Greenhouse Gases Mitigation CO_2 Capture and Utilization

Topic No: 6

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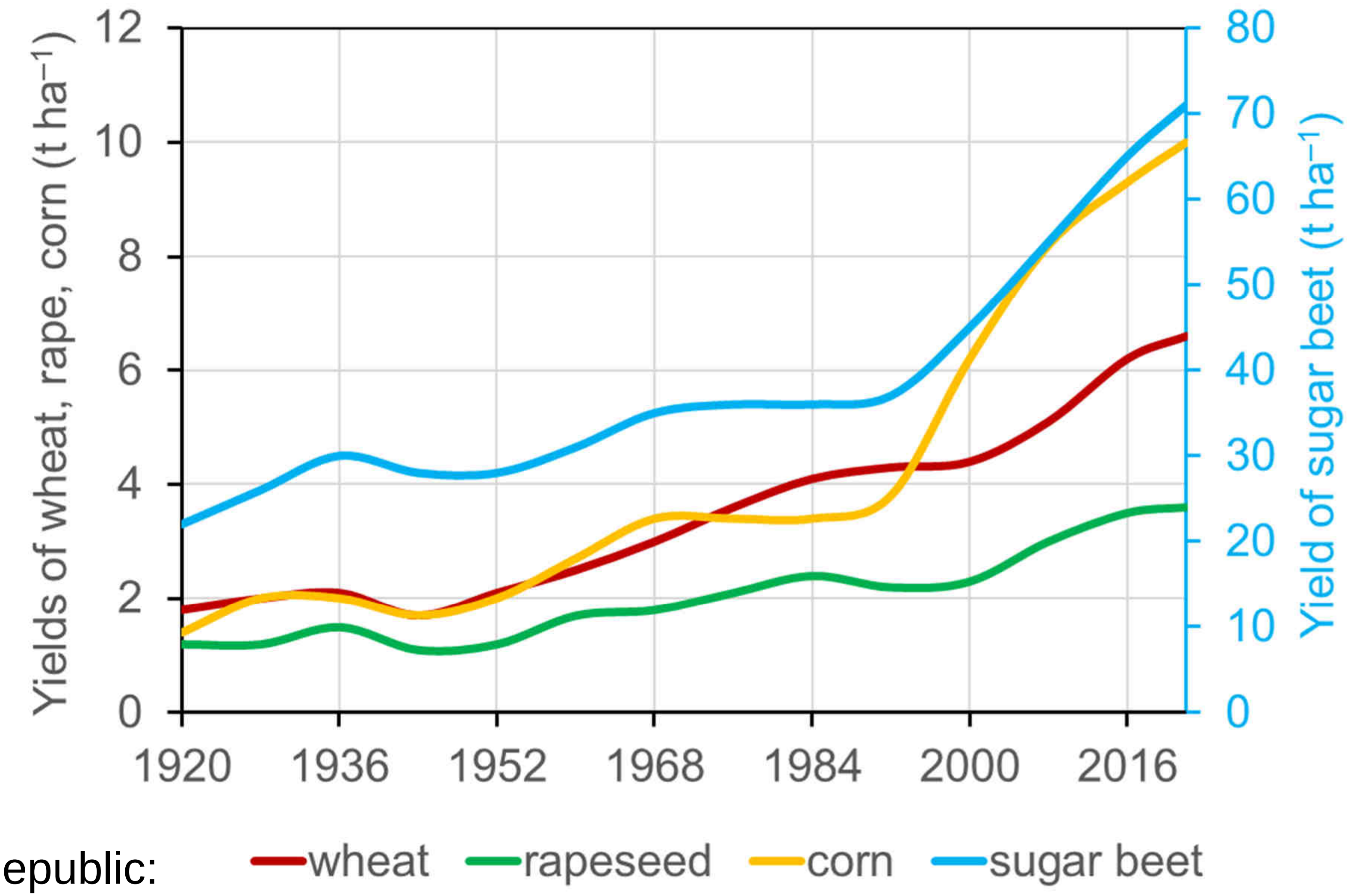
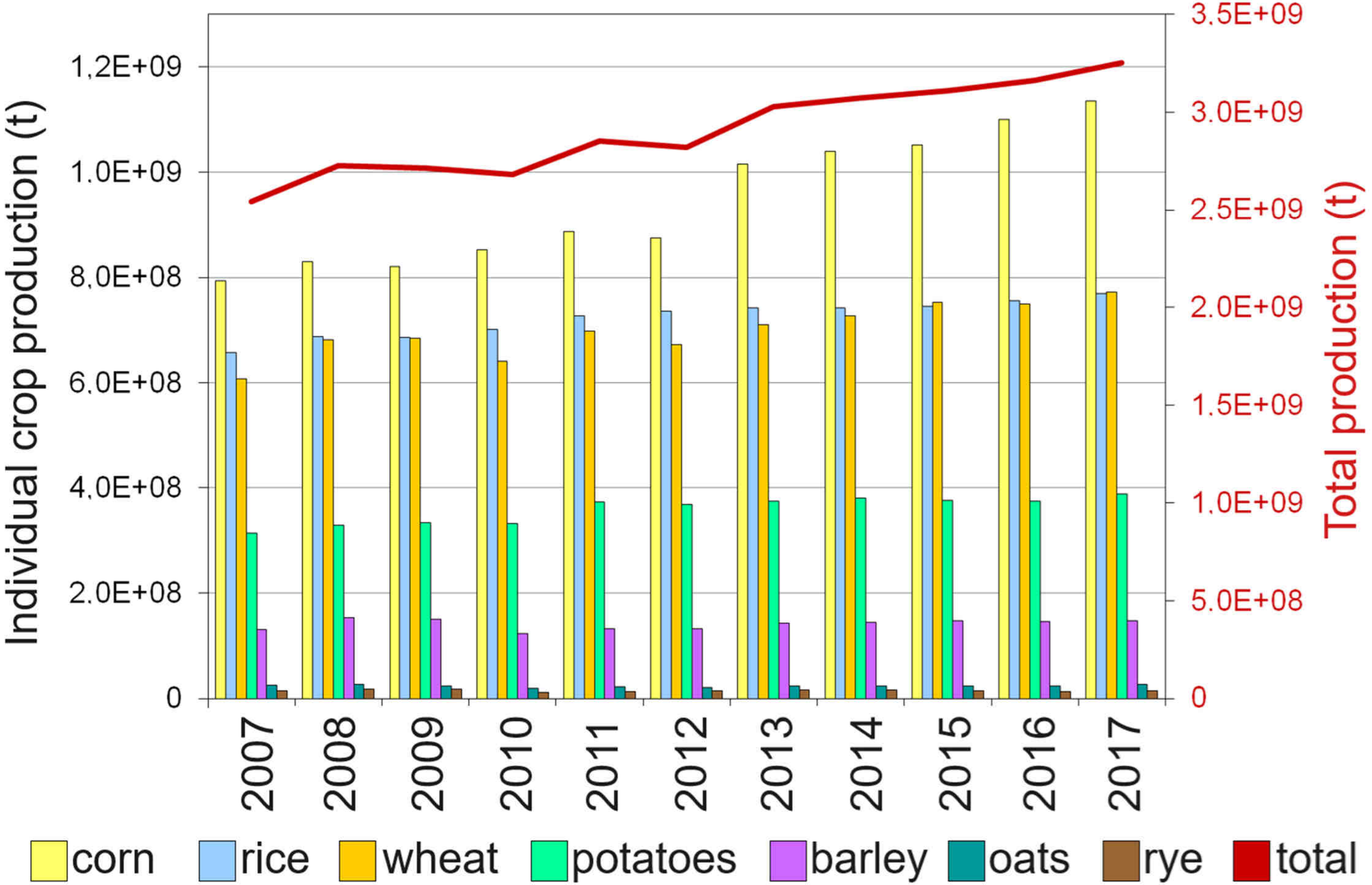
Population – agriculture – fertilizers - climate

