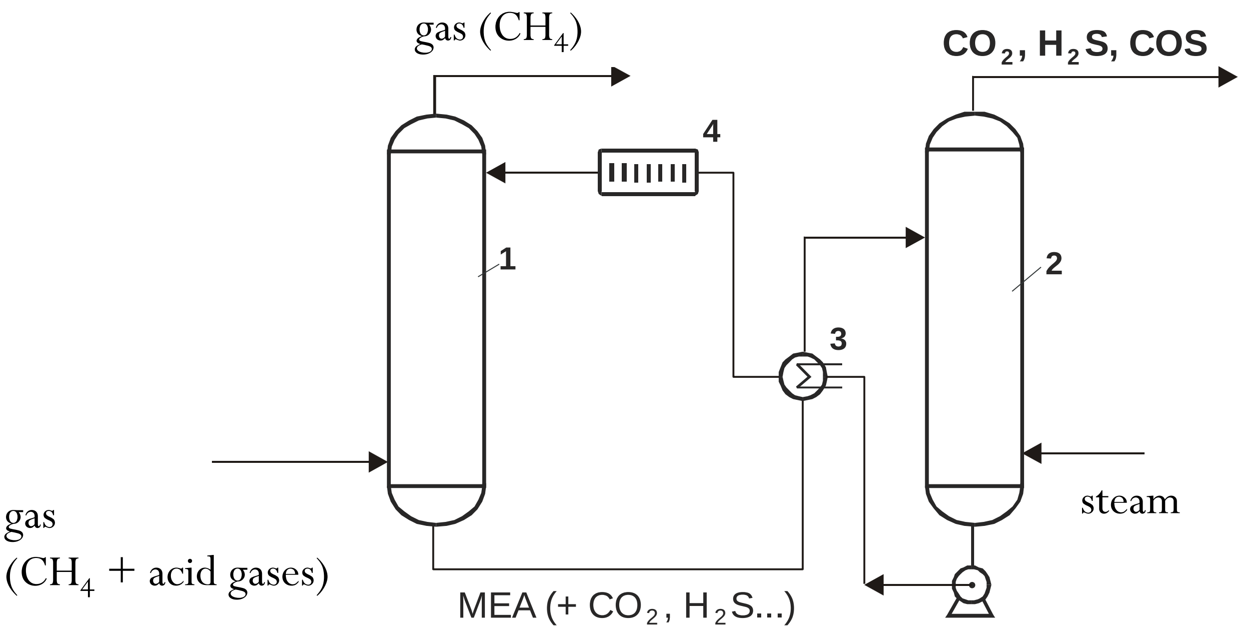
The process comprises of counter-current gas scrubbing in columns with aqueous solution of K_2CO_3 (5···10 %), at temperature of ~ 20 ^oC, and pressure of 20···70 bar.

Regeneration of saturated solution is done by heating, commonly by water vapor (steam) at room pressure:

$$K_2CO_3 + CO_2 + H_2O \quad = \quad 2\ KHCO_3$$

absorption: 20 bar, 20 ^oC desorption: 1 bar, 105 ^oC

Scheme of the removal procedure of acid gases from natural gas with MEA aqueous solution

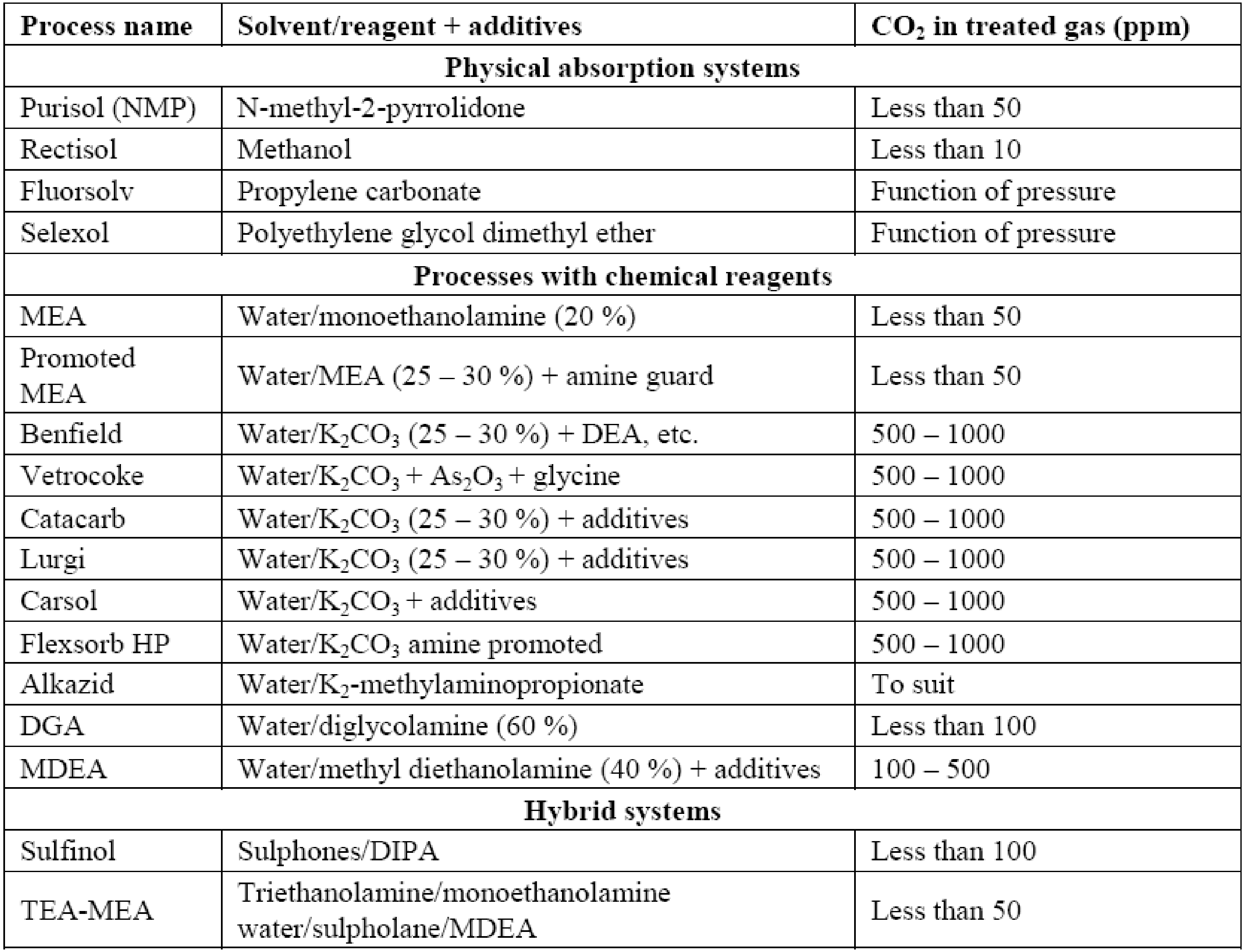


1 – absorber, 2 – regenerator, 3 – heat exchanger, 4 – cooler

The purified gas (CH_4) is separated at the top of the column and amino solution with absorbed acid gases is drained away to the regeneration column. The regeneration column has a similar design like the absorption column and there solution is heated usually with superheated steam to 130 °C at 0.3···1.0 bar.
From the top of the column desorbed gases are removed.
Amine solution is first cooled by heat exchanger (with a solution from absorber), followed by with cold water (which flow through the cooler) and then redosed into the reactor.

Overview of some CO_2 removal processes

[European Commission, 2000]



Process name	**Solvent/reagent + additives**	**CO_2 in treated gas (ppm)**
Physical absorption systems		
Purisol (NMP)	N-methyl-2-pyrrolidone	Less than 50
Rectisol	Methanol	Less than 10
Fluorsolv	Propylene carbonate	Function of pressure
Selexol	Polyethylene glycol dimethyl ether	Function of pressure
Processes with chemical reagents		
MEA	Water/monoethanolamine (20 %)	Less than 50
Promoted MEA	Water/MEA (25 – 30 %) + amine guard	Less than 50
Benfield	Water/K_2CO_3 (25 – 30 %) + DEA, etc.	500 – 1000
Vetrocoke	Water/K_2CO_3 + As_2O_3 + glycine	500 – 1000
Catacarb	Water/K_2CO_3 (25 – 30 %) + additives	500 – 1000
Lurgi	Water/K_2CO_3 (25 – 30 %) + additives	500 – 1000
Carsol	Water/K_2CO_3 + additives	500 – 1000
Flexsorb HP	Water/K_2CO_3 amine promoted	500 – 1000
Alkazid	Water/K_2-methylaminopropionate	To suit
DGA	Water/diglycolamine (60 %)	Less than 100
MDEA	Water/methyl diethanolamine (40 %) + additives	100 – 500
Hybrid systems		
Sulfinol	Sulphones/DIPA	Less than 100
TEA-MEA	Triethanolamine/monoethanolamine water/sulpholane/MDEA	Less than 50

(5) Methanation of remaining CO and CO_2

The small amounts of CO (about 0.2 %) and CO_2 (up to 500 mg kg^{-1}), remaining in the synthesis gas, can poison the ammonia synthesis catalyst and must be removed usually by conversion to CH_4 by hydrogenation in the methanator:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H = -206 \text{ kJ/mol}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H = -165 \text{ kJ/mol}$$

These reactions take place at a temperature of around 300 °C in a reactor filled with a nickel based catalyst.
The residual concentration of these carbon oxides is usually less than 10 ppmv.

Methane is not involved in the synthesis reaction, but the water formed must be removed before entering the converter. This is achieved by cooling, followed by condensation downstream of the methanator and finally by condensation/absorption in the product ammonia either in the loop or in a make-up gas drying unit.

(6) NH_3 synthesis

6.a. Compression

Modern ammonia plants use centrifugal compressors to pressurise the synthesis gas to the required level (100 – 250 bar, 350 – 550 °C) for ammonia synthesis.

Molecular sieves are sometimes used after the first compressor stage to remove the last traces of H_2O, CO and CO_2 from the synthesis gas. These compressors are usually driven by steam turbines, utilising steam produced from the excess process heat. A small quantity of condensates is removed from the synthesis gas during compression.
These condensates still contain ammonia.
Lubricating oils from mechanical equipment, which are typically removed in oil/water separators, can contaminate them.

6.b. Direct synthesis of NH_3 from elements

The synthesis of ammonia takes place on an iron catalyst at pressures usually in the range of 100 – 250 bar and at temperatures of between 350 and 550 °C:

$$N_2 + 3H_2 = 2NH_3 \qquad \Delta H_o = -46\ \text{kJ/mol}$$

Only 20 – 30 % of the synthesis gas is converted per pass to ammonia, due to unfavourable equilibrium conditions.
The unreacted gas is recycled after removing the ammonia formed.
Fresh synthesis gas is supplemented in the loop.

6.b. Overall reaction (1···6) :

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \xrightarrow{\text{air}} CO + H_2 + N_2 + H_2O \xrightarrow{-H_2O}$$

$$CO_2 + H_2 + N_2 \xrightarrow{-CO_2} H_2 + N_2 \longrightarrow NH_3$$

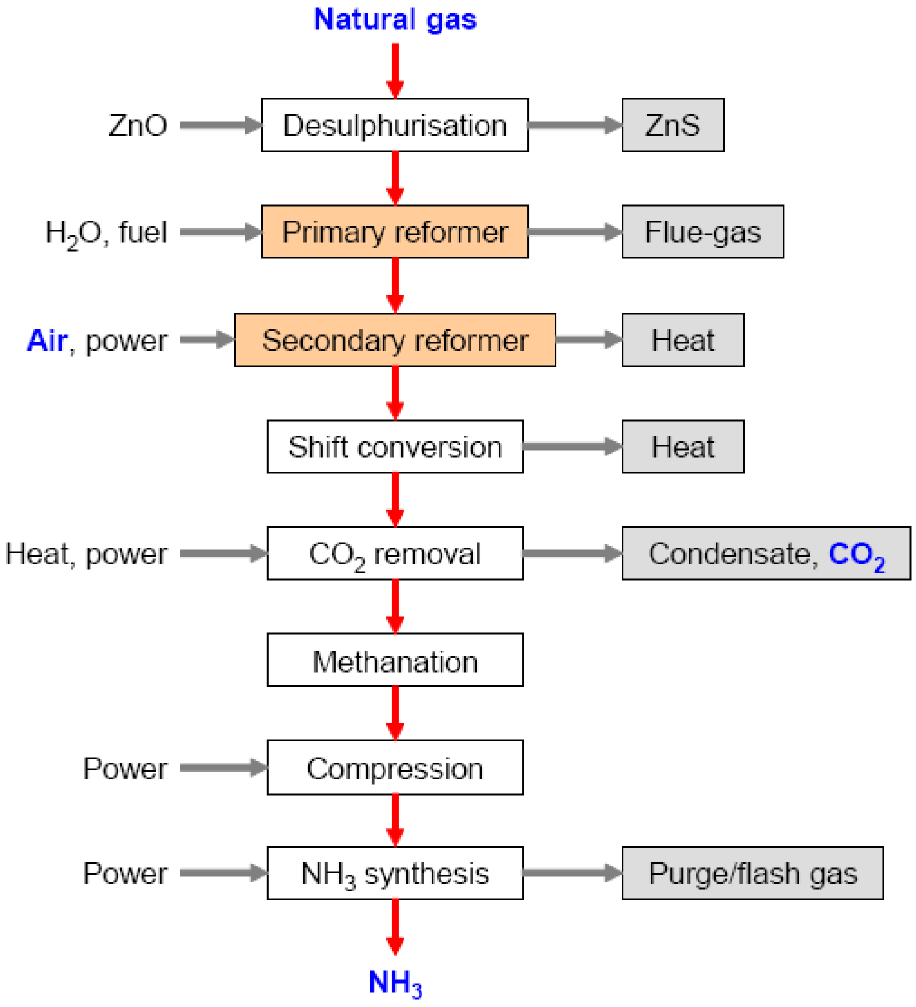
$$\mathbf{CH_4 + 0{,}3035\ O_2 + 1{,}131\ N_2 + 1{,}393\ H_2O \longrightarrow 2{,}262\ NH_3 + CO_2}$$

As the exothermic synthesis reaction proceeds, there is a reduction in volume and so a higher pressure and lower temperature favours the reaction.
The temperature of the catalyst needs to be controlled, as the heat of reaction at the necessary equilibrium and reaction rate produces a rise in temperature.
Subdividing the catalyst into several layers is one technique which can achieve this temperature control. In this technique, between the layers, the gases are cooled either directly by adding cooled synthesis gas or indirectly by generating steam.
Various converter designs can be utilised for this purpose.

