Faculty of Chemical Engineering and Technology
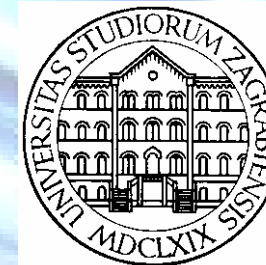University of Zagreb
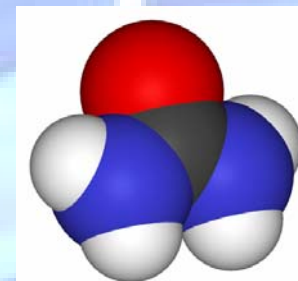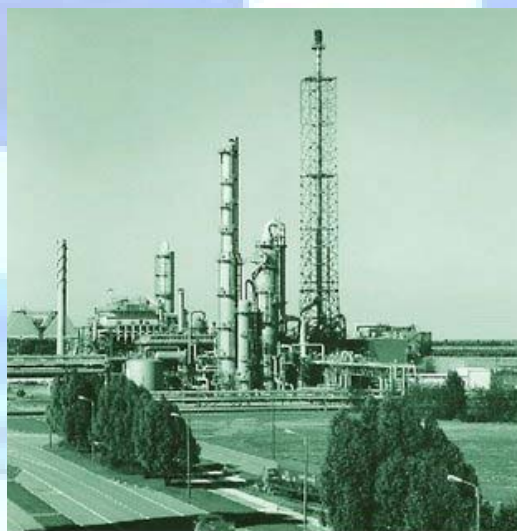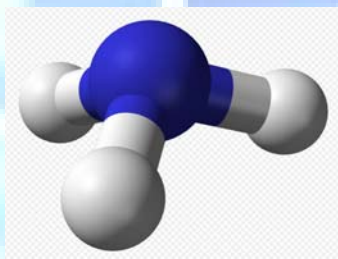
Petroleum Refining
and Petrochemical Processes

Ammonia & Urea

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FKITMCMXIX

AMMONIA

NH$_3$, t_v = −33.3 °C.

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

About 80 % of the ammonia is currently used as the <u>nitrogen source in fertilisers</u>, with the other 20 % being used in several industrial applications, such as the <u>manufacture of plastics, fibres, explosives, hydrazine, amines, amides, nitriles and other organic nitrogen compounds</u> 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.
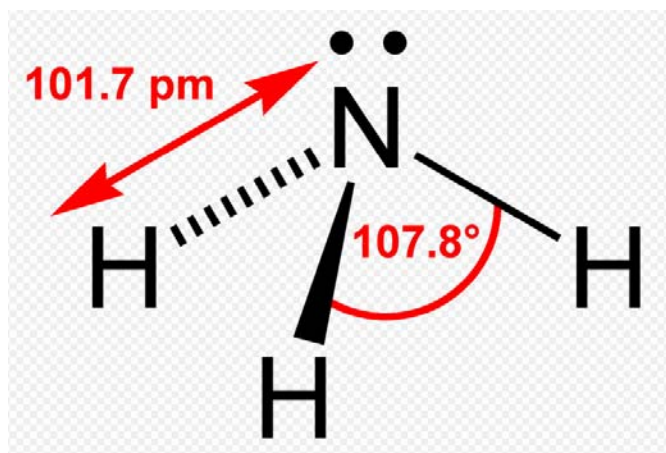
Ammonia is synthesised from nitrogen and hydrogen by the following reaction:

$$N_2 + 3\,H_2 \;\underset{k_2}{\overset{k_1}{\rightleftharpoons}}\; 2\,NH_3$$
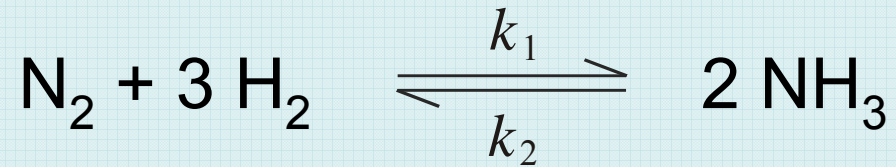
$$\Delta H = -92 \text{ kJ mol}^{-1}, \; \Delta S = -198 \text{ kJ mol}^{-1}, \; \Delta G = -16{,}3 \text{ kJ mol}^{-1}$$

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

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:

Nitrogen + Hydrogen $\rightleftharpoons$ Ammonia

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

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 °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)
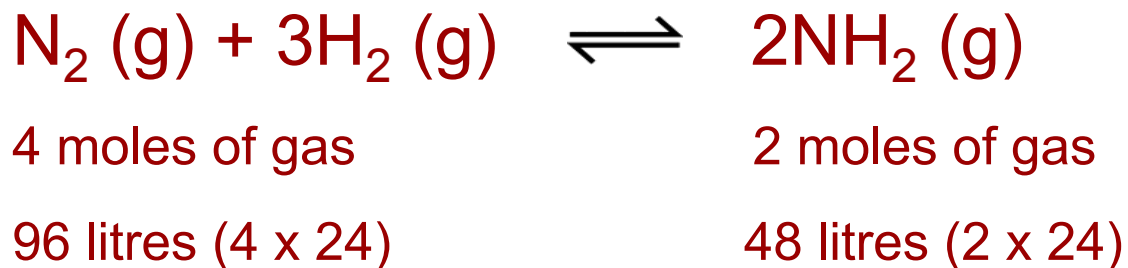
• If pressure is increased in reaction vessel, the reversible reaction favours ammonia production.