- World population growth: 1900: 1.7 bn. 1970: 3.7 bn. 2022: 8.0 bn.
- Key drivers of yield increases:
  - new varieties
  - pesticides
  - advances in agronomy
  - fertilizers



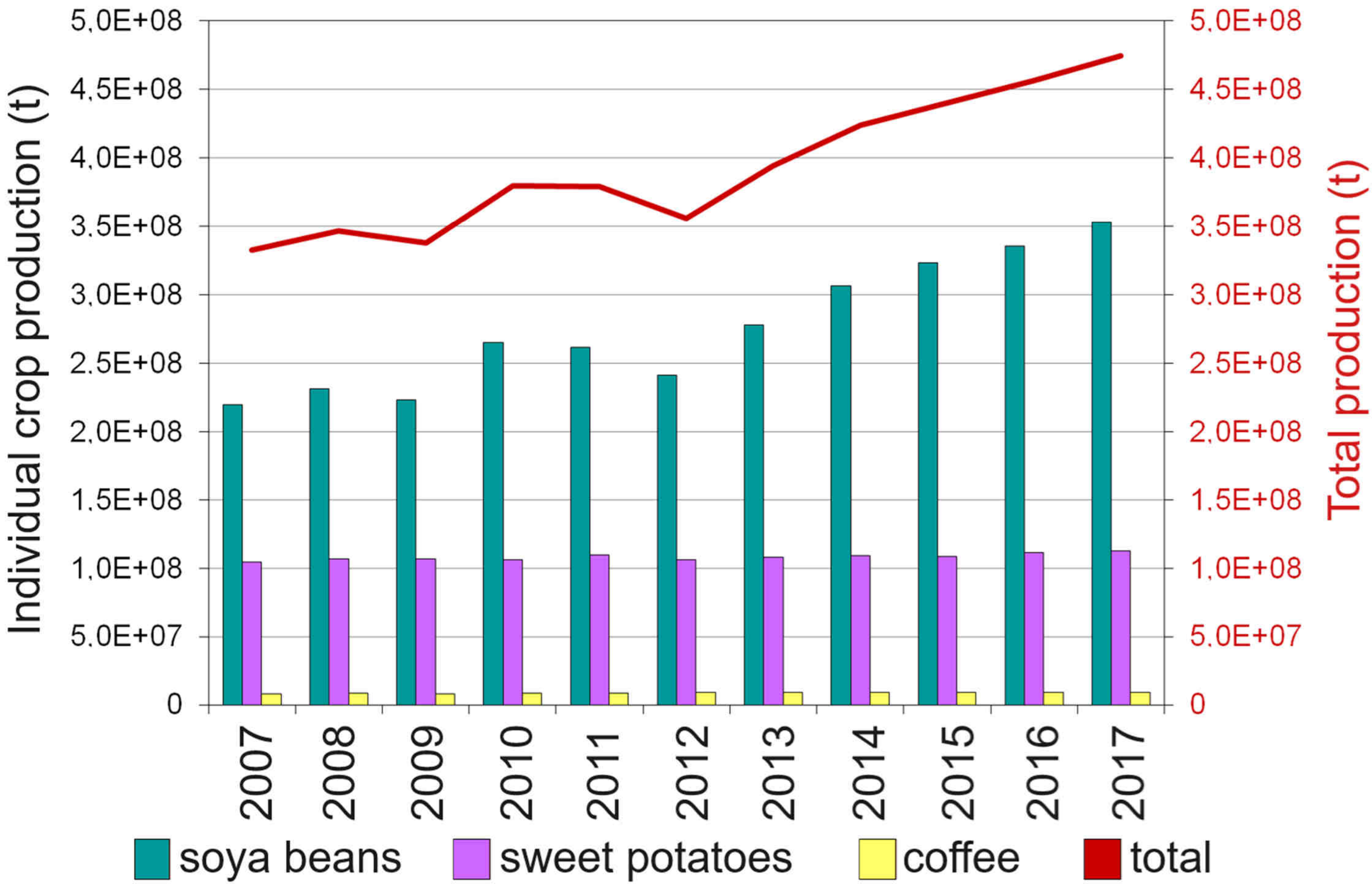
Example: Czech Republic:

Increase in production of selected crops



Reference(s): -

Increase in production of selected crops



Fertilizer consumption increased by biofuels

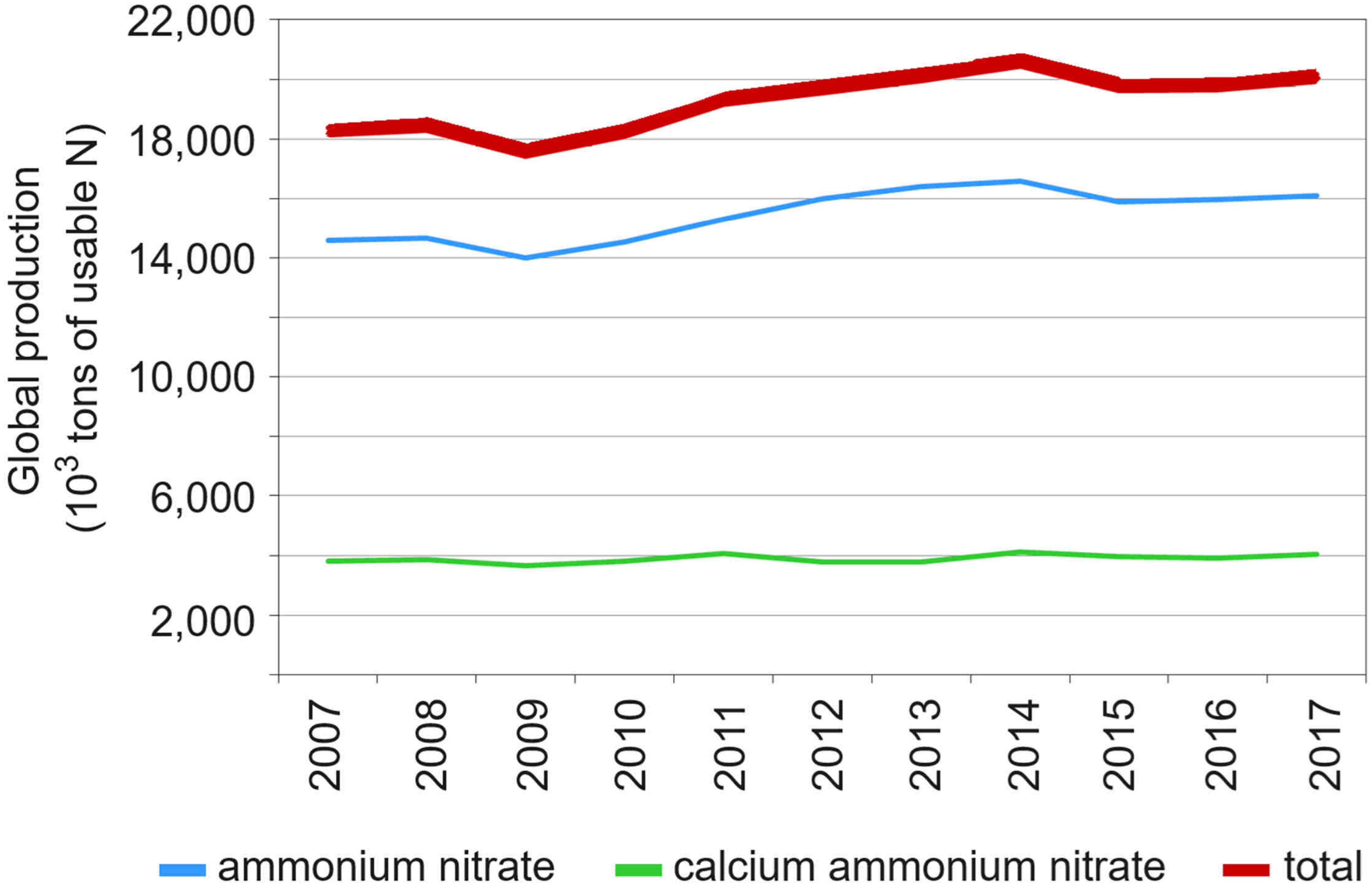
- Biofuels (FAME via transesterification, ethanol via fermentation and distillation
  - total: 82.3 10^6 t $year^{-1}$ (of petroleum equivalent)
  - ethanol: corn, other seeds, potatoes, sugar cane, sugar beet
  - FAME: soybean oil, palm oil, sunflower oil, rapeseed oil
- Starving people (according to UN): in 2016 815 mil.

  in 2023 825 mil.