For ammonia condensation from the loop, cooling with just water or air is insufficient to achieve low ammonia concentration at the inlet. For this reason, vaporising ammonia is used to chill the gas.
The ammonia vapours are liquefied by means of a refrigeration compressor.
The various synthesis configurations may differ with respect to the point where the make-up gas is added or where liquefied ammonia and purge gas is withdrawn.

New developments refer to the use of **more active catalysts** such as cobalt-promoted iron and ruthenium.
These catalysts allow a **lower synthesis pressure** and a **lower energy consumption** to be achieved.

NH$_3$ production by conventional steam reforming



Natural gas

ZnO → Desulphurisation → ZnS

H$_2$O, fuel → Primary reformer → Flue-gas

Air, power → Secondary reformer → Heat

Shift conversion → Heat

Heat, power → CO$_2$ removal → Condensate, **CO$_2$**

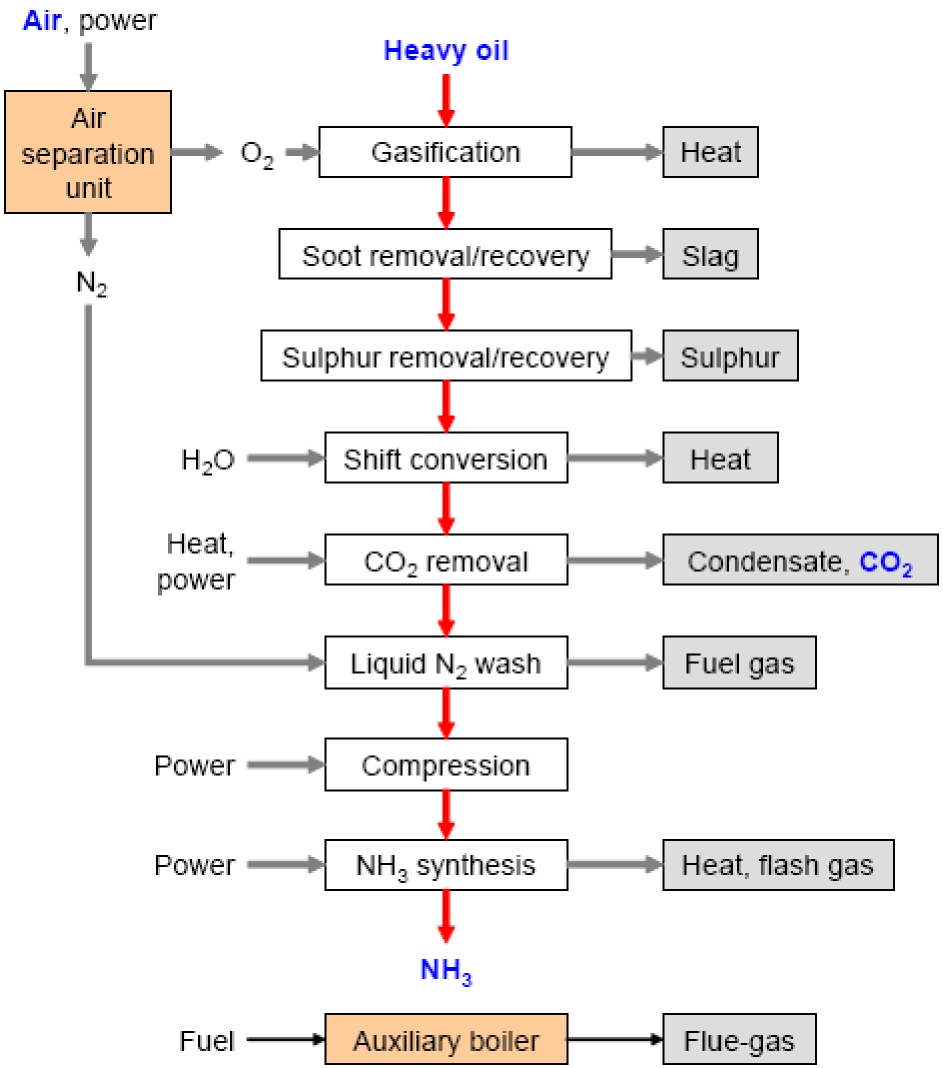
Methanation

Power → Compression

Power → NH$_3$ synthesis → Purge/flash gas

NH$_3$

NH$_3$ production by partial oxidation



Air, power

Air separation unit → O$_2$

N$_2$

Heavy oil

O$_2$ → Gasification → Heat

Soot removal/recovery → Slag

Sulphur removal/recovery → Sulphur

H$_2$O → Shift conversion → Heat

Heat, power → CO$_2$ removal → Condensate, **CO$_2$**

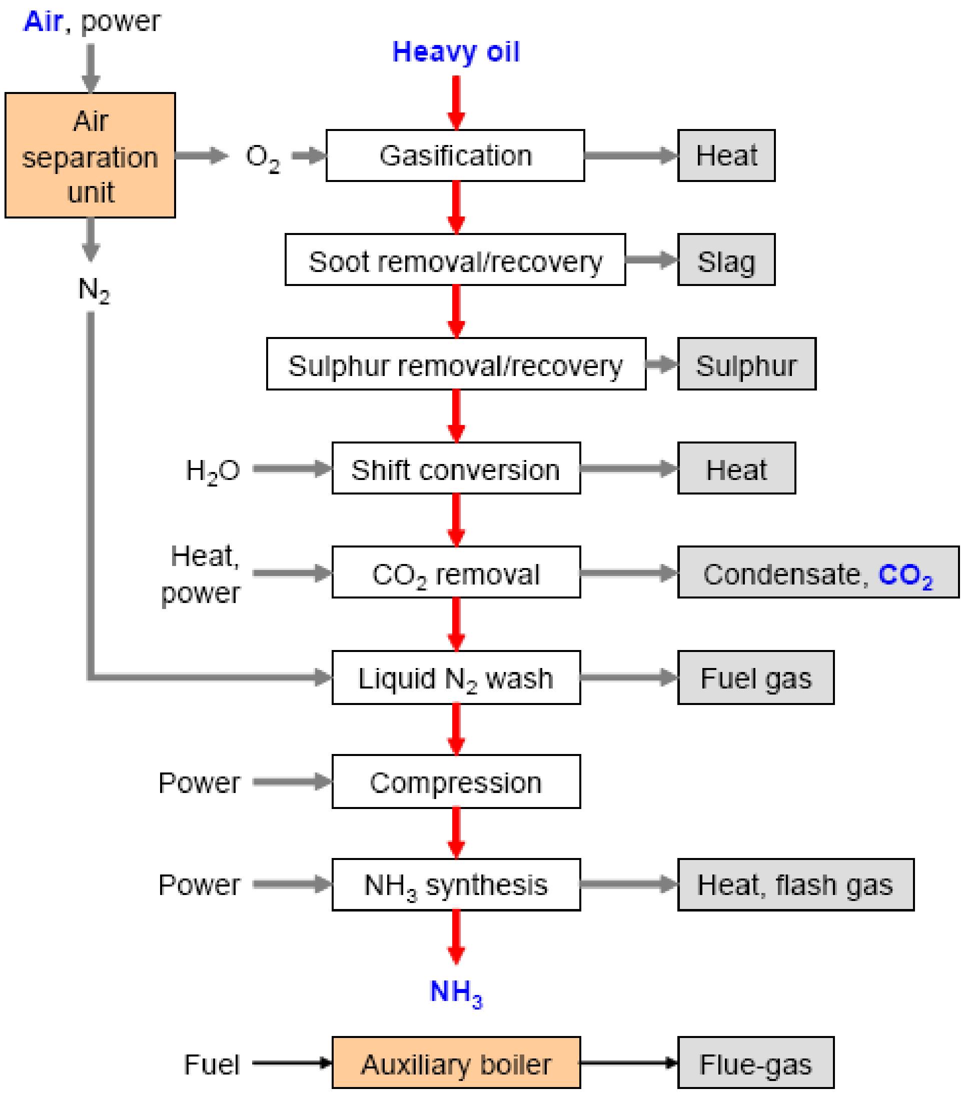
N$_2$ → Liquid N$_2$ wash → Fuel gas

Power → Compression

Power → NH$_3$ synthesis → Heat, flash gas

NH$_3$

Fuel → Auxiliary boiler → Flue-gas



Air, power
Air separation unit
O_2
N_2
Heavy oil
Gasification → Heat
Soot removal/recovery → Slag
Sulphur removal/recovery → Sulphur
H_2O → Shift conversion → Heat
Heat, power → CO_2 removal → Condensate, CO_2
Liquid N_2 wash → Fuel gas
Power → Compression
Power → NH_3 synthesis → Heat, flash gas
NH_3
Fuel → Auxiliary boiler → Flue-gas

The **partial oxidation** process is used for the gasification of *heavy feedstocks* such as residual oils and coal.

Figure gives an overview of the process steps.

The process is very flexible and can handle the full range of hydrocarbon feedstock, from natural gas up to the heaviest asphalt including waste materials such as plastics.

Ammonia plants which incinerate waste require compliance with the waste incineration Directive 76/2000/EC and the emissions of dioxins may be a concern.

Output from ammonia production

1. Ammonia

A typical size for a single stream ammonia production plant is
1000 – 1500 tonnes/day (300000 – 500000 tonnes/year) [1, EFMA, 2000].
The product is stored if not utilised.

Commercial anhydrous ammonia has two grades of purity:

- anhydrous ammonia min. 99.7 wt-%, water content approximately 0.2 wt-%
- anhydrous ammonia min. 99.9 wt-%.

Output from ammonia production

2. Carbon dioxide

Carbon dioxide is produced in accordance with stoichiometric conversion and can be recovered for **further use** as feedstock in a urea plant, for use in fertiliser production (ODDA process) and/or methanol production or liquefaction, in the beverage industry or as a coolant gas in nuclear reactors.

There is, however, an inevitable excess of CO_2 which is released as an emission from the process.

The carbon dioxide production in the ***steam/air reforming*** of natural gas is **1.15 – 1.40 kg / kg NH_3**, dependent on the degree of air reforming (the figures do not include carbon dioxide in the combustion gases).

A CO_2/NH_3 mole ratio of 0.5 (weight ratio 1.29), the stoichiometric ratio for urea production, is obtainable in the heat exchange reformer concepts.

In ***partial oxidation*** of residual oils, CO_2 production is **2 – 2.6 kg / kg NH_3**, dependent on the feedstock C/H ratio.

Output from ammonia production

3. Sulphur

In partial oxidation, **87 – 95 % of the sulphur** content of the gasifier feed **is recovered** in a Claus unit.

4. Steam

Modern steam reforming processes can be designed with no steam export or with some export if this is favourable for the site energy balance of low/medium pressure steam.

Surplus steam is usually produced in reforming processes where the process air compressor is driven by a gas turbine and in cases when electric power is used for the main compressors and can be used as export.
Processes with gas heated primary reforming may be designed for zero steam export even though some power import or gas turbine drive steam input is needed.

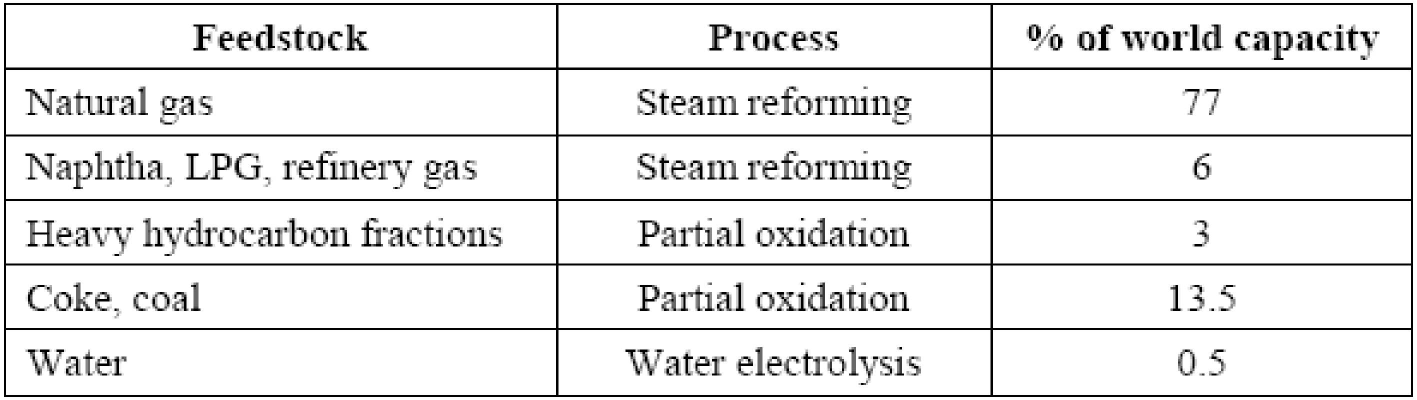
The partial oxidation process will have a steam deficit if all of the compressors are driven by steam.