• Increase external pressure $\longrightarrow$ 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
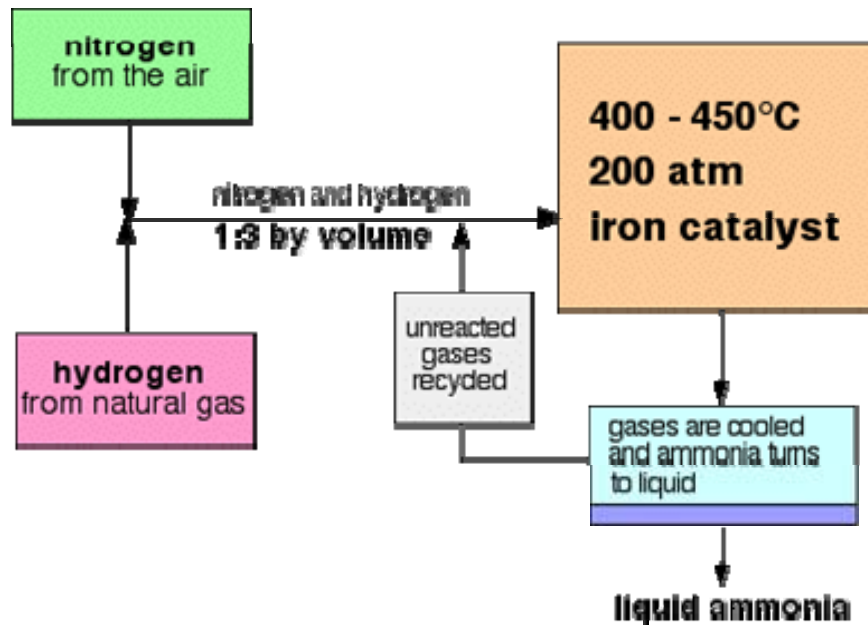
Catalyst - mechanism of action

$N \equiv N$ / 945 kJ mol^{-1}

$C-C$ / 347 kJ mol^{-1}

$H-H$ / 436 kJ mol^{-1}

catalytically active center (*)

$$N_2 + 2^* \rightarrow 2\,N^*$$
$$H_2 + 2^* \rightarrow 2\,H^*$$

$\left.\right\}$ kemisorpcija

$$NH^* + H^* \rightarrow NH_2$$
$$NH_2{}^* + H^* \rightarrow NH_3 + 2^*$$

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

chemisorption = r.d.s.

Overall reaction: $\qquad 2\,N + 6\,H \rightarrow 2\,NH_3$
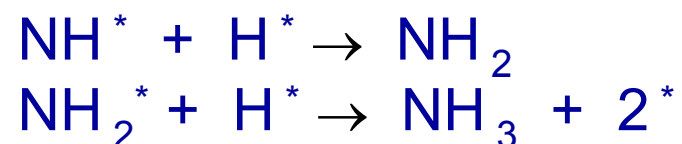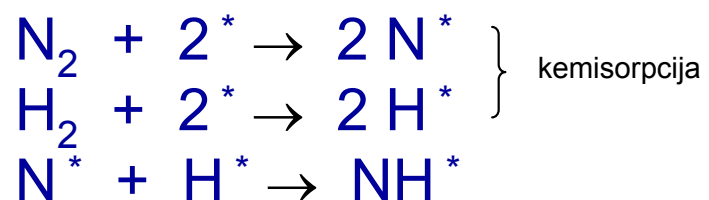
Influence of reaction pressure and temperature on ammonia conversion
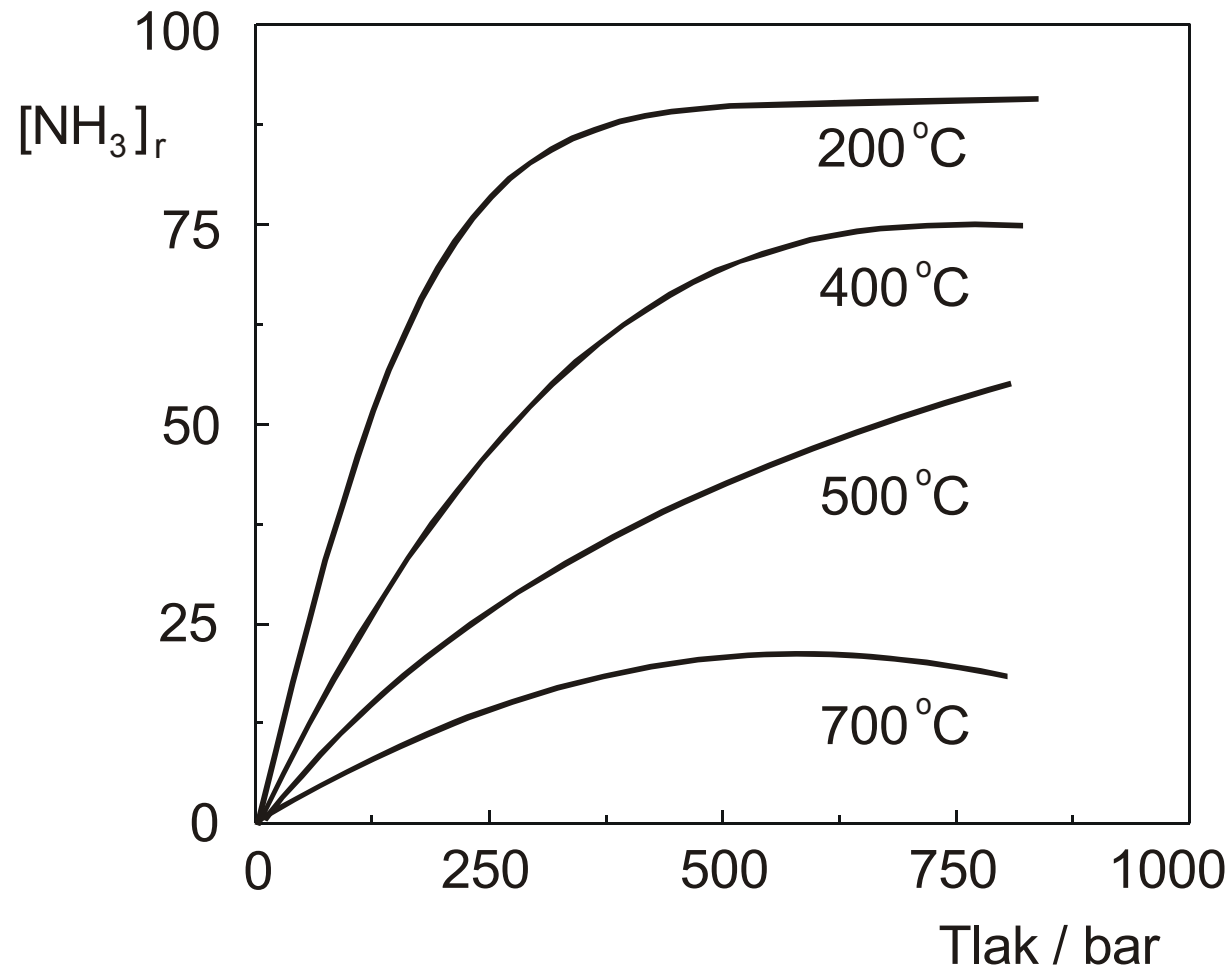
t / °C	K_r	p (NH$_3$)		
		1 bar	10 bar	100 bar
25	5.27×10^5	0.937	9.80	99.3
100	0.275×10^3	0.660	8.76	95.9
200	0.382×10^0	0.172	5.37	81.9
300	0.452×10^{-2}	0.031	2.07	58.0
400	0.182×10^{-3}	0.00781	0.682	34.1
500	0.160×10^{-4}	0.00271	0.259	18.2