In what form is nitrogen bound in fertilizers?

Nitrates	$Ca(NO_3)_2$; $CaMg(NO_3)_4$
Ammonia and ammines	$(NH_4)_2SO_4$; NH_3 (l, 100%)
Amides	$CO(NH_2)_2$; $CaCN_2$ (cyanamide)
Multiple forms together	NH_4NO_3 with additives Ca^{2+}, Mg^{2+}
Nitrogen with slow effect	Urea aldehyde fertilizers

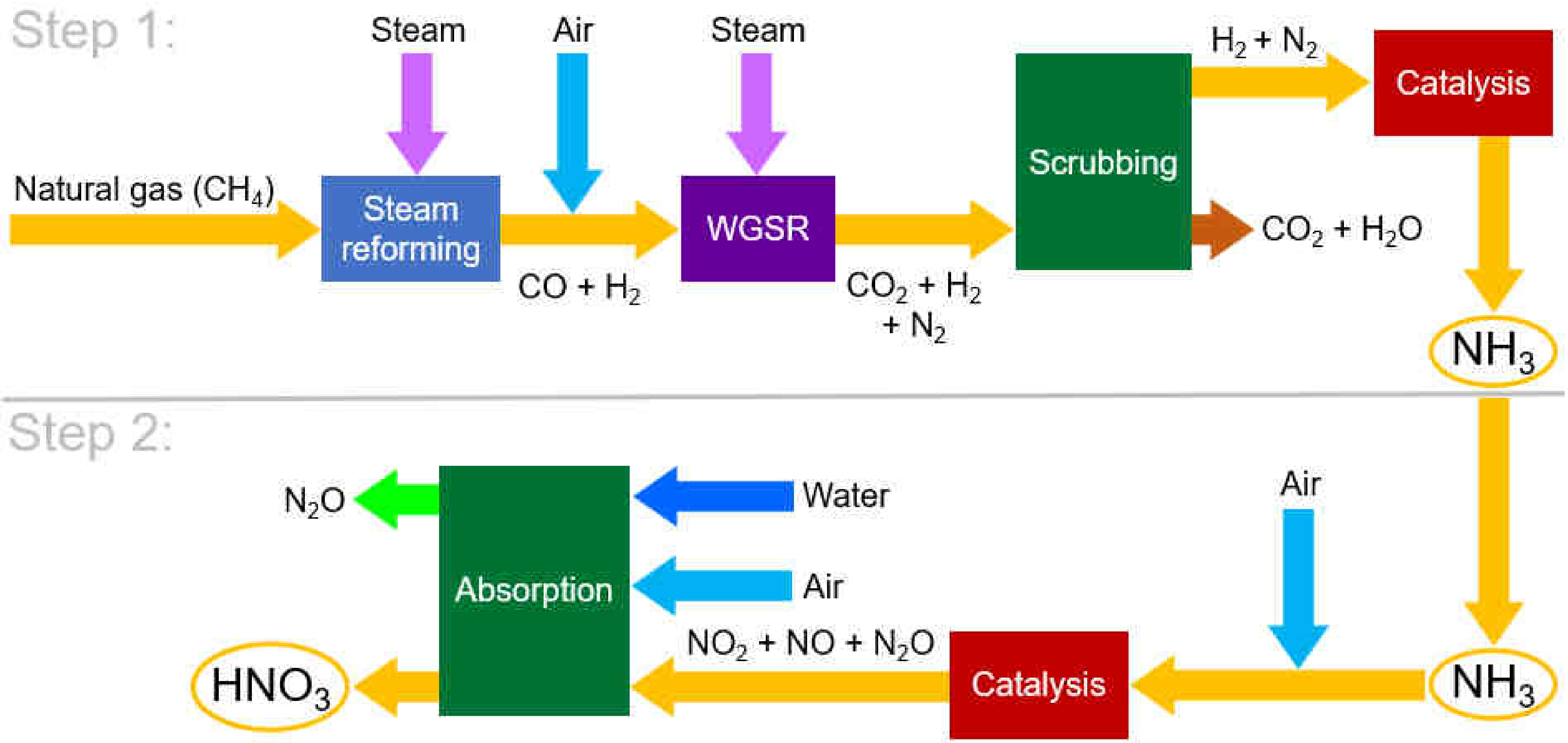
Annual production of Synthetic fertilizers