Process development

Currently, about 80 % of the ammonia production capacity worldwide is provided by the well-developed steam reforming process.
High level process integration, innovative equipment design and improved catalysts are the main characteristics of ammonia plants today.

Applied processes and feed stocks in the production of ammonia

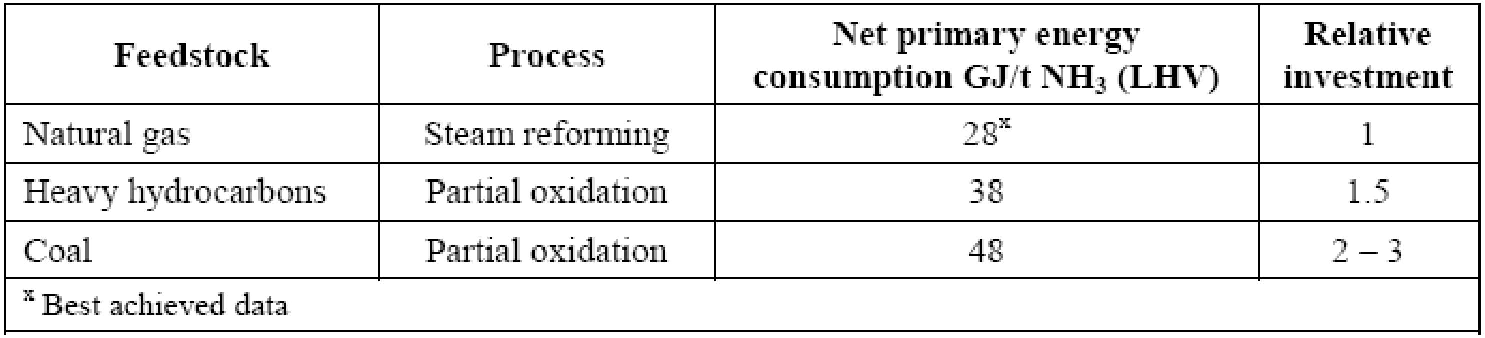
The third column shows the related share of world capacity (1990)



Feedstock	Process	% of world capacity
Natural gas	Steam reforming	77
Naphtha, LPG, refinery gas	Steam reforming	6
Heavy hydrocarbon fractions	Partial oxidation	3
Coke, coal	Partial oxidation	13.5
Water	Water electrolysis	0.5

Cost differences and total energy demands for ammonia production

[European Commission, 1997]



Feedstock	**Process**	**Net primary energy consumption GJ/t NH_3 (LHV)**	**Relative investment**
Natural gas	Steam reforming	28[x]	1
Heavy hydrocarbons	Partial oxidation	38	1.5
Coal	Partial oxidation	48	2 – 3

[x] Best achieved data

Urea // $H_2N\text{–}CO\text{–}NH_2$, $t_t = 132.7\ ^{o}C$

The commercial synthesis of urea is achieved by the reaction of ammonia and carbon dioxide at high pressure forming ammonium carbamate, which is then dehydrated by applying heat, forming urea and water:

$$2\ NH_3 + CO_2 \overset{1.}{\rightleftharpoons} \underset{\text{Ammonium carbamate}}{NH_4COONH_2} \xrightarrow{2} \underset{\text{Urea}}{NH_2\text{–}CO\text{–}NH_2} + H_2O$$

Both reactions take place in the liquid phase in the same reactor and are in equilibrium.
The yield depends on various operating parameters.
Reaction 1 is fast and exothermic and essentially goes to completion under the industrial reaction conditions used. Reaction 2 is slower and endothermic and does not go to completion. The conversion (on a CO_2 basis) is usually in the order of 50 – 80 %. The conversion increases with increasing temperature and NH_3/CO_2 ratio and decreases with increasing H_2O/CO_2 ratio.

Typical urea production parameters

Parameter		Unit
Pressure	140 – 250	bar
Temperature	180 – 210	°C
NH_3/CO_2 ratio	2.8:1 – 4:1	molar ratio
Retention time	20 – 30	minutes

Several side reactions may occur in urea synthesis.

The most relevant equilibrium reactions are:

- hydrolysis of urea:

$$CO(NH_2)_2 + H_2O \; = \; NH_2COONH_4 = \; 2\,NH_3 + CO_2$$

- formation of biuret:

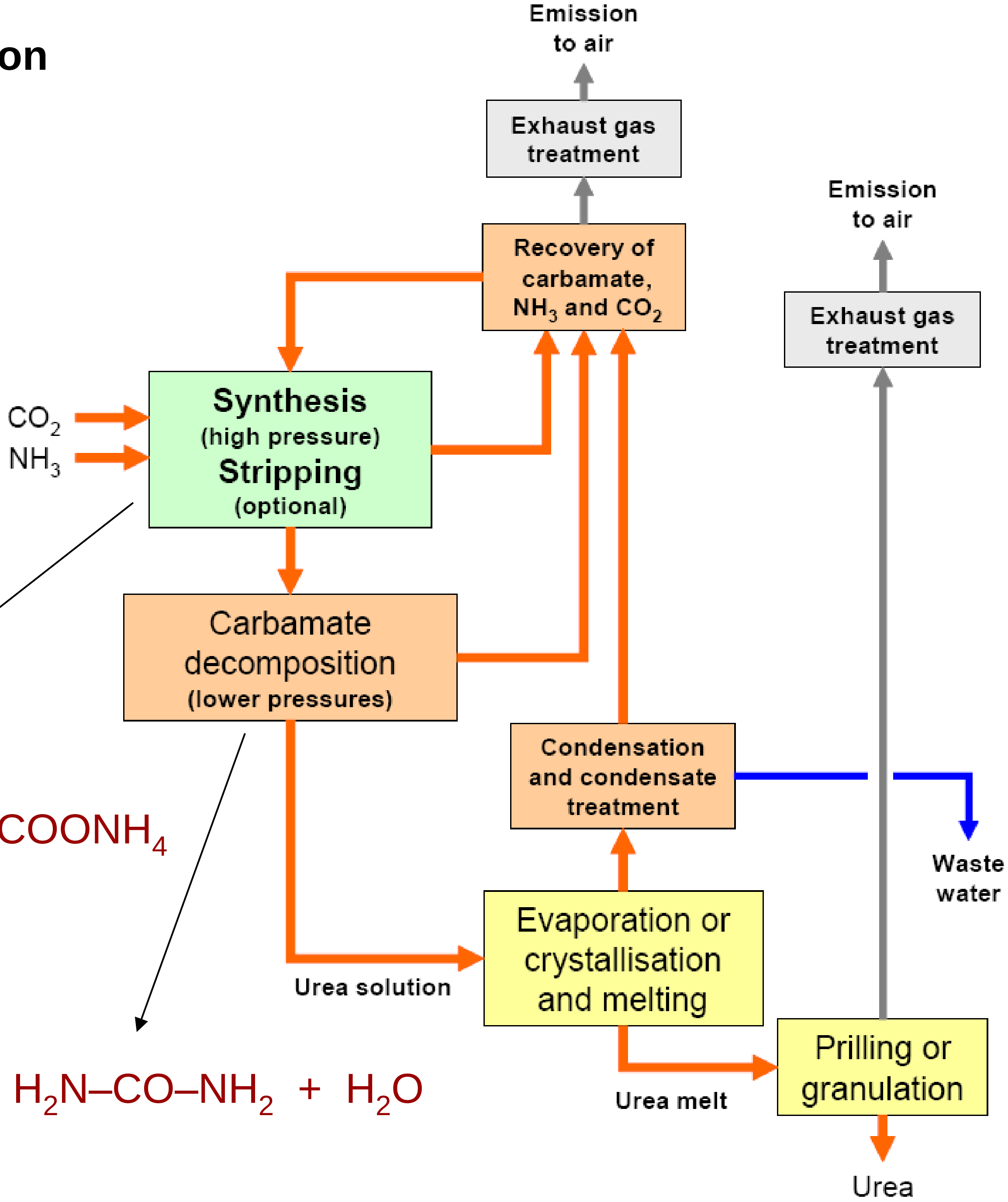
$$2\,CO(NH_2)_2 = NH_2CONHCONH_2 + NH_3$$

- formation of isocyanic acid:

$$CO(NH2)_2 = NH_4NCO = NH_3 + HNCO$$

The hydrolysis reaction is the reverse reaction of the urea formation and only takes place in the presence of water.
Acids or alkaline solutions can also accelerate the rate of hydrolysis. In practice, residence times of urea solutions with low NH_3 content at high temperatures must be minimised. Biuret must be limited in fertiliser urea (preferably maximum of 1.2 % EC), since biuret might cause crop damage, notably during foliage spraying. In technical urea (e.g. used in the production of synthetic resins), the biuret content is generally up to 0.3 – 0.4 % or much lower (even <0.15 %) depending on customer requirements.
Low NH_3 concentrations and high temperatures also favour the formation of isocyanic acid, especially in the evaporation section of the plant, the reaction equilibrium forming isocyanic acid is shifted to the right.
At an economical conversion rate of NH_3 and CO_2 to urea, the process design intends nowadays to efficiently separate product urea from the other reaction components, to recover excess NH_3, and to decompose residual ammonium carbamate to NH_3 and CO_2 for recycling into the process (“total recycling processes”). This is usually realised by stripping (still at high pressure)
And subsequent depressurisation/heating of the urea solution or combinations of both.

Overview of the production of urea by total recycling processes



Emission to air

Exhaust gas treatment

Recovery of carbamate, NH_3 and CO_2

Emission to air

Exhaust gas treatment

CO_2

NH_3

Synthesis
(high pressure)
Stripping
(optional)

Carbamate decomposition
(lower pressures)

Condensation and condensate treatment

Waste water

Urea solution

Evaporation or crystallisation and melting

Urea melt

Prilling or granulation

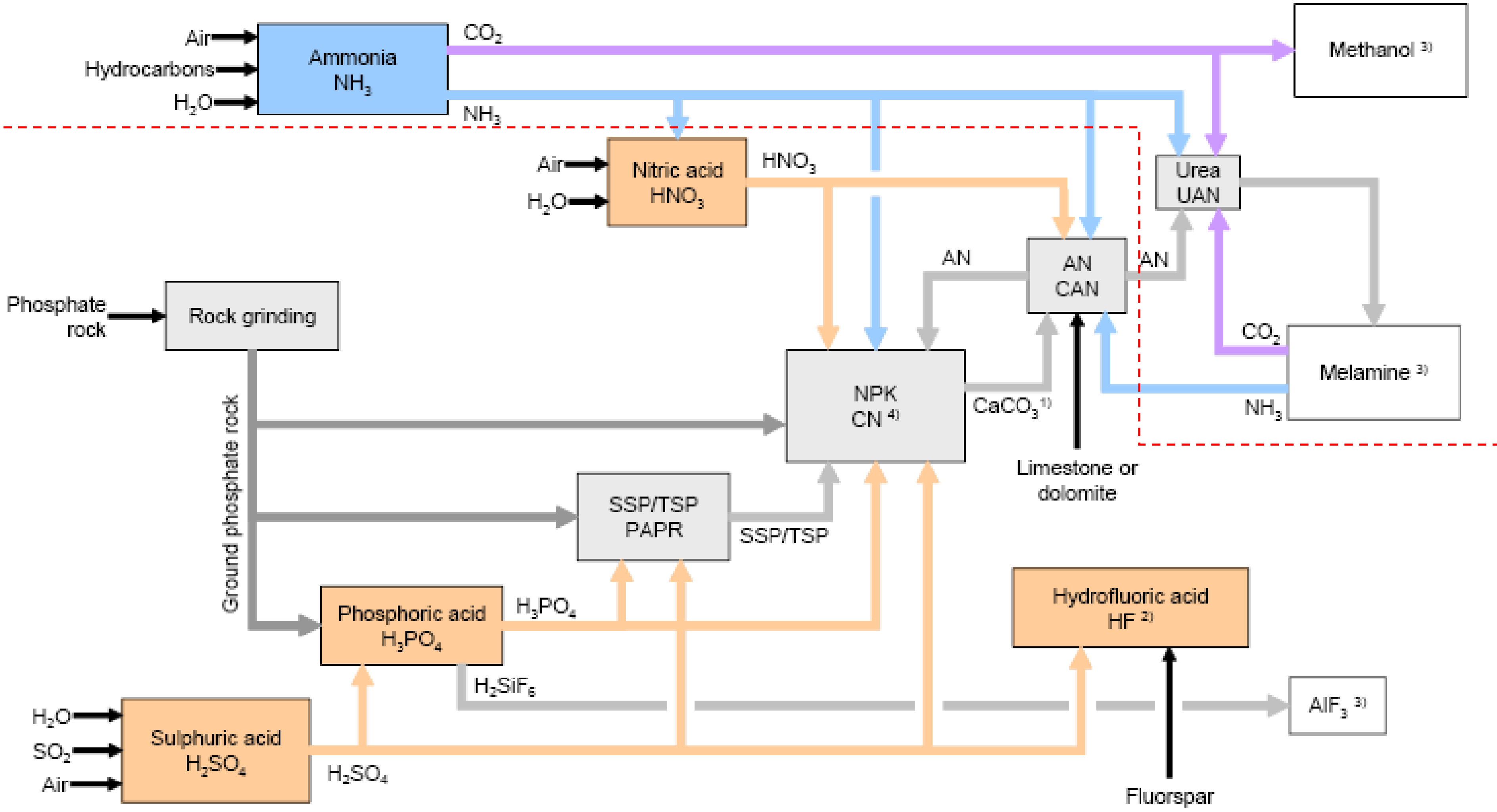
Urea

$$2\,NH_3 + CO_2 \rightleftharpoons NH_2COONH_4$$

$\Delta H = -100.5$ kJ mol^{-1}

$$H_2NCOONH_4 \underset{CO_2,\ NH_3}{\overset{180°C}{\rightleftharpoons}} H_2N{-}CO{-}NH_2 + H_2O$$