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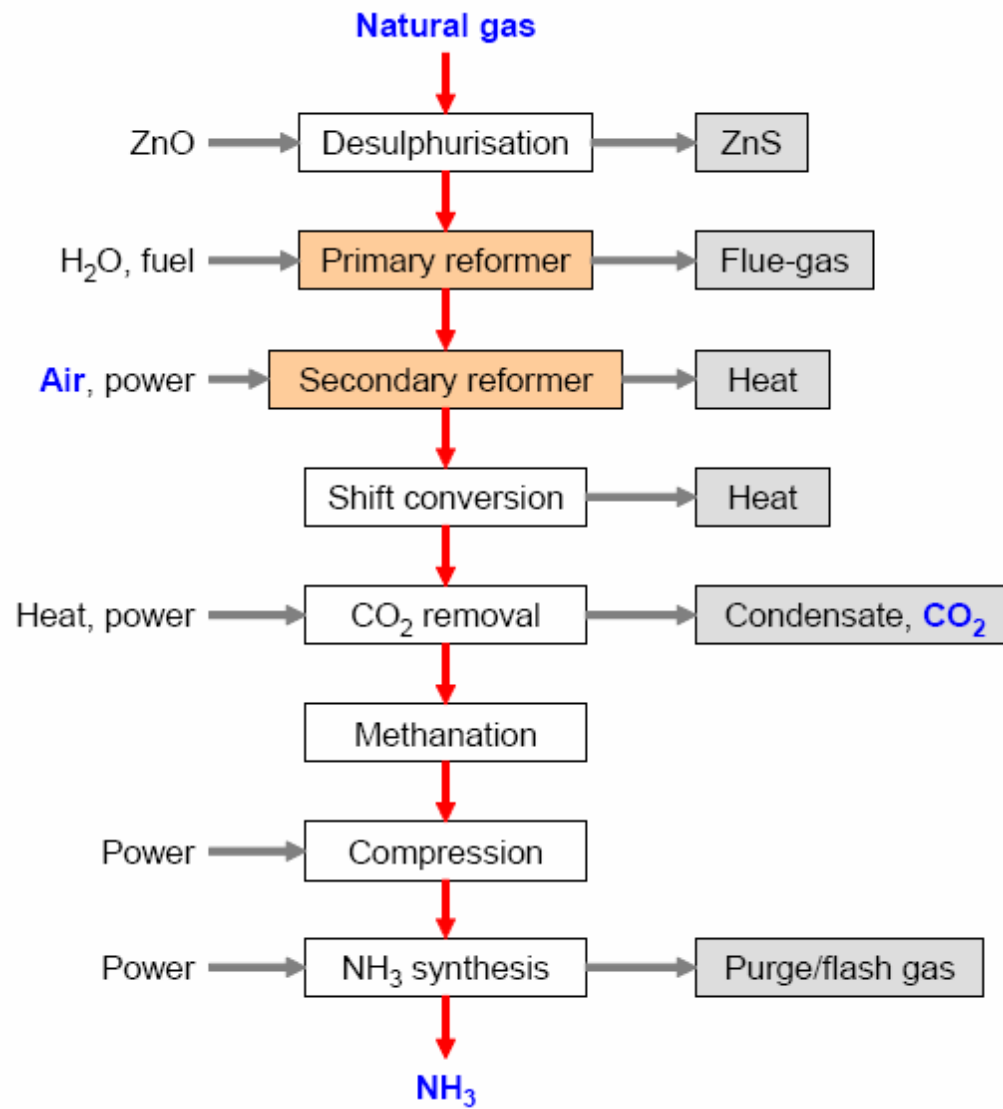
(1) Desulphurisation – removal of S-compounds (catalyst poisons) from natural gas

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$_2$S,
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) $H_2S + ZnO \rightarrow ZnS + H_2O$
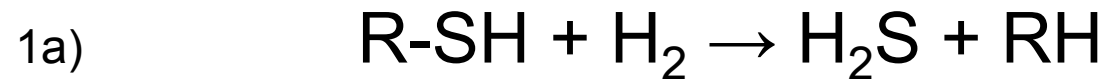
(2) Steam reforming of methane (hydrogen production)