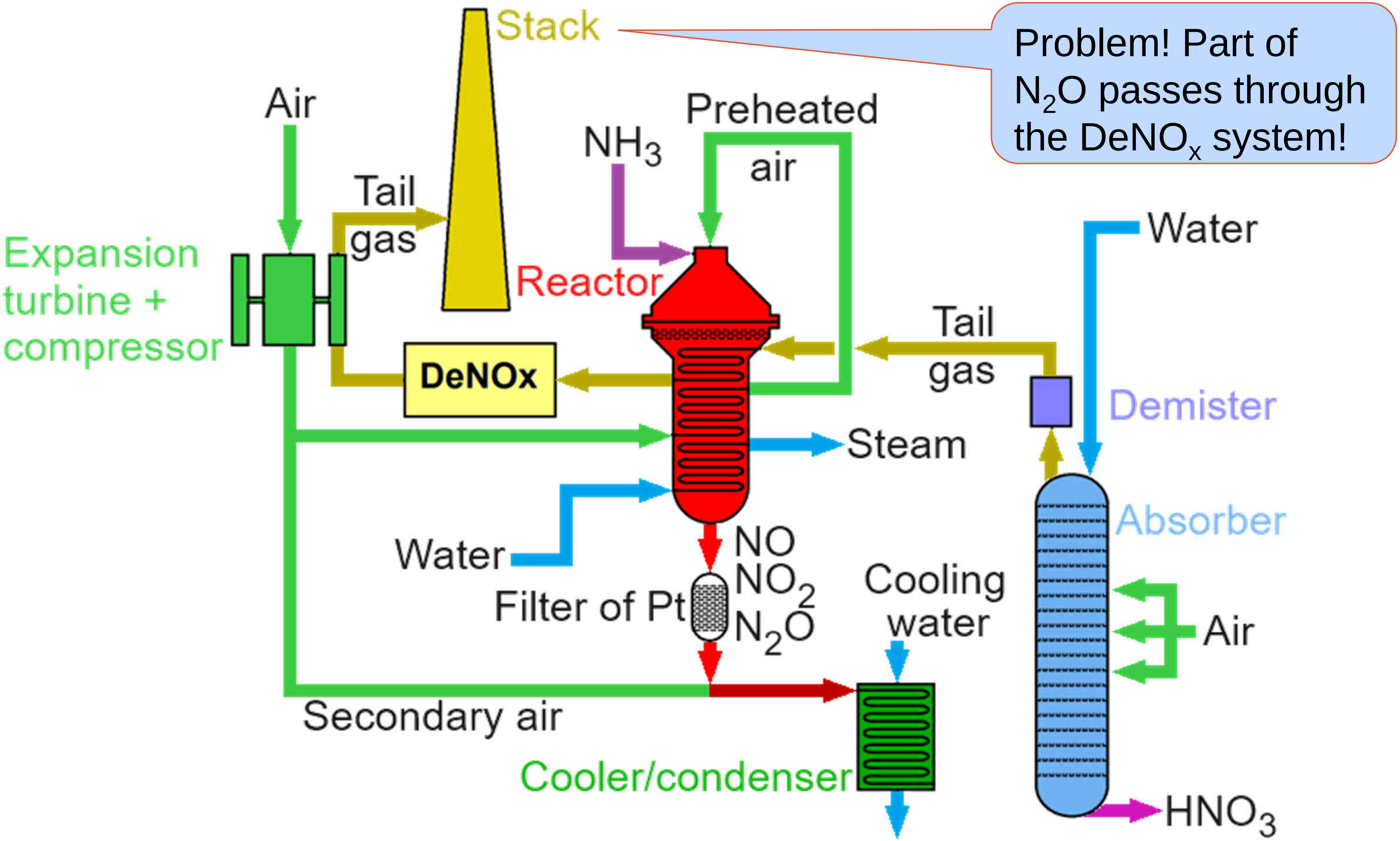
Reference(s): -

How are fertilizers made?

- The process consists of 2 main steps, which result in GHG emissions.
  - Haber-Bosch synthesis of ammonia ⇒ emissions of CO_2
  - Ostwald synthesis of nitric acid ⇒ emissions of N_2O

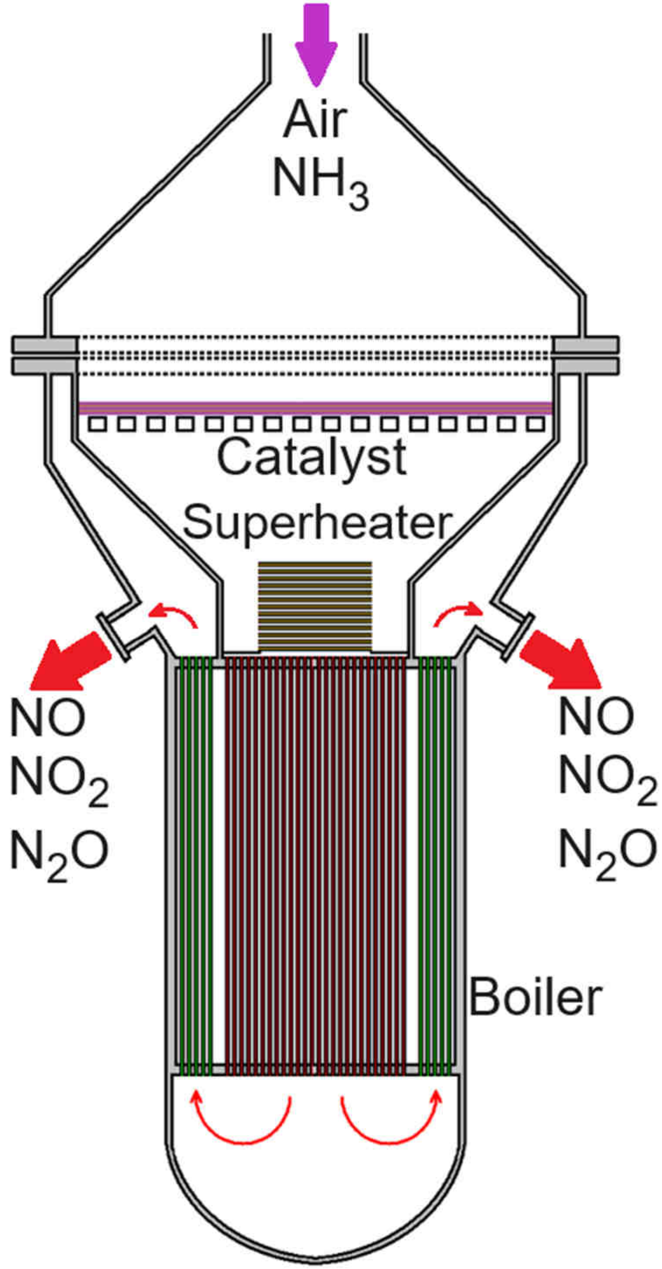


How is nitric acid made?



Reactor = the core of the Ostwald system

- Catalytic converter (oxidizer) of NH_3
  - temperature = 890 – 920 °C
  - pressure = 4 – 8 bar



Reactor = the core of the Ostwald system

Two reactors in the hall

Absorber

Reactor hall

For which application is HNO_3 used?

Nitric acid (regardless if diluted up to 65% or concentrated)

- **nitrogen fertilizers (ca. 70% of production)**
  - ammonium nitrate, calcium n., potassium n., sodium n.
- **explosives (ca. 10% of production)**
  - ammonium nitrate, TNT etc.
- **other uses (ca. 20% of production)**
  - direct use → steel pickling
  - sodium nitrate → oxidizer for silicates
  - adipic acid → polymers production
  - nitrobenzene → aniline production
  - dinitrotoluene → polyurethane production

Reference(s): -
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Technical aspect of nitric acid production

- Example of operating parameters of a modern reactor Grande Paroisse® (later GPN)

► Average production	990 t HNO_3 / day
► Typical PtRh primary catalyst lifespan	100 days or 99,000 t HNO_3
► Oxidation pressure	7.4 bar abs.
► Catalyst temperature	920 ℃
► Effective oxidizer diameter	3,000 mm
► Weight of precious metals in the catalyst	43 kg Pt 3 kg Rh 26 kg Pd.

Primary N_2O emissions: 800 – 1,600 ppm_V

- Use as an inhalation anesthetic... but also as a psychotropic substance

- Use as a booster, e.g. for "muscle cars„

$$2N_2O \xrightarrow{T} 2N_2 + O_2$$

- But, nitrous oxide is a significant greenhouse gas!

N_2O has markedly high GWP

- The biggest anthropogenic emissions = production and use of synthetic nitrogen fertilizers
- The Average lifetime in the atmosphere 114 years
- GWP(N_2O) for the 100 years horizon (according to IPCC):
  - 2nd report stated GWP = 310
  - 4th report stated GWP = 298
  - 5th report stated GWP = 265
- Approx. 600 nitric acid production plants worldwide operated in the continuous production regime.
- The overall N_2O emissions estimated at 1.2 10^6 t/year
- From the point of view of the greenhouse effect, it is comparable to the operation of 80 10^6 passenger cars …. but:
  - the cars riding 24 hours per day / 7 days a week / 365 days per year
  - how many cars drive this way?