$\Delta H = +27.6$ kJ mol^{-1}



Overview of boundaries and links between the **Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers** / LVIC-AAF industries

(1) only with NPK production using the nitrophosphate route (2) not typically produced on fertiliser sites
(3) not described in this document 4) CN is $Ca(NO_3)_2$, and is alternatively produced by neutralisation of HNO_3 with lime

BAT - Example - Ammonia production

Process types

- Two basic types of NH_3 synthesis:

1. Steam reforming of natural gas or light hydrocarbons
   (85 % of world NH_3 production)
2. Partial oxidation of heavy gas oil or vacuum residue

Steam reforming of natural gas

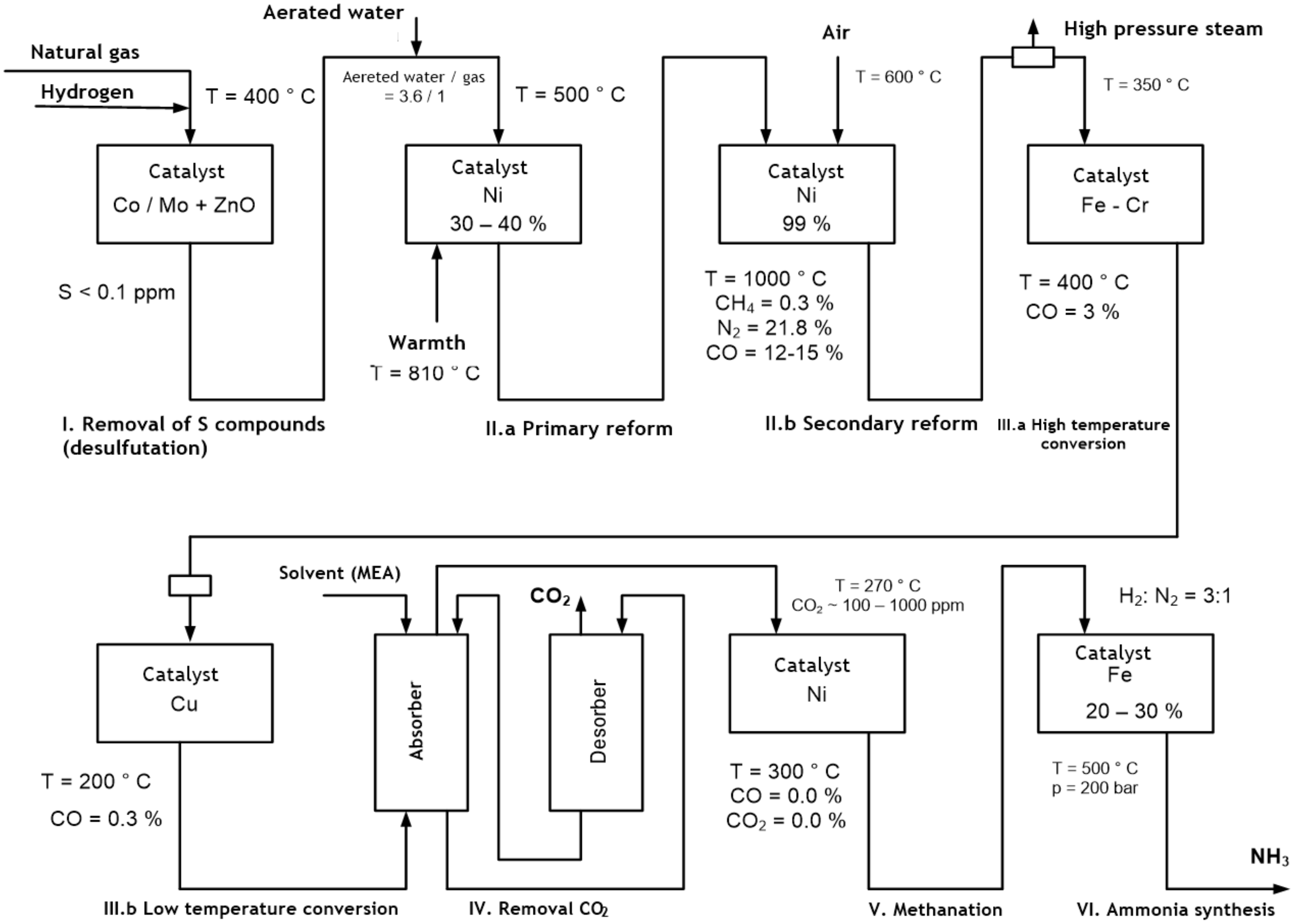
- the easiest and the most efficient way of NH_3 synthesis
- **dominant BAT for ammonia production**
- other types of synthesis (partial oxidation of heavy gas oil, coal gasification) - it can be considered as BAT only in special conditions

	Natural gas	Heavy gas oil	Coal
Energy consumption	1.0	1.3	1.7
Investment costs	1.0	1.4	2.4
Production costs	1.0	1.2	1.7

Process description: steam reforming of natural gas – 6 basic steps

Main raw materials: **air** (N_2, O_2, Ar, CO_2), **natural gas** ($CH_4 \rightarrow H_2$) & **aerated water**

Synthesis conditions: *p* = 200 bar, *T* = 500 °C; BAT capacity = 1500 t d^{-1} NH_3



Natural gas
Hydrogen
T = 400 ° C
Catalyst
Co / Mo + ZnO
S < 0.1 ppm
I. Removal of S compounds (desulfutation)

Aerated water
Aereted water / gas = 3.6 / 1
T = 500 ° C
Catalyst
Ni
30 – 40 %
Warmth
T = 810 ° C
II.a Primary reform

Air
T = 600 ° C
Catalyst
Ni
99 %
T = 1000 ° C
CH_4 = 0.3 %
N_2 = 21.8 %
CO = 12-15 %
II.b Secondary reform

High pressure steam
T = 350 ° C
Catalyst
Fe - Cr
T = 400 ° C
CO = 3 %
III.a High temperature conversion

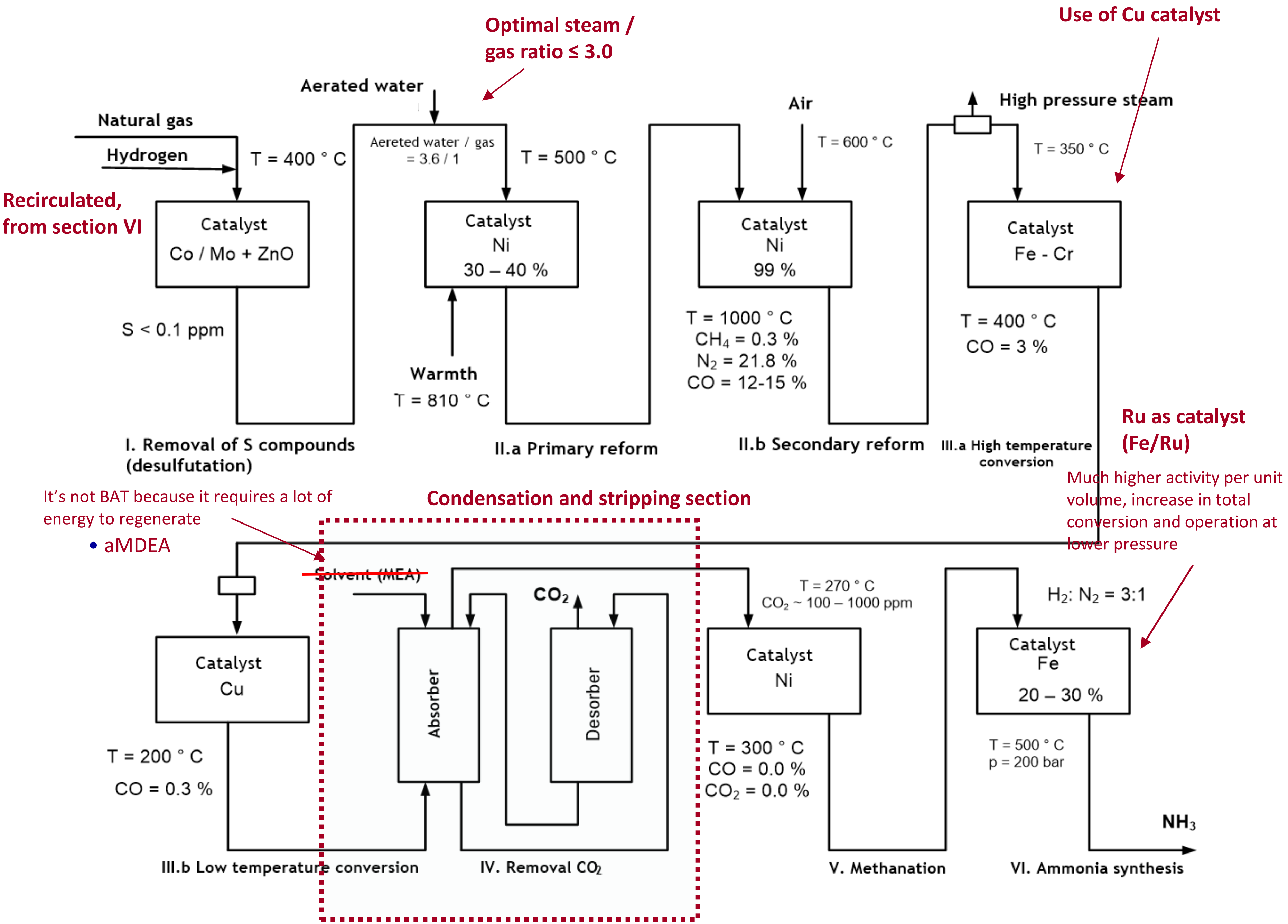
Catalyst
Cu
T = 200 ° C
CO = 0.3 %
III.b Low temperature conversion

Solvent (MEA)
Absorber
CO_2
Desorber
IV. Removal CO_2

T = 270 ° C
CO_2 ~ 100 – 1000 ppm
Catalyst
Ni
T = 300 ° C
CO = 0.0 %
CO_2 = 0.0 %
V. Methanation

H_2: N_2 = 3:1
Catalyst
Fe
20 – 30 %
T = 500 ° C
p = 200 bar
NH_3
VI. Ammonia synthesis

Steam reforming of natural gas – **BAT –** energy independent plant



Optimal steam / gas ratio ≤ 3.0

Use of Cu catalyst

Recirculated, from section VI

Natural gas

Hydrogen

T = 400 ° C

Catalyst
Co / Mo + ZnO

S < 0.1 ppm

I. Removal of S compounds (desulfutation)

Aerated water

Aereted water / gas = 3.6 / 1

T = 500 ° C

Catalyst
Ni
30 – 40 %

Warmth
T = 810 ° C

II.a Primary reform

Air

T = 600 ° C

Catalyst
Ni
99 %

T = 1000 ° C
CH_4 = 0.3 %
N_2 = 21.8 %
CO = 12-15 %

II.b Secondary reform

High pressure steam

T = 350 ° C

Catalyst
Fe - Cr

T = 400 ° C
CO = 3 %

III.a High temperature conversion

Ru as catalyst (Fe/Ru)

Much higher activity per unit volume, increase in total conversion and operation at lower pressure

It’s not BAT because it requires a lot of energy to regenerate

- aMDEA

Condensation and stripping section

~~Solvent (MEA)~~

Catalyst
Cu

T = 200 ° C
CO = 0.3 %

III.b Low temperature conversion

Absorber

Desorber

CO_2

IV. Removal CO_2

T = 270 ° C
CO_2 ~ 100 – 1000 ppm

Catalyst
Ni

T = 300 ° C
CO = 0.0 %
CO_2 = 0.0 %

V. Methanation

H_2: N_2 = 3:1

Catalyst
Fe
20 – 30 %

T = 500 ° C
p = 200 bar

NH_3

VI. Ammonia synthesis

Application of BAT on new ammonia synthesis plants

Development directions:

- reduction of steam/gas ratio
- load transfer from primary to the secondary reformer
- improve the final purity of the product
- improve the efficiency of the synthesis loop
- improve the energy efficiency
- reduce NOx emissions
- find a better catalyst for ammonia synthesis

Harmful emissions and solid waste

Air emissions

Main sources:

- flue gases from the primary reformer – CO_2, NO_x, SO_2 and CO
- exhaust gases from the CO_2 removal units – CO_2
- waste gas from the ammonia synthesis section – NH_3, NO_x
- discontinuous emissions – NO_2

Emissions into water

Main sources:

- condensate after low-temperature section
- waste gas washing water

Solid waste

Main sources:

- spent catalyst
- molecular sieves

Air emissions

I. source: flue gases from the primary reformer

CO_2: 500 kg CO_2 / t NH_3
NO_x: 0.6 – 1.3 kg NO_2 / t NH_3
SO_2: 0.01 kg SO_2 / t NH_3 – depending on the fuel
CO: 0.03 kg CO / t NH_3

Basic steps to reduce harmful NO_x emissions:

- low content of NH_3 in the waste gas
- a small excess of O_2

II. source: exhaust gases from the CO_2 removal unit

More or less CO_2 must be released into the atmosphere, and this gas contains NH_3 in traces

- if CO_2 is needed in other production units then it can be used (urea production)

III. source: waste gas from the ammonia synthesis section

It is necessary to remove as much NH_3 as possible from the waste gas because it contributes significantly to harmful NO_x emissions in/from flue gases

Ammonia is separated from the waste gas by washing with water, then it separates from the water by distillation and returns to the process

IV. source: discontinuous emissions

NO_x: 10-20 kg h^{-1}

Emissions to water

I. source: condensate after low-temperature section

- The process gas after the low-temperature section contains H_2, N_2, CO_2 and aereted water in excess which need to condense

CONDENSATE: if it's left untreated it may contain 1 kg NH_3 / m_3 and 1 kg methanol / m^3
- recovery by stripping and recirculation into a process where it can be used as boiler water

II. source: waste gas washing water

- the amount of ammonia depends on the success of the distillation process which leads to the separation of water and ammonia

Solid waste

Sources: spent catalyst and molecular sieves

BAT ammonia production process does not generate solid waste because these sources are separated from the process, and precious metals are recovered

Monitoring and control of harmful emissions into the air

Monitoring is necessary for:

NO_x emmisions – in flue gas

SO_2 emmisions – in flue gas

Monitoring is not required for:

CO_2 emisions

CO emisions

- discontinuous emissions are difficult to track/follow!