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

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

$$H_2 + air\ (O_2 + N_2) \longrightarrow H_2O + N_2$$

... 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
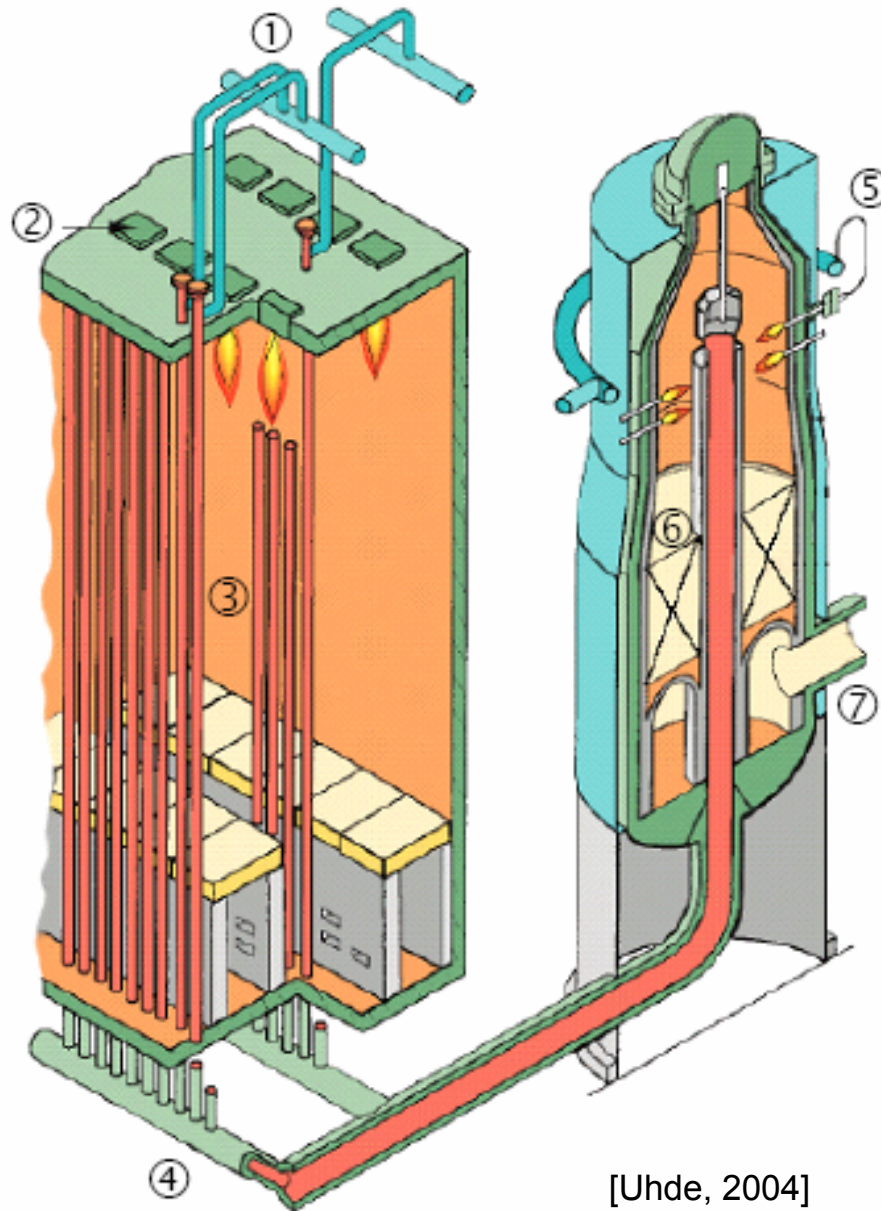

[Uhde, 2004]

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 :

$$CO + H_2O \xrightarrow[\text{2. Cu, 225 }^{o}C]{\text{1. Fe, 450 }^{o}C} CO_2 + H_2 \qquad \Delta H = -41.2 \text{ kJ mol}^{-1}$$
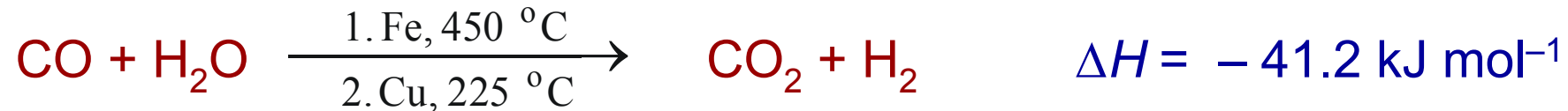
3.a. High-temperature conversion
Reaction temperature 350-450 °C, Fe/Cr-catalyst, CO < 3 vol. %
3.b. Low-temperature conversion
Reaction temperature 200-225 °C, Cu/Zn-catalyst, CO < 0.2 vol. %

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$_2$.
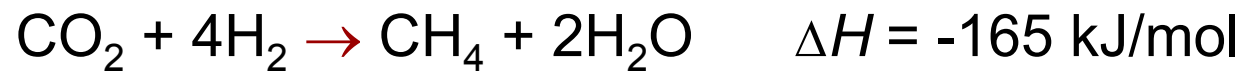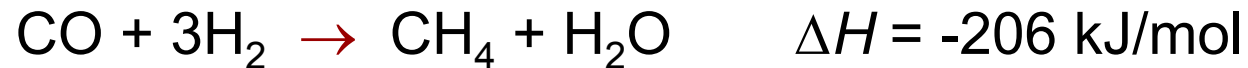
Overview of some CO_2 removal processes
[European Commission, 2000]

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:

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

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

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:

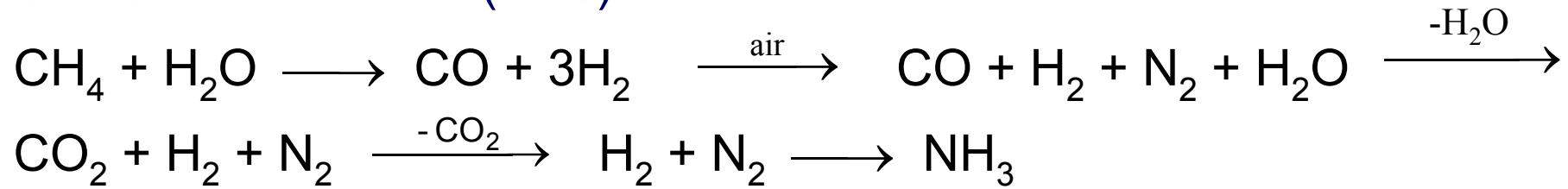$$N_2 + 3H_2 = 2NH_3 \qquad \Delta H_o = \text{-46 kJ/mol}$$

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) :