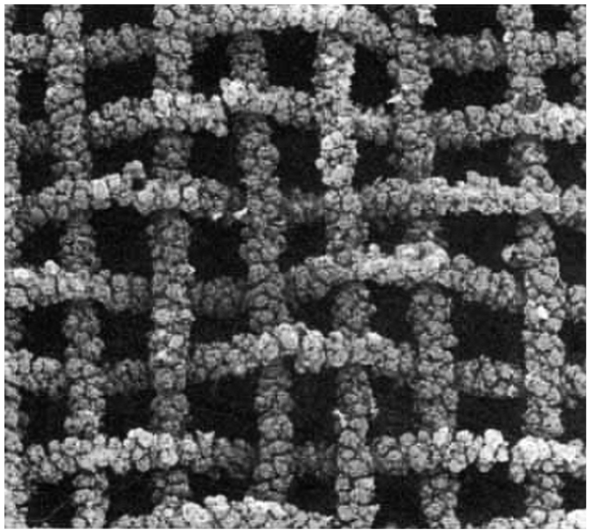
- Basically only 3 economically viable options:

1 ► to improve the primary catalyst - „gauzes" for NH_3 oxidation

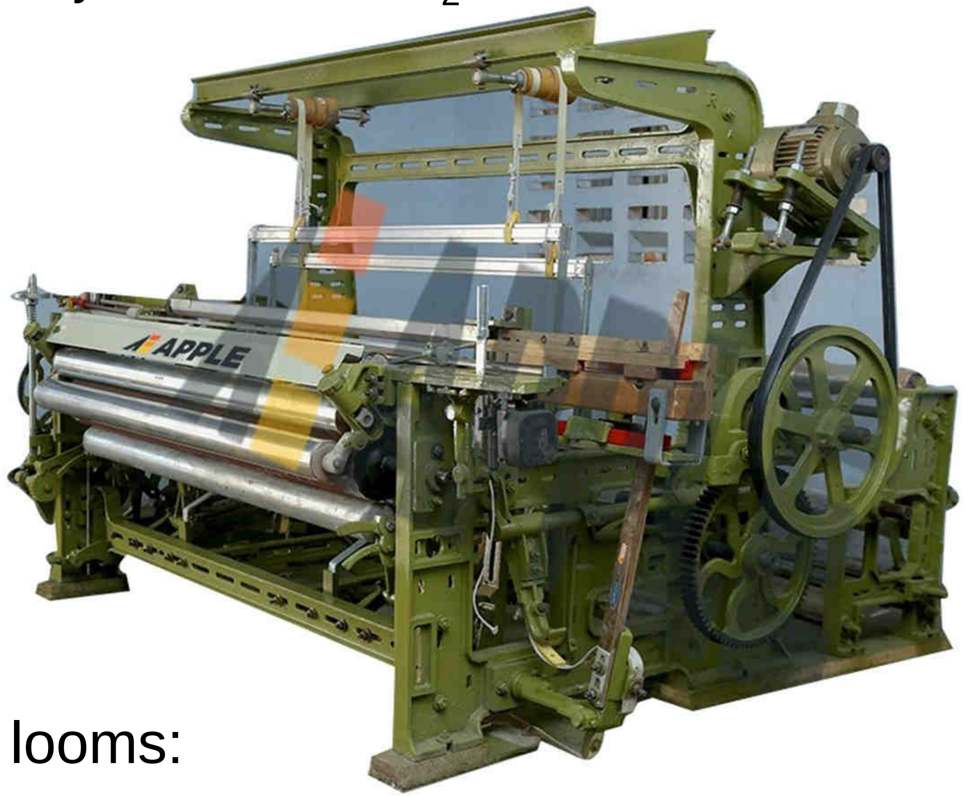
2 ► to install a secondary (high temperature) catalyst directly under the gauzes - high temperature decomposition of N_2O

3 ► to install the final reduction catalyst (tail gas treatment)

- First, the problem with mechanical strength was solved.
  - long-term proven alloys Pt/Rh: 90/10, 92/8 or 95/5 (wt. %)
  - historically the oldest woven sieves – tearing due to low elasticity
  - standard fabric mesh density 1,024 mesh cm^2
  - elasticity of woven gauzes limited by Pt/Rh alloy
  - hole in the sieve = decrease in efficiency = increased N_2O emissions

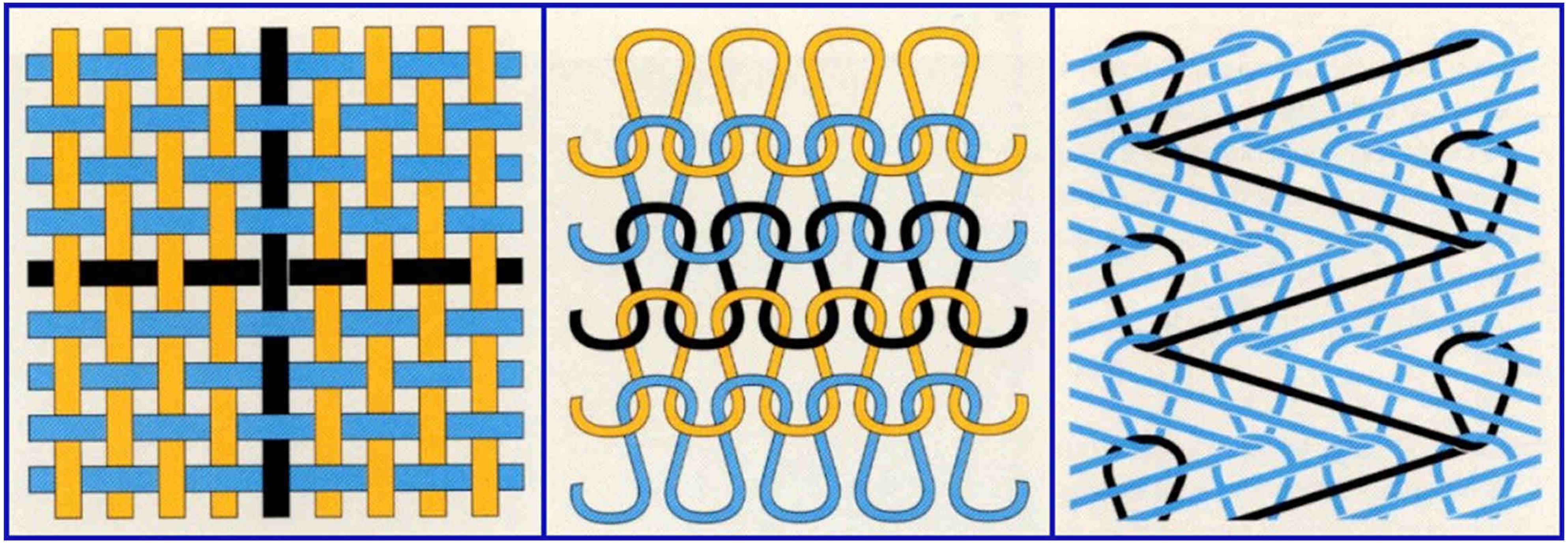


weaving on classic mechanical looms:

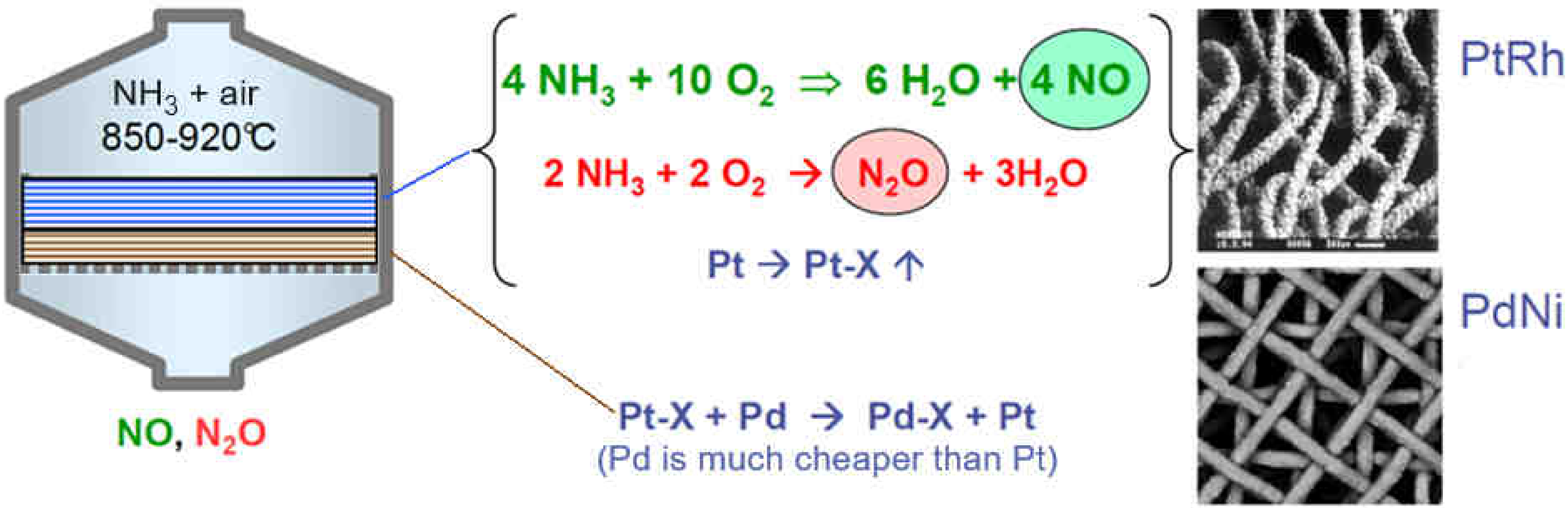


- First, the problem with mechanical strength was solved.
  - increasing elasticity (and endurance) by applying knitted and warp-knitted gauzes

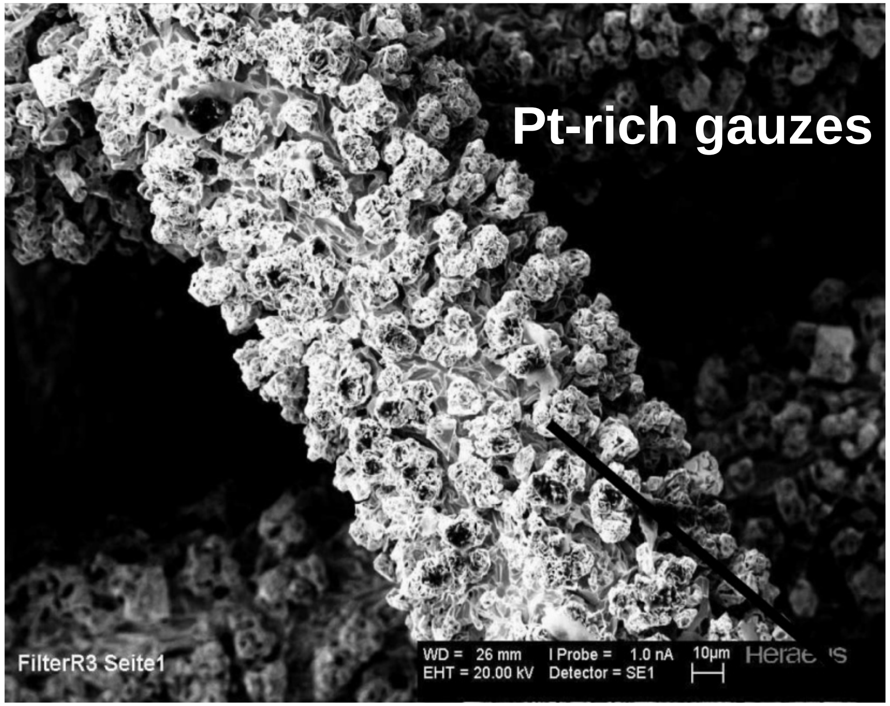
woven	knitted	warp-knitted
(poor elasticity)	**(good elasticity)**	**(good elasticity)**

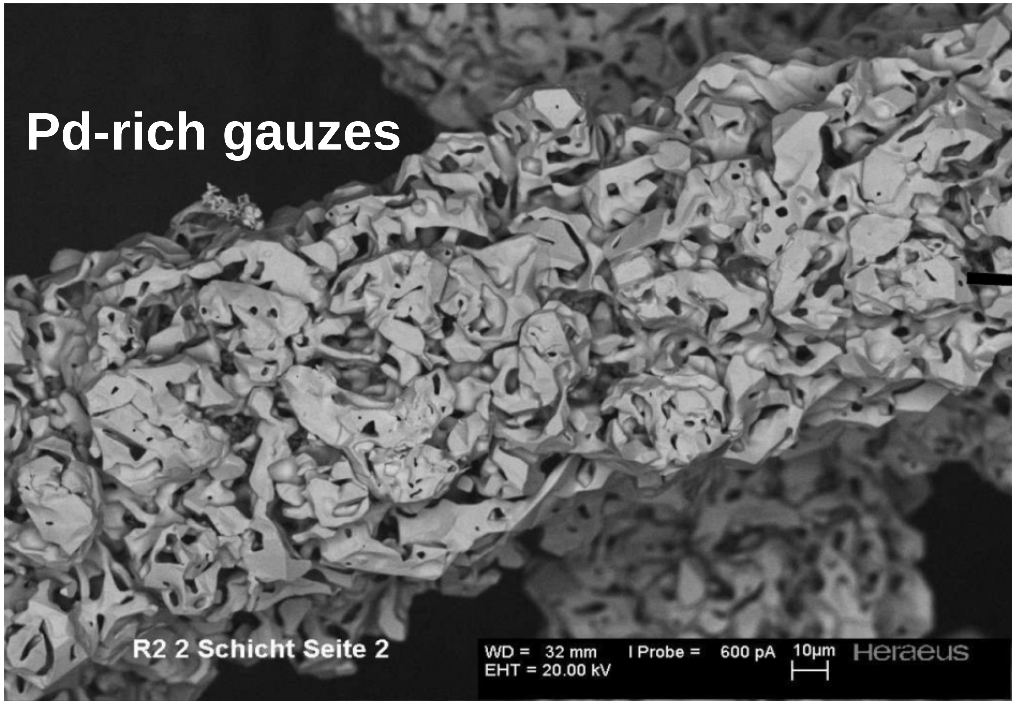


- By changing the composition of the alloy, the parallel reaction to N_2O can be reduced.
- History
  - ▶ Pd or Pd/Ni screens have been installed under catalytic screens for decades.
  - ▶ Only Pt/Rh gauzes had a catalytic effect.
  - ▶ Pd/Ni screens were only used to capture flying Pt particles:



- Today state of the art = changed composition of alloys
  - The gauzes are not divided into catalytic and catching ones
  - Pt/Rh/Pd ratio is changed from top to bottom from Pt predominance to Pd predominance
  - Pt remains in active form throughout the set and the lower layers oxidize N_2O to NO (e.g. FTC® system by W.C. Heraeus, GmbH)
  - reduction of N_2O emissions by up to 30%