Frequency of control: **1 per month**

Analytical control methods:

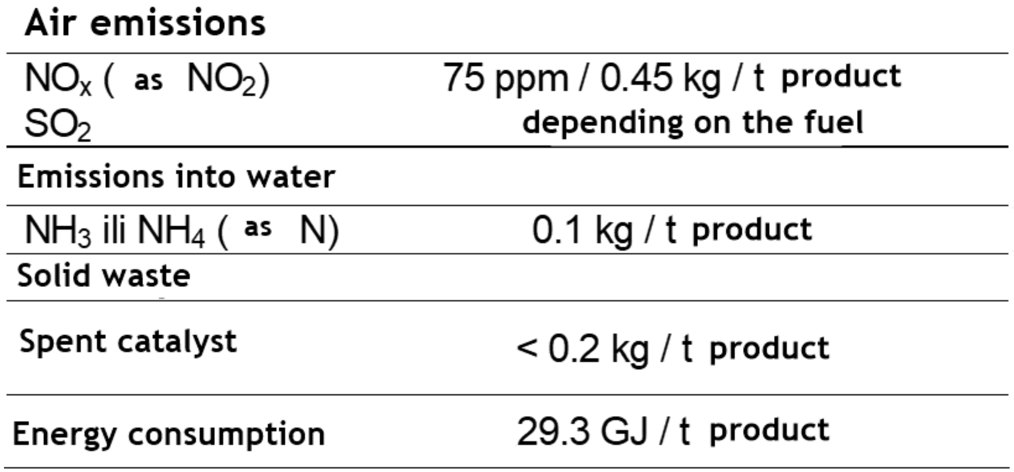
For NO_x emissions – Photometry

For SO_2 emissions – IR spectrometry

Monitoring and control of harmful emissions into water

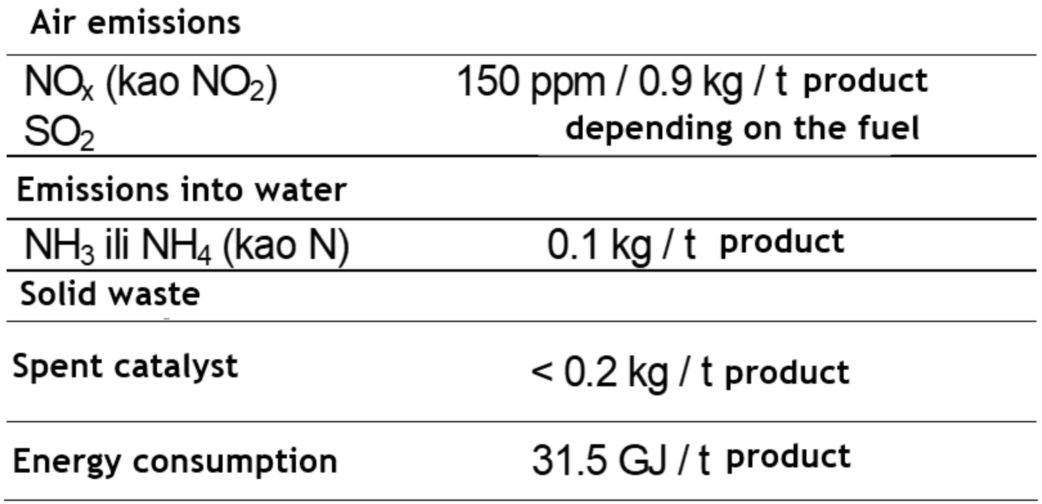
- Monitoring is not required if there is recirculation of condensate into the process;
- If there is no condensate recirculation, it is necessary to measure the amount of ammonia and methanol in the effluent (spectrophotometry).

Harmful emission limit values (ELVs) that can be achieved at new NH_3 synthesis plants:

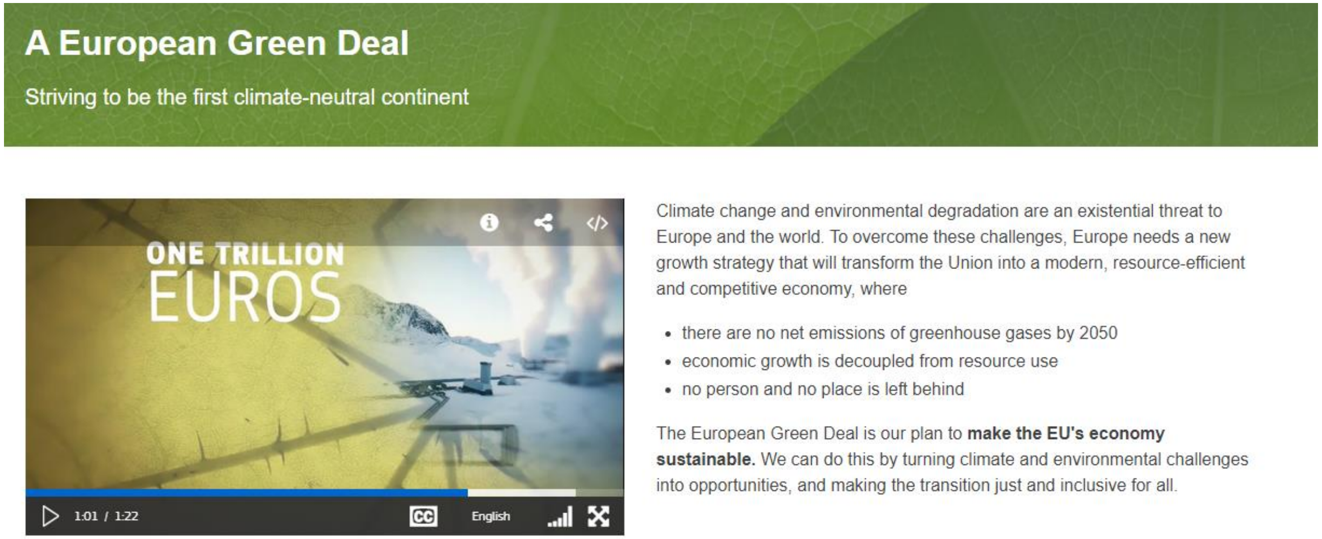


Air emissions	
NO_x (as NO_2)	75 ppm / 0.45 kg / t product
SO_2	depending on the fuel
Emissions into water	
NH_3 ili NH_4 (as N)	0.1 kg / t product
Solid waste	
Spent catalyst	< 0.2 kg / t product
Energy consumption	29.3 GJ / t product

Harmful emission limit values (ELVs) that can be achieved at existing NH_3 synthesis plants:



Air emissions	
NO_x (kao NO_2)	150 ppm / 0.9 kg / t product
SO_2	depending on the fuel
Emissions into water	
NH_3 ili NH_4 (kao N)	0.1 kg / t product
Solid waste	
Spent catalyst	< 0.2 kg / t product
Energy consumption	31.5 GJ / t product



A European Green Deal

Striving to be the first climate-neutral continent

Climate change and environmental degradation are an existential threat to Europe and the world. To overcome these challenges, Europe needs a new growth strategy that will transform the Union into a modern, resource-efficient and competitive economy, where

- there are no net emissions of greenhouse gases by 2050
- economic growth is decoupled from resource use
- no person and no place is left behind

The European Green Deal is our plan to **make the EU's economy sustainable.** We can do this by turning climate and environmental challenges into opportunities, and making the transition just and inclusive for all.

Action plan to boost the efficient use of resources by moving to a clean, circular economy, restore biodiversity and cut pollution. The plan outlines investments needed and financing tools available.

The EU aims to be climate neutral in 2050. We proposed a European Climate Law to turn this political commitment into a legal obligation. Reaching this target will require action by all sectors of our economy, including:

- investing in environmentally-friendly technologies
- supporting industry to innovate
- rolling out cleaner, cheaper and healthier forms of private and public transport
- decarbonising the energy sector
- ensuring buildings are more energy efficient

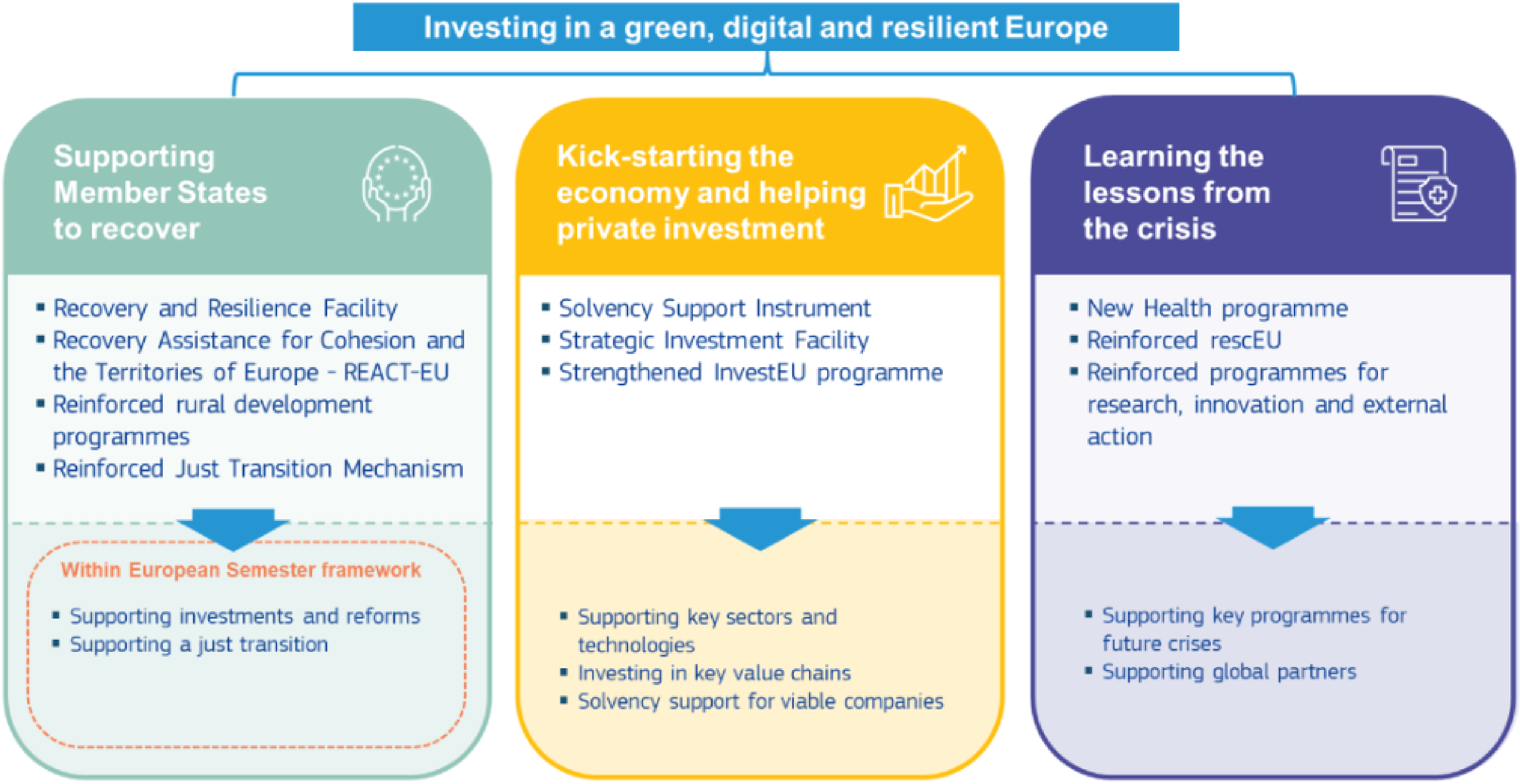
The EU will also provide financial support and technical assistance to help those that are most affected by the move towards the green economy. This is called the Just Transition Mechanism. It will help mobilise at least €100 billion over the period 2021-2027 in the most affected regions.