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

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

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

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.
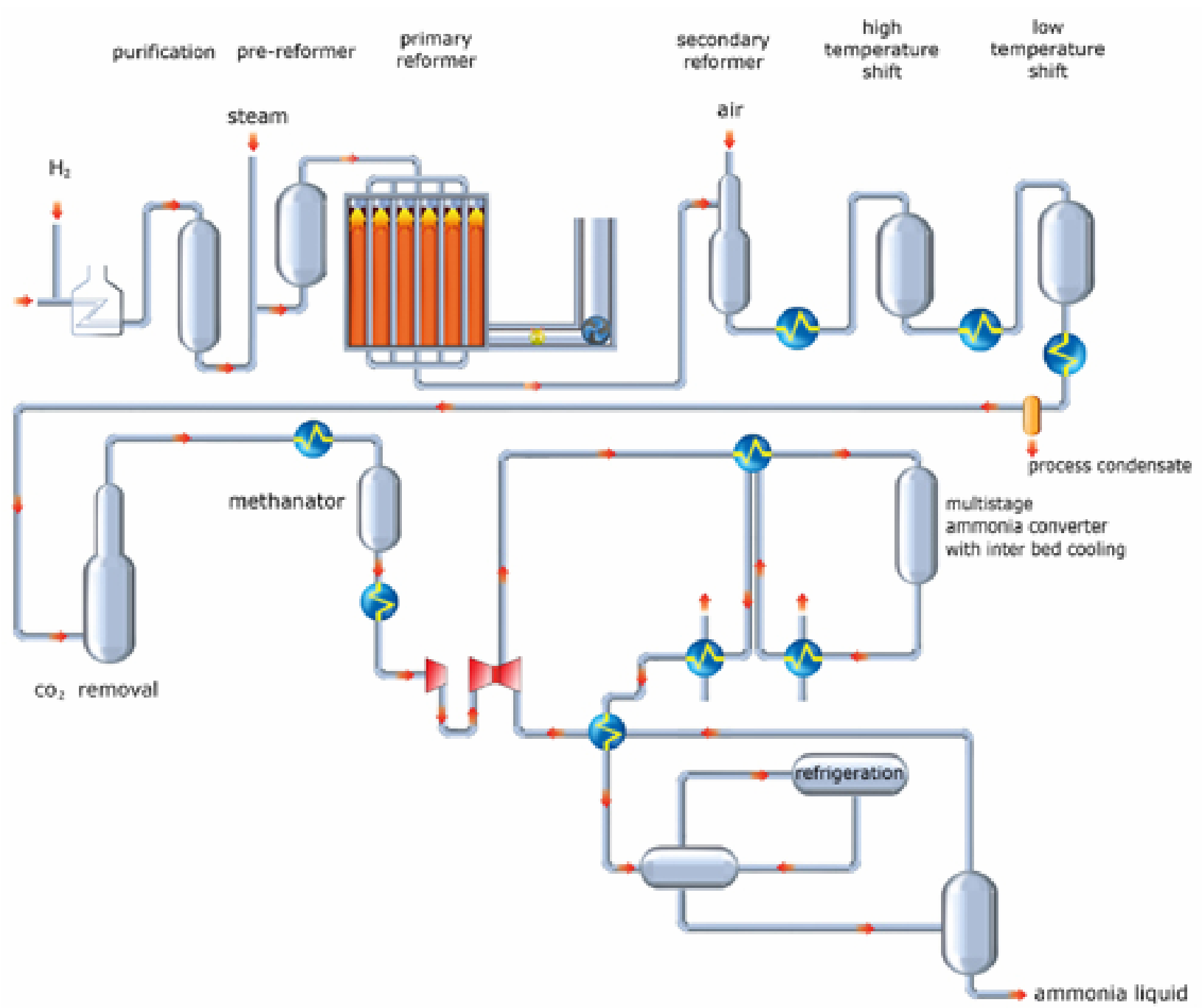Various converter designs can be utilised for this purpose.

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
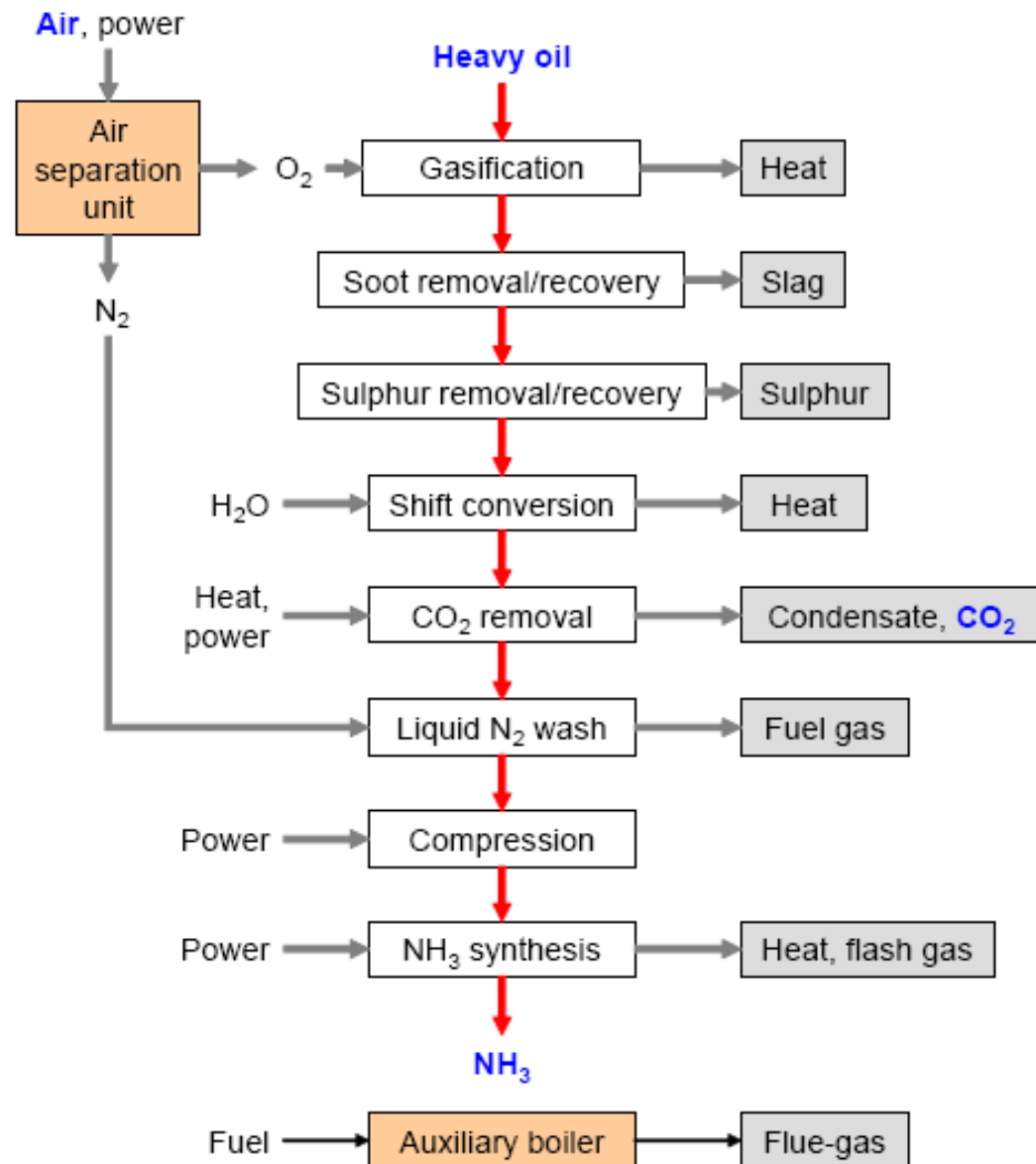and ruthenium.
These catalysts allow a **lower synthesis pressure** and a **lower energy consumption**
to be achieved.