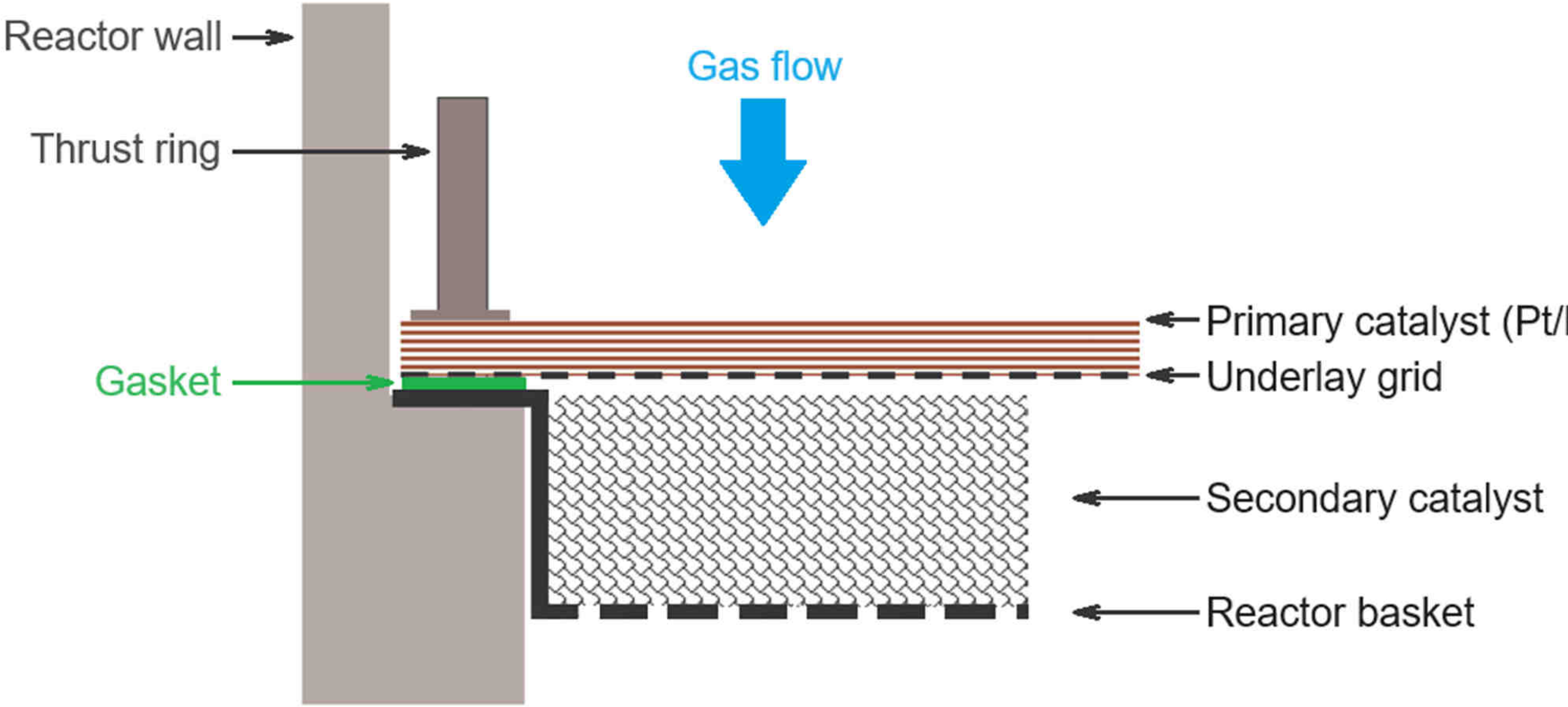
- N_2O secondary decomposition catalysts placed immediately below the Pt/Rh/Pd gauzes
  - function principle = high temperature decomposition

$$2N_2O \xrightarrow{850-920\ °C;\ catalysis} 2N_2 + O_2$$

  - modern reactors with a basket filled with Raschig rings (homogenizing T and gas flow) → easy installation → replacement of ceramic rings with a catalyst
  - older reactors without a basket, but with a grate → small space for installation = problem → lower efficiency
  - More types of secondary catalysts:
    - precious metals-based catalysts (Pt/Rh/Pd on alumina)
    - base metals-based catalysts (zeolites, Co, Fe_2O_3 etc.)
  - reduction of N_2O emissions by up to 60 - 85%

Secondary (high temperature) catalyst

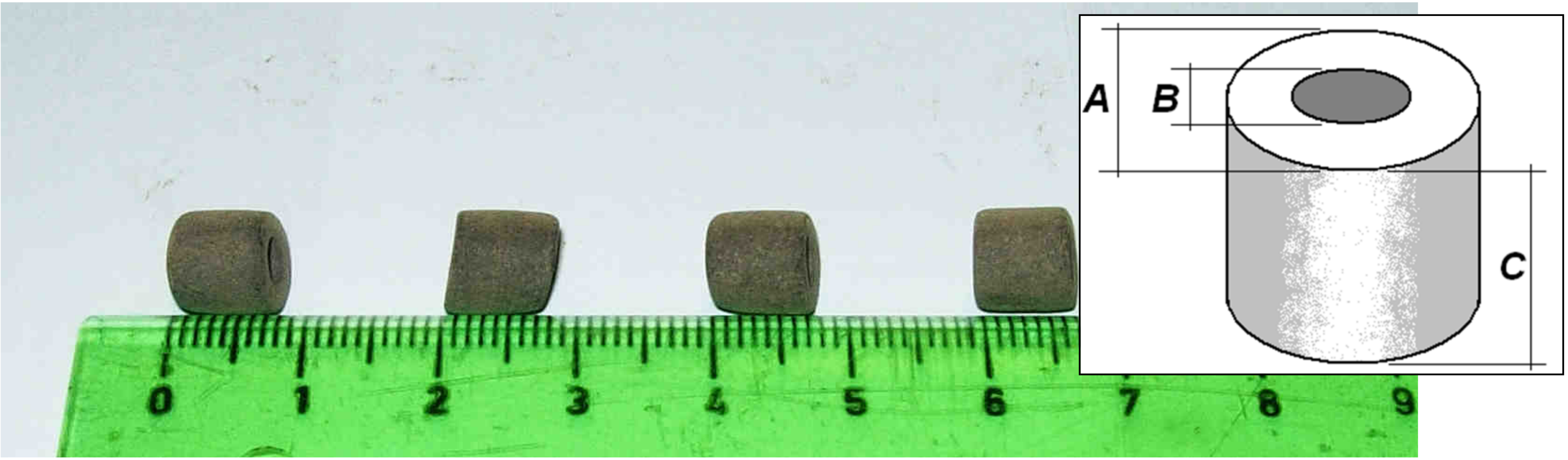
- Location of the secondary catalyst in the basket-designed reactors
  - N_2O emissions reduction by 60–70% (new types up to 85%), Δp = 4,5–5 kPa

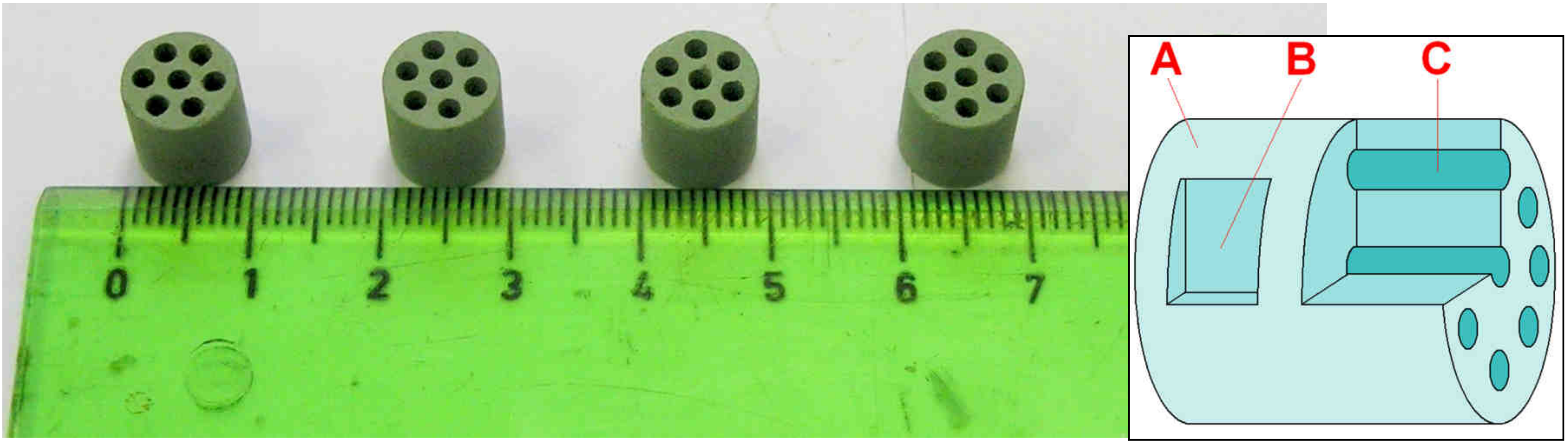


- Location of the secondary catalyst in the basket-designed reactors
  - ► An example of the secondary precious metals-based catalyst installation