Povoljne okolnosti

Next Generation EU - a new recovery instrument of €750 billion which will boost the EU budget with new financing raised on the financial markets for 2021-2024

Postizanje samodostatnosti:

- Proizvodnja hrane (površine, voda, gnojivo, sjeme)
- Proizvodnja energije (goriva) i strateških materijala
- Proizvodnja aktivnih komponenti lijekova (povratak proizvodnje iz Azije)



Investing in a green, digital and resilient Europe

Supporting Member States to recover

- Recovery and Resilience Facility
- Recovery Assistance for Cohesion and the Territories of Europe - REACT-EU
- Reinforced rural development programmes
- Reinforced Just Transition Mechanism

Within European Semester framework

- Supporting investments and reforms
- Supporting a just transition

Kick-starting the economy and helping private investment

- Solvency Support Instrument
- Strategic Investment Facility
- Strengthened InvestEU programme

- Supporting key sectors and technologies
- Investing in key value chains
- Solvency support for viable companies

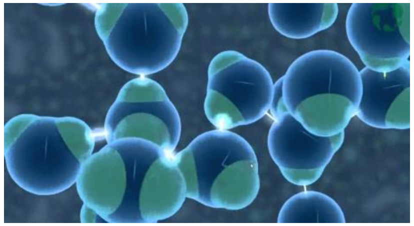
Learning the lessons from the crisis

- New Health programme
- Reinforced rescEU
- Reinforced programmes for research, innovation and external action

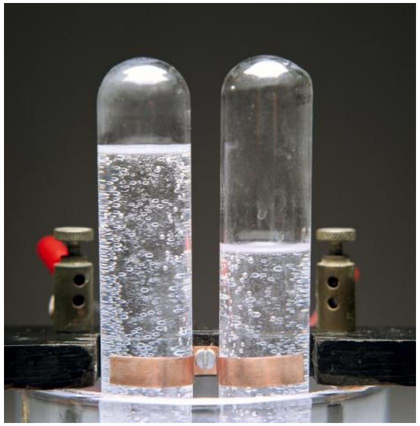
- Supporting key programmes for future crises
- Supporting global partners

Source: European Commission

Green Hydrogen by Water Electrolysis



$2\ H_2O\ (l) \rightarrow 2\ H_2(g) + O_2(g)$



More in News, Power Plants, Projects, Markets & Finance, Policy, Europe

France backs green hydrogen as part of €30bn green energy package

By Jules Scully | Sep 07, 2020 11:16 AM BST | 0

Image: Twitter/LANGA Group.

Almost a third of France's €100 billion (US$118.2 billion) coronavirus recovery package will be directed towards greener energy policies, as the country ramps up expenditure on hydrogen production.

Some €30 billion of the plan will be spent on an "ecological transition", including efforts to make buildings more energy efficient and ensure France is at the forefront of green hydrogen, the country's prime minister, Jean Castex, noted. "Relaunch France is first and foremost a plan intended to serve the climate and biodiversity," he said.

Announcing the package – which has employment, environment and competitiveness as its three pillars – last week, Castex said the money would be spent over the next two years to help the economy to recover to its pre-crisis level by 2022.

„With energy consumption representing nearly 70% of France's greenhouse gas emissions, the government said the scheme should be an opportunity for the country to spearhead low-carbon hydrogen production. A total of €7 billion will be spent by 2030 to develop green hydrogen, including funding for research projects focused on carbon-free solutions based on hydrogen for the maritime and aviation industries."

11

JUN 2020

The Netherlands Preparing for GW-Scale Hydrogen Production

5 potential industrial regions have been designated for large-scale green hydrogen production.

Currently the Dutch annual industrial hydrogen demand is 1.2 million ton. This demand will significantly increase in the coming decade and the production methods need to be "green", fueled by renewable electricity. New markets like transport will need to be serviced. More than 10 GW electricity will be needed as input and most will come from offshore North Sea wind. Currently electrolyzers are in the MW range, not GW. The GW-hydrogen plant will need up to 8 hectare. In all 5 regions locations with sufficient space can be found. Bottleneck is the electricity infrastructure, not so much the gas infrastructure. Bringing renewable electricity from all those turbines and panels to the hydrogen plants will be more costly than handling the resulting hydrogen.

Next stop, hydrogen-powered trains

'World's first' hydrogen-powered train enters into service

PUBLISHED MON, SEP 17 2018 5:29 AM
UPDATED TUE, APR 21 2020 5:41 AM

European railway manufacturer Alstom has launched what it says is the world's first hydrogen fuel cell train. Alstom's Coradia iLint uses fuel cells that turn hydrogen and oxygen into electricity, and can travel up to 140 kilometers per hour. Two models of the low-noise, zero-emissions train will enter commercial service in Lower Saxony, Germany, today.

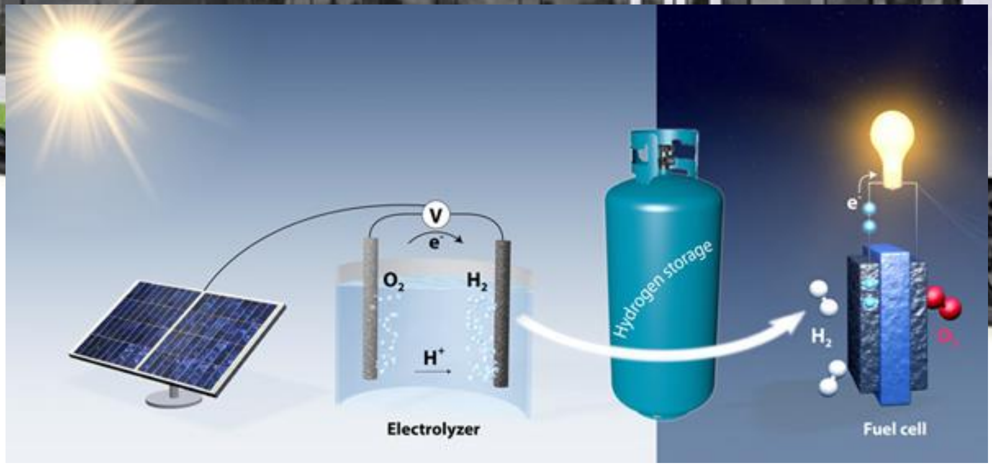
Engineers working on the Hydroflex say that hydrogen-powered trains could be the answer to decarbonising the UK's rail system without incurring the high cost of electrifying its track. According to an assessment of 20 lines in Britain and mainland Europe, electrifying a single kilometer of track can cost £750,000 to £1m ($965,000 to $1.3m). Hydrogen-powered trains are less expensive, because they don't require massive track overhauls and they can be created by retrofitting existing diesel trains. This is especially beneficial in rural areas where there are more miles to cover, but fewer passengers to justify the expense.

https://www.bbc.com/future/article/20200227-how-hydrogen-powered-trains-can-tackle-climate-change

FORBES / EDITORS' PICK|23,342 views|Dec 29, 2019,08:00am EST

Heavy-Duty Hydrogen: Fuel Cell Trains And Trucks Power Up For The 2020s

The first zero-emission “hydrail” project in the U.S. will be in southern California, where the San Bernardino County Transportation Authority plans to operate a FLIRT H2 train from Swiss supplier Stadler from 2024. The first train, with two cars and a rooftop power pack containing fuel cells and hydrogen tanks, will run on a 9-mile commuter rail line between San Bernardino and Redlands, under a contract worth $23.5 million, according to the SBCTA, with an option to purchase four more trains.



Rosen Group headed for hydrogen

9/3/2020

With more than 30 years of experience in pipeline integrity management, the ROSEN Group is investing in a new challenge to support operators in the transition towards a low-carbon future. The company has been developing a holistic approach for managing the integrity of hydrogen pipelines. This approach can be applied to the conversion of existing natural gas pipeline grids to hydrogen, or used to new build networks.

Canada has big plans to use hydrogen to cut emissions - and produce more oil

9/4/2020

Alberta will announce no later than October a strategy to develop "blue hydrogen" as a cleaner alternative to using natural gas to extract crude at steam-driven oil sands sites, Associate Minister of Natural Gas Dale Nally told Reuters in an interview. "Reducing the carbon intensity of the oil sands would allow of course more expansion."

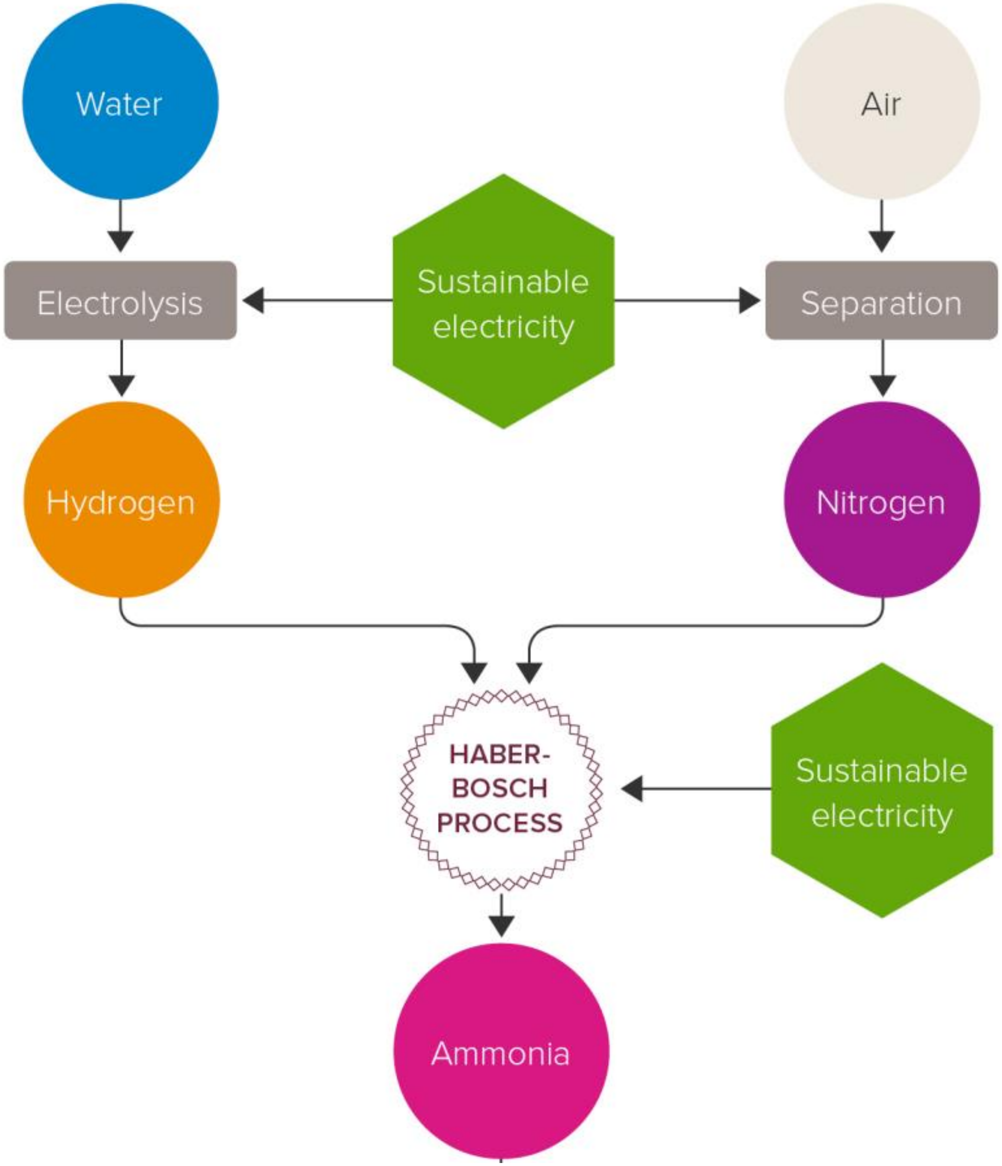
Blue hydrogen is produced from natural gas, with the carbon byproduct captured and stored.

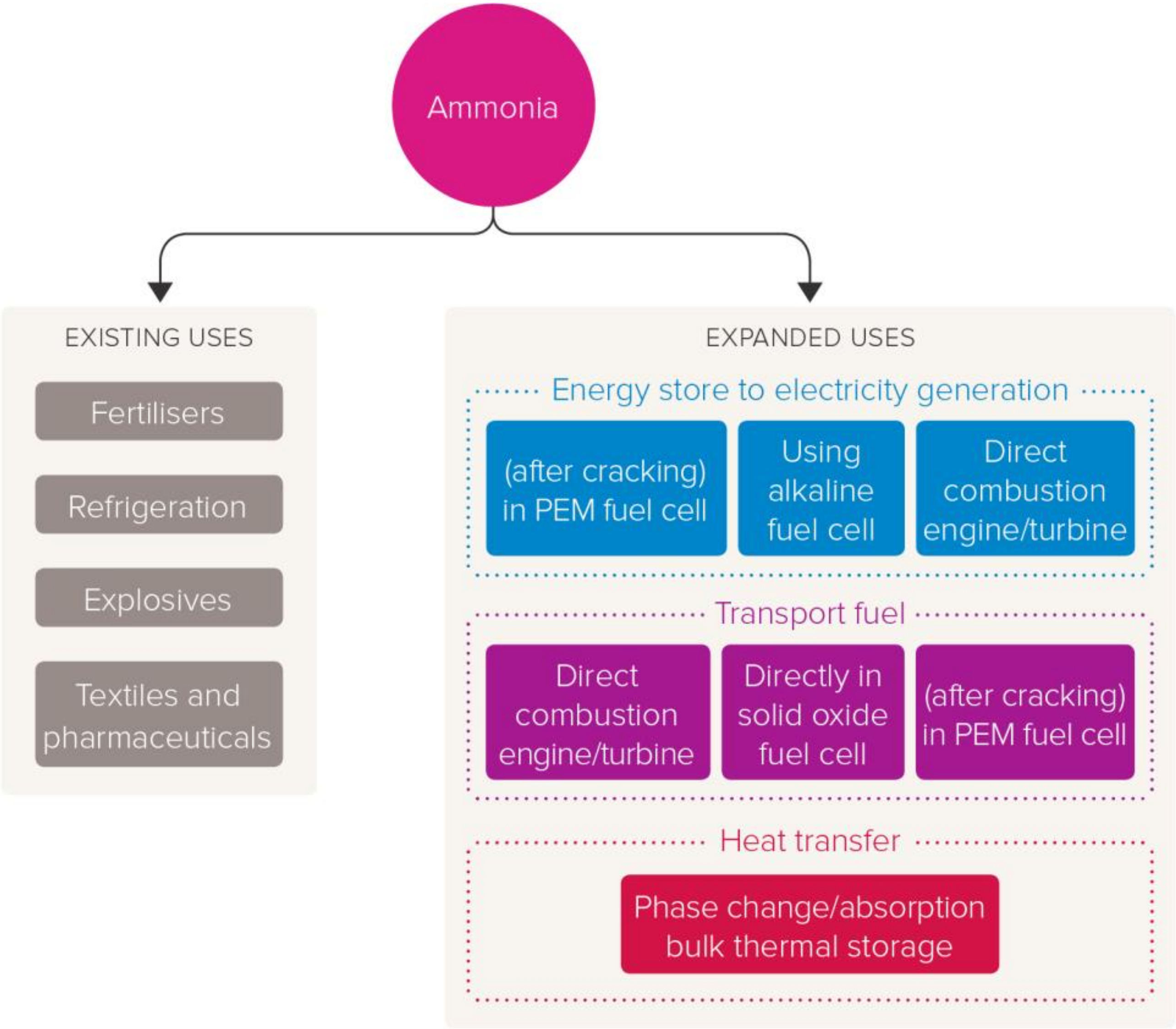
A green agenda to be launched by Trudeau this month is expected to map out a course to the 2050 zero-emissions target, and likely to include a strategy describing hydrogen as a "net-zero moon shot" for the petroleum sector.