NH₃ production by conventional steam reforming

NH₃ production by conventional
steam reforming

NH₃ production by partial oxidation
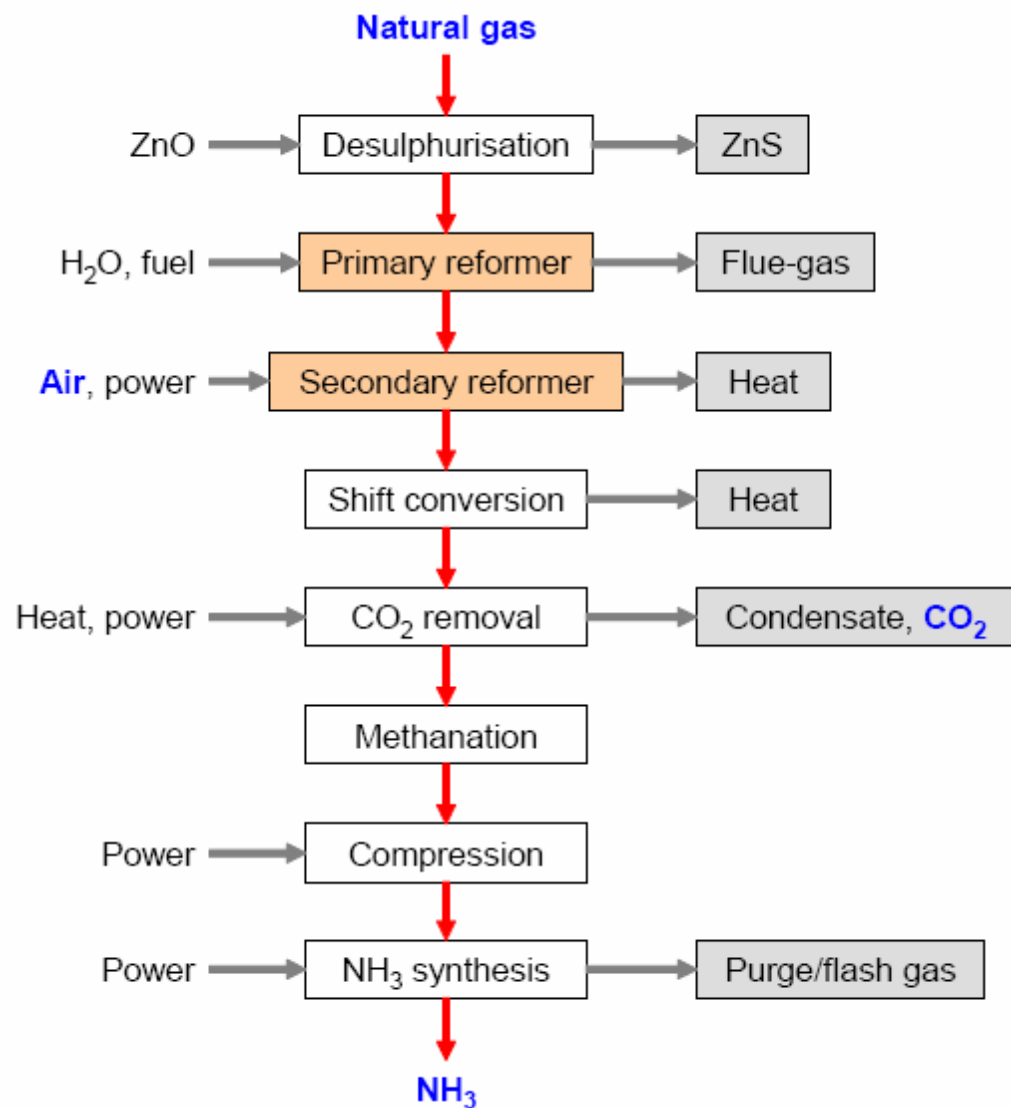
NH₃ production by partial oxidation
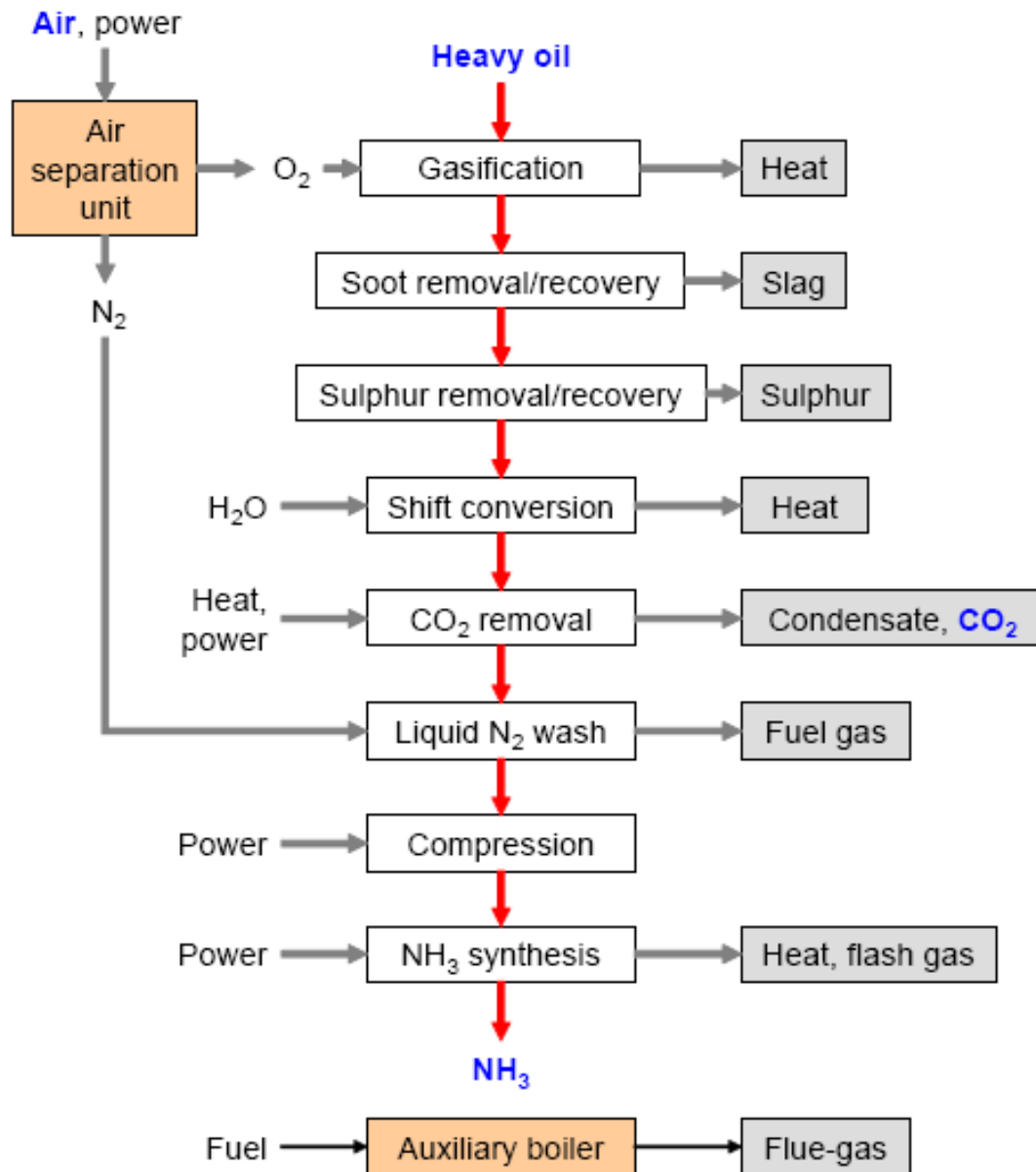
The **partial oxidation** process is used for the gasification of *heavy feedstocks* such as residual oils and coal.

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)

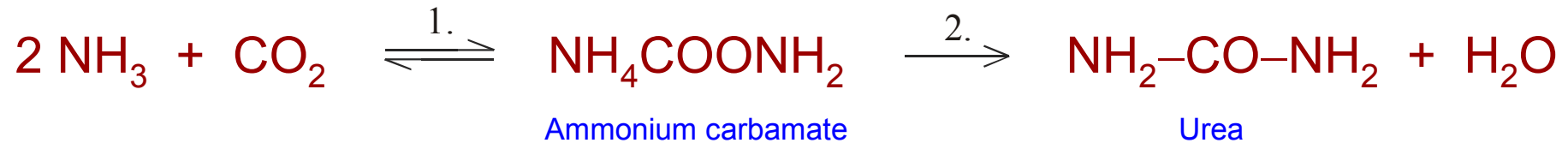| Feedstock	Process	% of world capacity
Natural gas	Steam reforming	77
Naphtha, LPG, refinery gas	Steam reforming	6
Heavy hydrocarbon fractions	Partial oxidation	3
Coke, coal	Partial oxidation	13.5
Water	Water electrolysis	0.5

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 // $H_2N-CO-NH_2$, t_t = 132.7 °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:

$$2\ NH_3\ +\ CO_2\ \underset{\longleftarrow}{\overset{1.}{\longrightarrow}}\ NH_4COONH_2\ \overset{2.}{\longrightarrow}\ NH_2-CO-NH_2\ +\ H_2O$$

<div align="center">Ammonium carbamate   Urea</div>

Both reactions take place <u>in the liquid phase in the same reactor and are in equilibrium</u>. The yield depends on various operating parameters.
Reaction 1 is fast and exothermic and essentially goes to completion under the industrial r eaction 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:

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

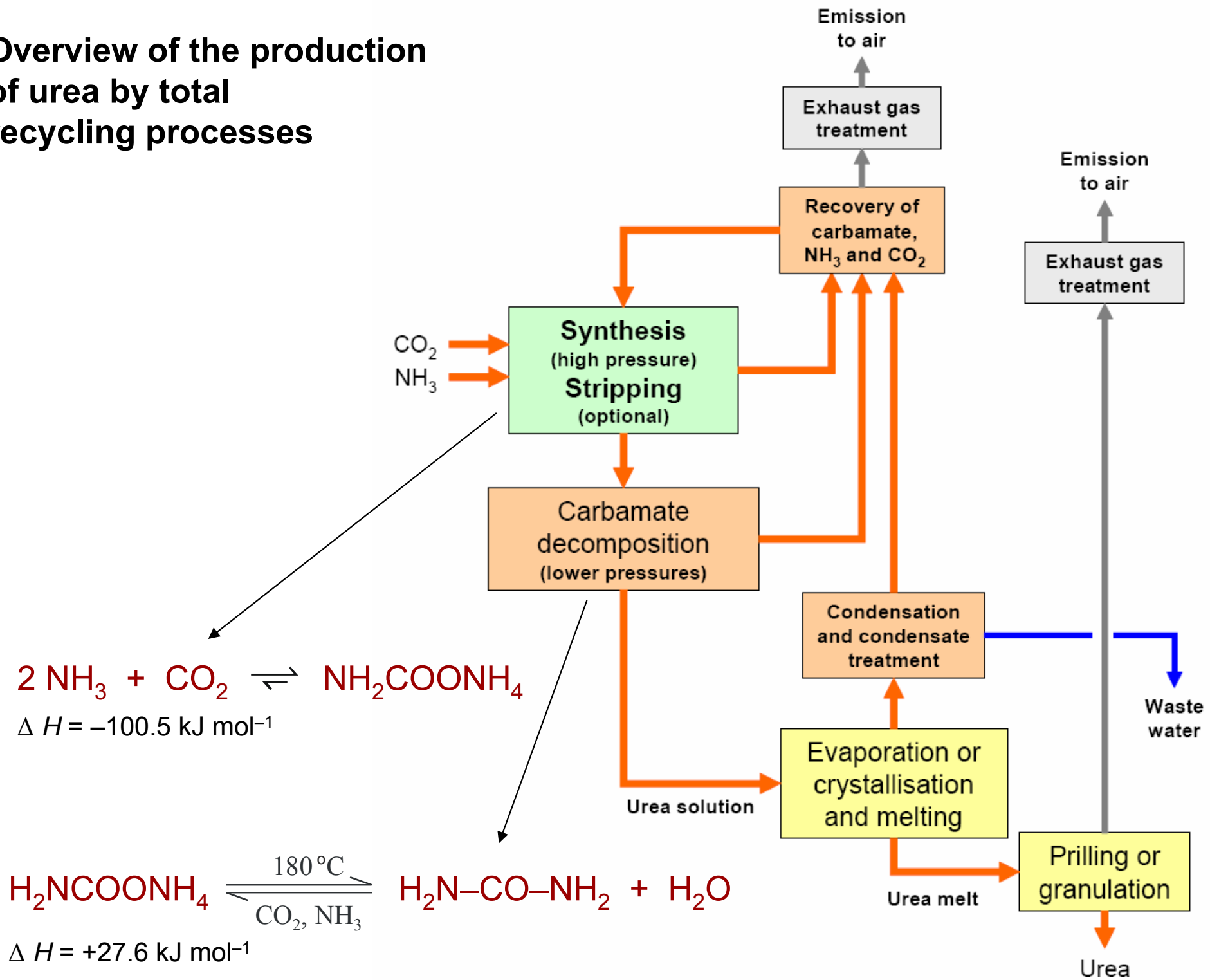• formation of isocyanic acid:

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

The hydrolysis reaction is the reverse reaction of the urea formation and only takes place in the presence of water.
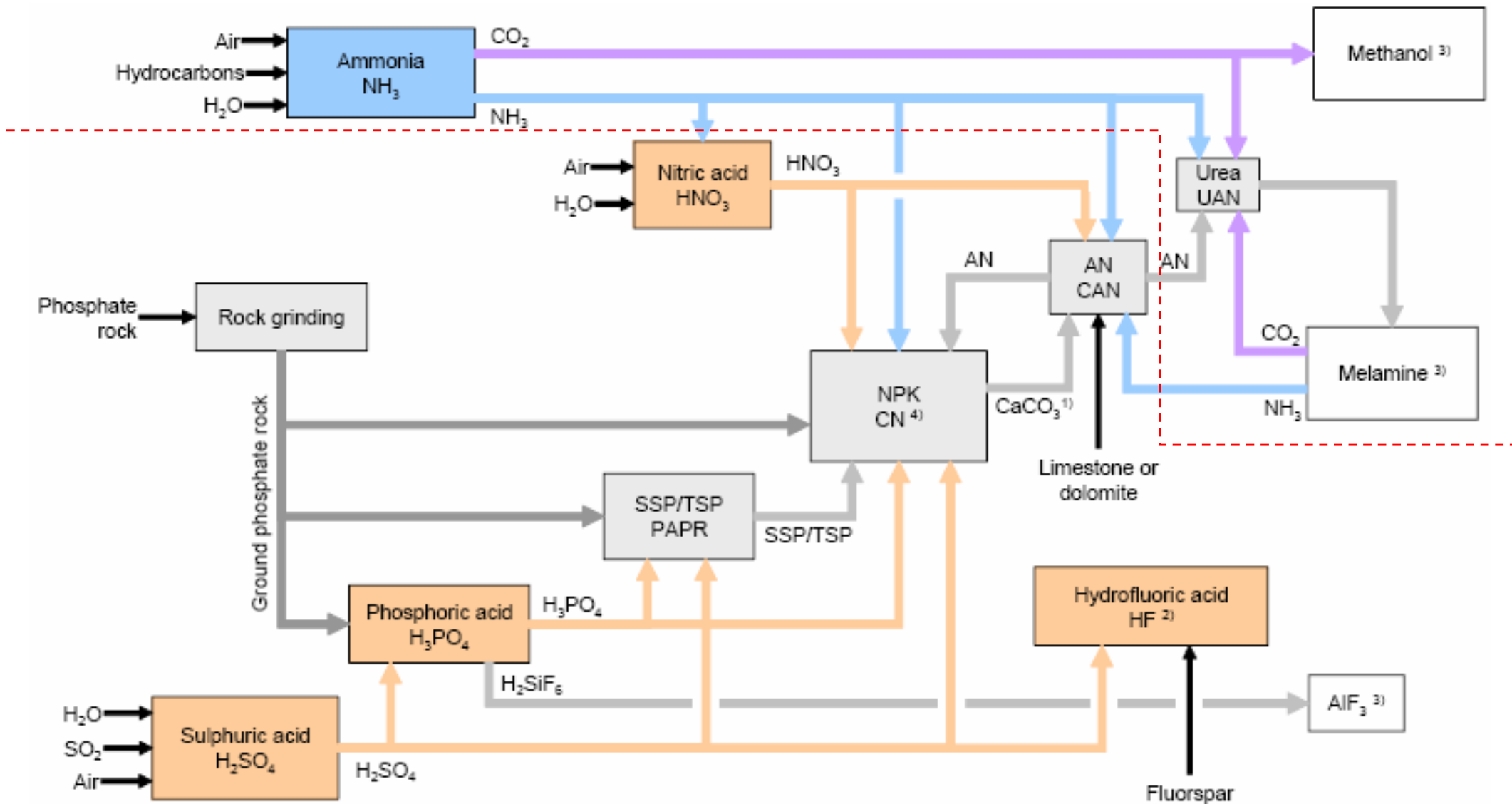Acids or alkaline solutions can also accelerate the rate of hydrolysis. In practice, residence times of urea solutions with low NH_3 content at high temperatures must be minimised. Biuret must be limited in fertiliser urea (preferably maximum of 1.2 % EC), since biuret might cause crop damage, notably 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

Synthesis (high pressure) **Stripping** (optional)

CO_2

NH_3

Carbamate decomposition (lower pressures)

Condensation and condensate treatment

Waste water

Evaporation or crystallisation and melting

Urea solution

Prilling or granulation

Urea melt

Urea

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

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

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

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

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