"Cleaning up the oil and gas sector is going to be a necessary event if we are going to meet our 2050 target" of net-zero emissions, the source added.

The federal government's draft plan - three years in the making - says several provinces could produce hydrogen, some using renewable energy, and by 2050 the industry could create 100,000 jobs, generate more than C$5 billion in annual revenue and reduce annual greenhouse gas emissions by 100 megaton.

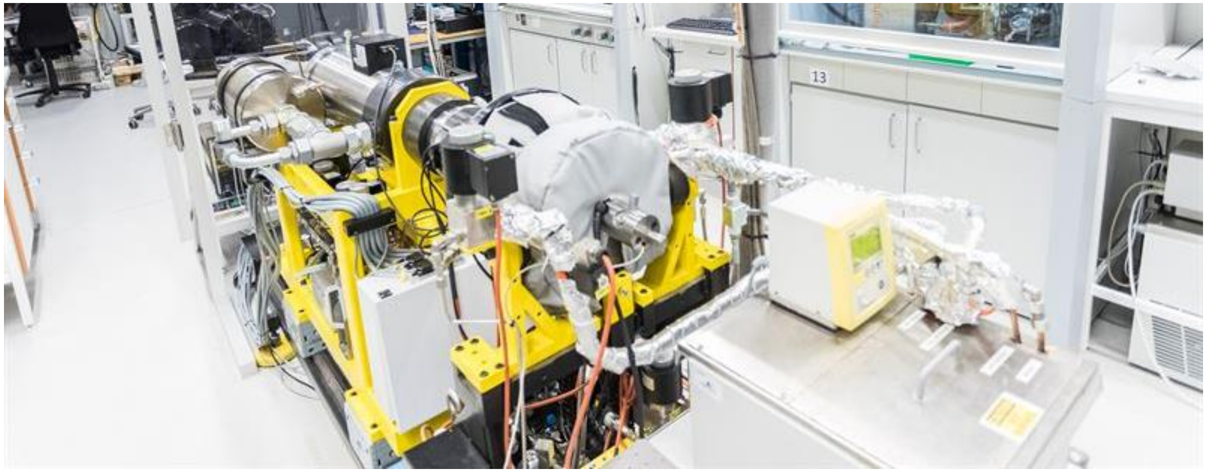
Green Ammonia




Ammonia
EXISTING USES
Fertilisers
Refrigeration
Explosives
Textiles and pharmaceuticals
EXPANDED USES
Energy store to electricity generation
(after cracking) in PEM fuel cell
Using alkaline fuel cell
Direct combustion engine/turbine
Transport fuel
Direct combustion engine/turbine
Directly in solid oxide fuel cell
(after cracking) in PEM fuel cell
Heat transfer
Phase change/absorption bulk thermal storage

Ammonia-Powered Internal Combustion Engines

Ammonia energy proponents look forward to the day when their fuel is used in internal combustion engines – but the state of this art is unsettled and it is not clear which combustion technologies will win in the end.



$NH_3 + O_2 \rightarrow N_2 + H_2O$

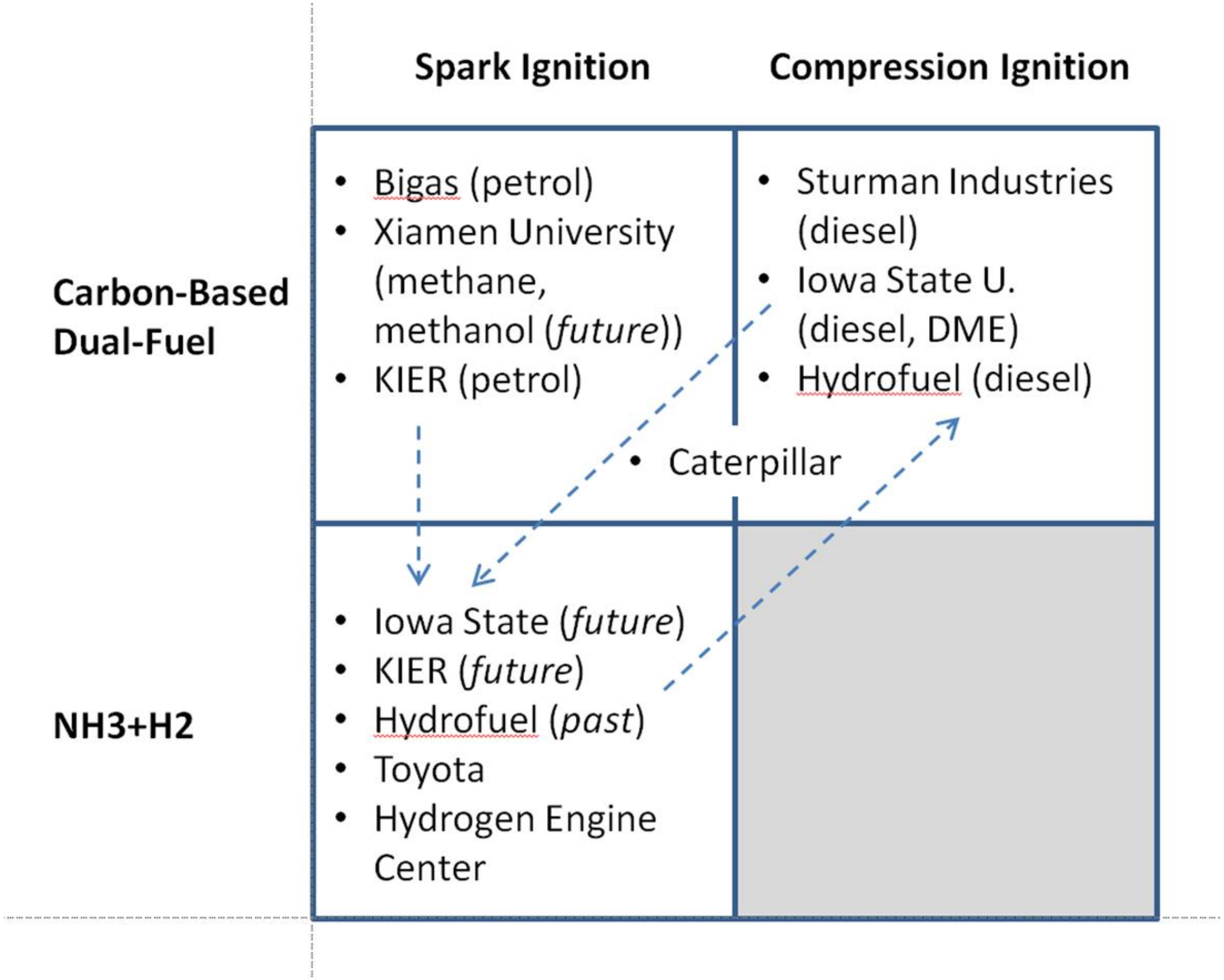
The Caterpillar Corporation put it succinctly in their 2008 patent application that covers a "power system having an ammonia-fueled engine": "When ammonia is combusted, the combustion produces a flame with a relatively low propagation speed . . . This low combustion rate of ammonia causes combustion to be inconsistent under low engine load and/or high engine speed operating conditions. Most existing combustion engines that use ammonia as engine fuel typically require a combustion promoter (i.e., a second fuel such as gasoline, hydrogen, diesel, etc.) for ignition, operation at low engine loads and/or high engine speed."

In other words, one option is to use a liquid combustion promoter. However, as the patent subsequently notes, this approach "generally requires dual fuel storage systems, dual delivery systems, and dual injection systems, thus adding additional weight, complexity, and cost to the engine system."

The second option is to use hydrogen as the combustion promoter. A promising variant of this approach is to place an on-board reformer between the fuel tank and the engine. The reformer can be set up to "crack" enough of the ammonia into hydrogen and nitrogen to support viable combustion.

https://www.ammoniaenergy.org/articles/ammonia-powered-internal-combustion-engines/

AmmoniaEnergy has assembled data on nine current and recent ICE development programs. They are about evenly distributed across three camps.



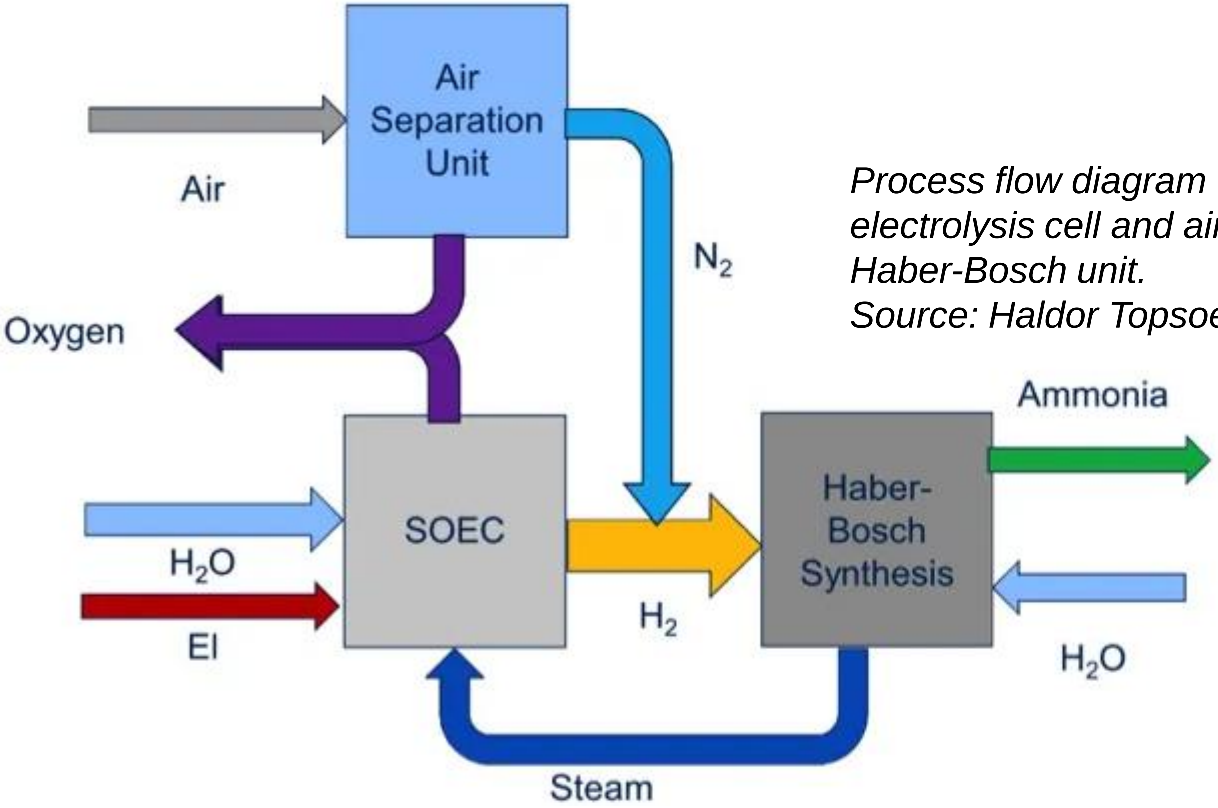
	Spark Ignition	**Compression Ignition**
Carbon-Based Dual-Fuel	• Bigas (petrol) • Xiamen University (methane, methanol (*future*)) • KIER (petrol)	• Sturman Industries (diesel) • Iowa State U. (diesel, DME) • Hydrofuel (diesel)
NH3+H2	• Iowa State (*future*) • KIER (*future*) • Hydrofuel (*past*) • Toyota • Hydrogen Engine Center	

- Caterpillar

Green ammonia: Haldor Topsoe's solid oxide electrolyzer (SOEC)

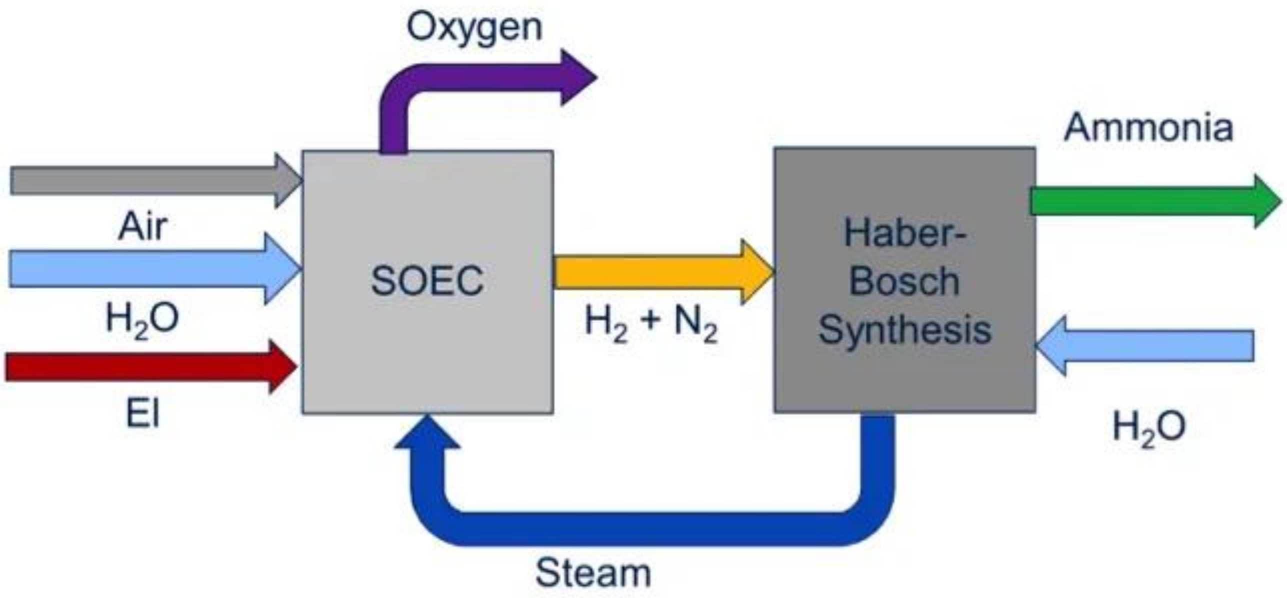
- SOC4NH3 project (2019-2022; USD $36 million)
- feasibility study for a small industrial-scale green ammonia pilot plant (1-2 metric ton per day), which it hopes to build by 2025; could be commercially available by 2030.

It has the potential to reduce both capex and opex, relative to other electrolyzer technologies but also relative to conventional ammonia plants using natural gas. The system has been designed to reduce capex by eliminating the need for an air separation unit (ASU). For opex, which is dominated by energy costs in any ammonia technology, the SOEC-HB is estimated to produce green ammonia with a specific energy consumption of about 7.2 MWh per ton, which is 26 GJ per ton. In other words, its green ammonia plant could be more energy efficient than today's best state-of-the-art natural gas-fed ammonia plant, which consumes around 28 GJ per ton.

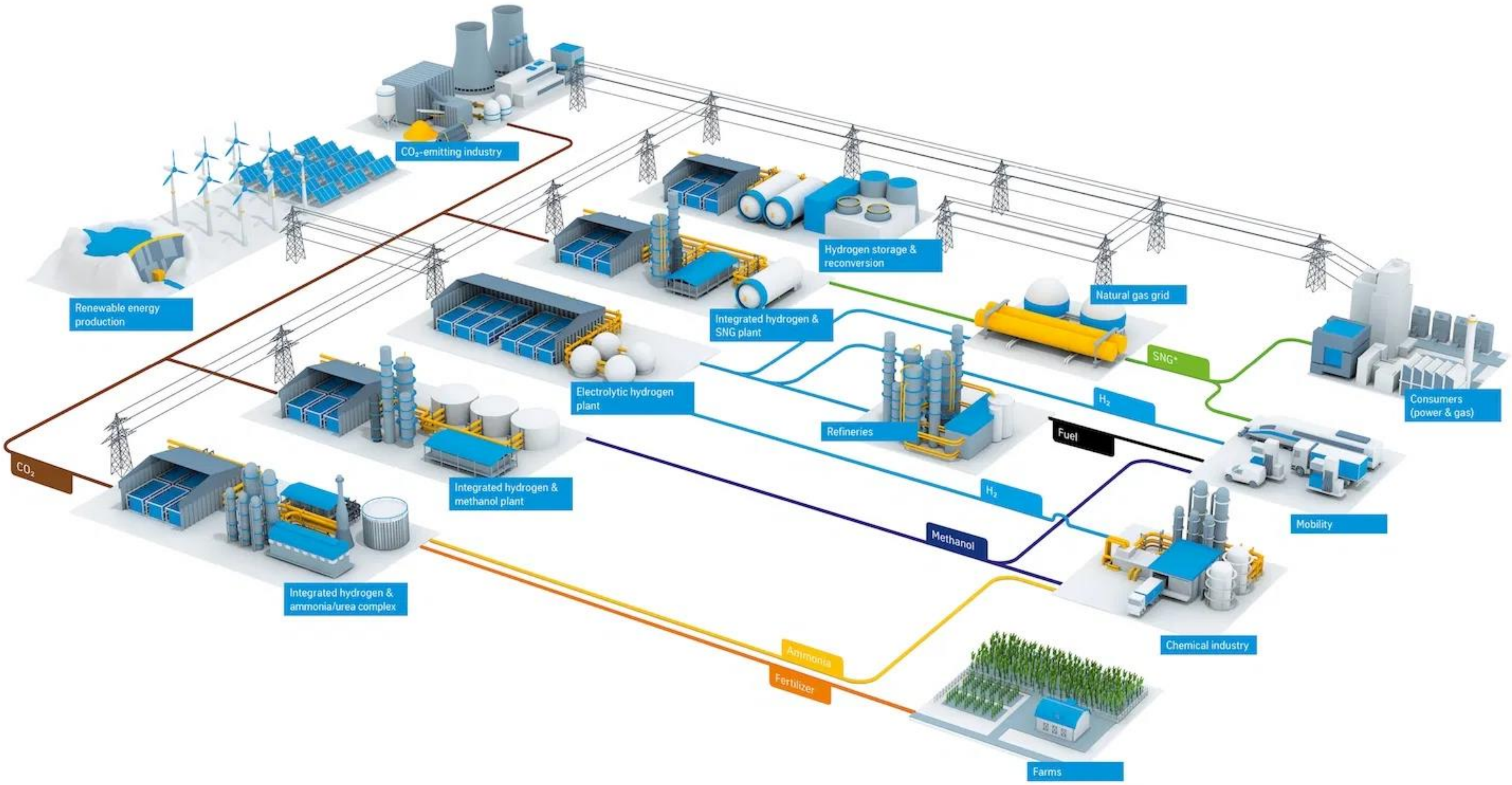


Process flow diagram to show solid oxide electrolysis cell and air separation unit feeding Haber-Bosch unit.
Source: Haldor Topsoe.

Process flow diagram to show solid oxide electrolysis cell producing both hydrogen and nitrogen to feed Haber-Bosch unit.
Source: Haldor Topsoe.

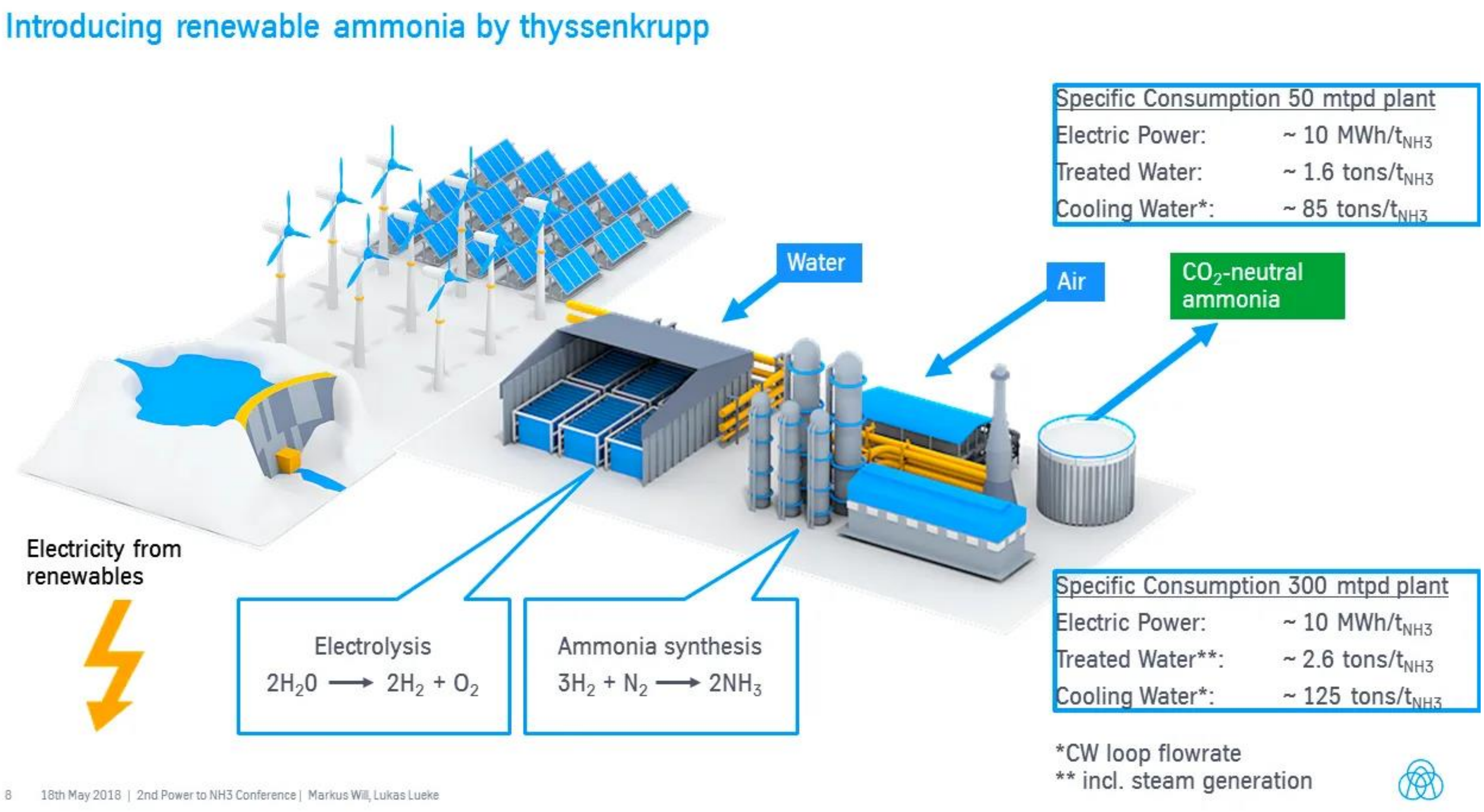


https://ammoniaindustry.com/haldor-topsoes-solid-oxide-electrolyzer/



Hydrogen value chains, ThyssenKrupp press release, 07/03/2018

The advanced water electrolysis features a well-proven cell design paired with an especially large active cell area of 2.7 m^2. By further optimizing the proven ‘Zero-Gap’ electrolysis technology (leaving virtually no gap between membrane and electrodes), very high efficiencies of more than 82% are achieved.
Sami Pelkonen, CEO of the Electrolysis & Polymers Technologies business unit
ThyssenKrupp press release, Key to a sustainable future: thyssenkrupp launches advanced water electrolysis, *06/20/2018*



Introducing renewable ammonia by thyssenkrupp

Specific Consumption 50 mtpd plant	
Electric Power:	~ 10 MWh/t_{NH3}
Treated Water:	~ 1.6 tons/t_{NH3}
Cooling Water*:	~ 85 tons/t_{NH3}

Water

Air

CO_2-neutral ammonia

Electricity from renewables

Electrolysis
$2H_20 \longrightarrow 2H_2 + O_2$

Ammonia synthesis
$3H_2 + N_2 \longrightarrow 2NH_3$

Specific Consumption 300 mtpd plant	
Electric Power:	~ 10 MWh/t_{NH3}
Treated Water**:	~ 2.6 tons/t_{NH3}
Cooling Water*:	~ 125 tons/t_{NH3}

*CW loop flowrate
** incl. steam generation

TASK - Option A. Green Ammonia Production - calculate and fill the table !

- 10 mass. % of annual anmonia produced by hydrogen from water electrolysis
- compressed green hydrogen is introduced into the ammonia synthesis loop; nitrogen is obtained conventionally
- emisions from fuel combustion and energy efficiency are not considered

1. Desulfurization (ZnO / HDS)

2.a Primary Reforming

2.b Secundary Reforming

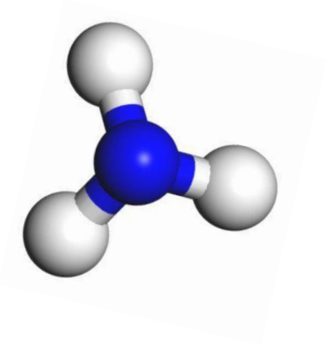
3. Water Gas Shift

4. CO_2 removal / H-T / L-T

5. CO & CO_2 Metanation

6. Ammonia Synthesis

	100 % NH_3	90 % NH_3	10 % NH_3	Δ
	t/y.	t/y.	t/y.	t/y.
NH_3	448.800	403.920	44.880	
CO_2				
CH_4				
O_2				
N_2				
H_2O				
H in NH_3				
H_2				
N in NH_3				



(1-6) $$CH_4 + 0{,}3035\ O_2 + 1{,}131\ N_2 + 1{,}393\ H_2O \longrightarrow 2{,}262\ NH_3 + CO_2$$

(water electrolysis) $$2\ H_2O \longrightarrow 2\ H_2 + O_2$$