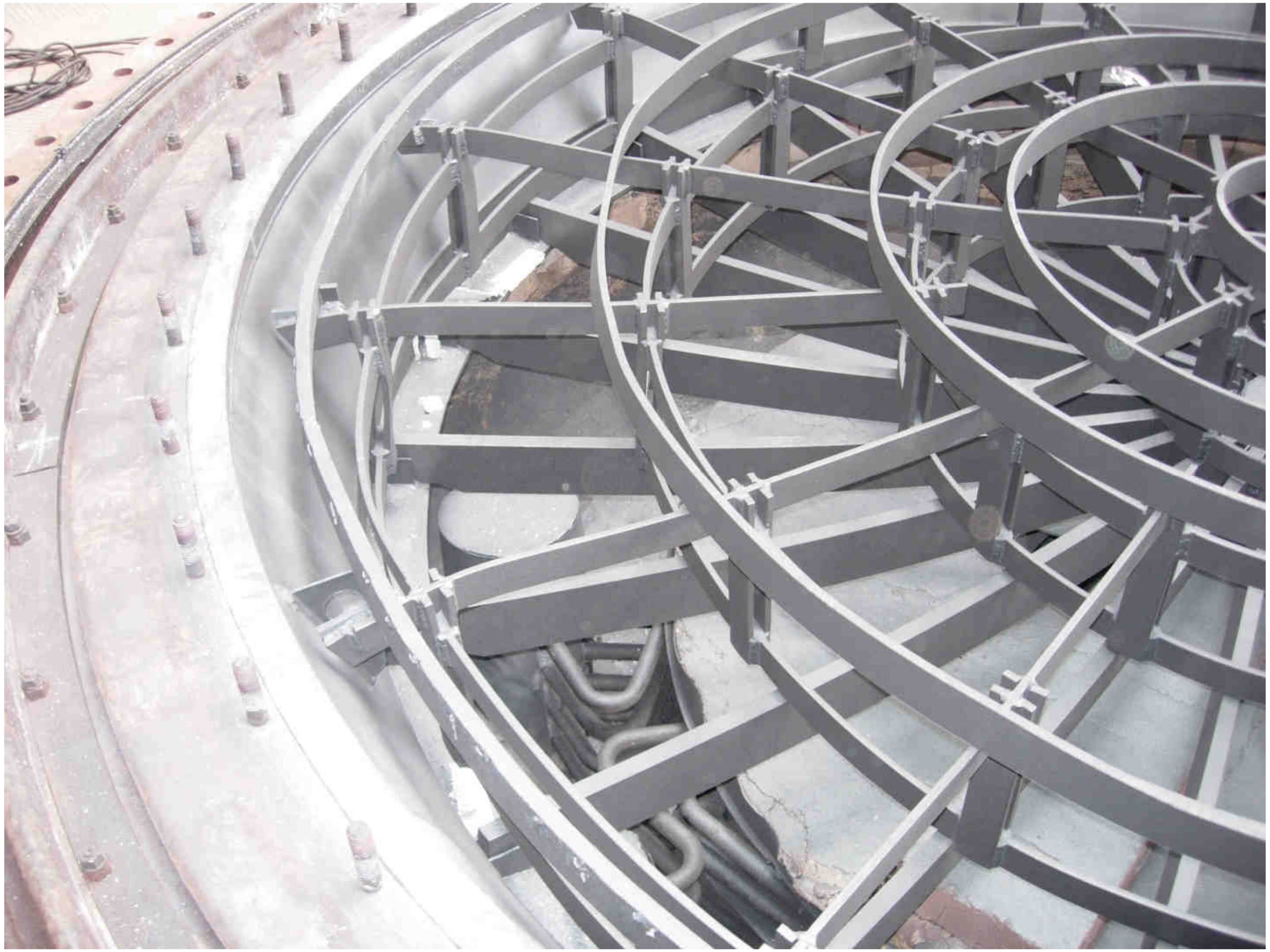
Reference(s): -

- Top figure: Pt, Rh, Pd on alumina, bottom figure: zeolitic with Ce + Cr





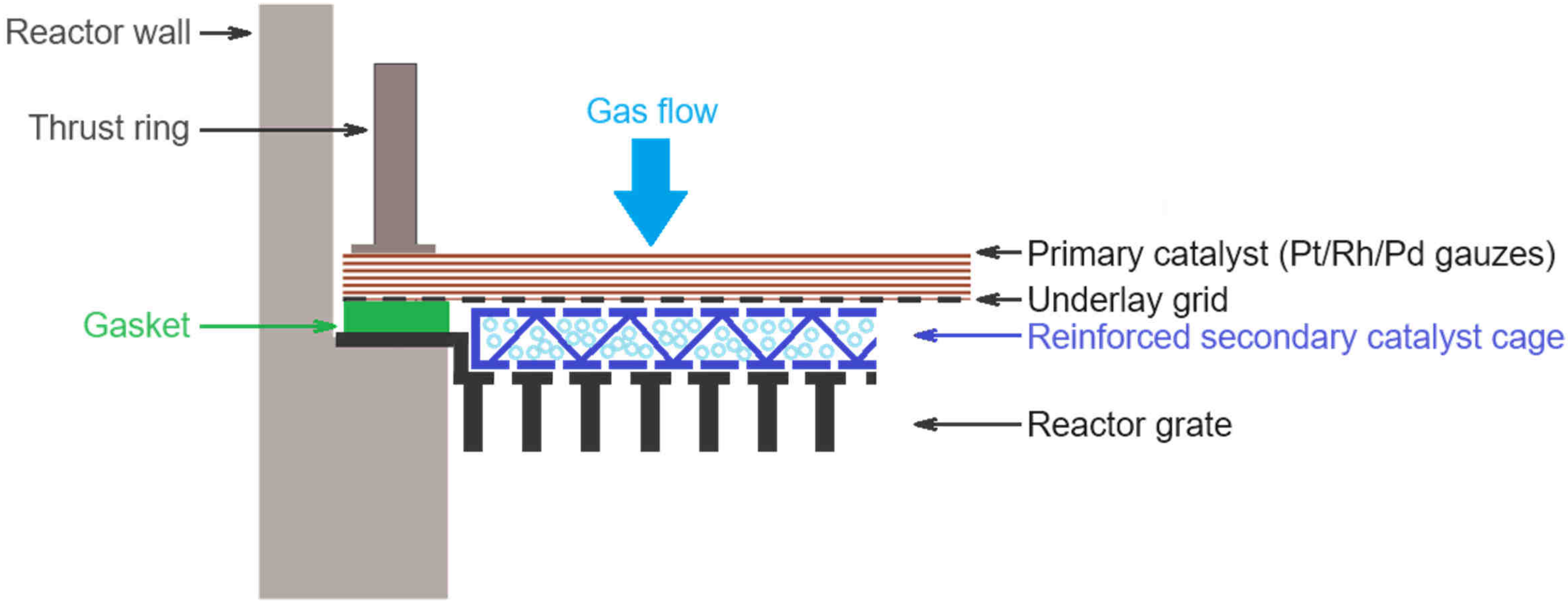
- Older reactors do not have baskets, but steel grates ⇒ problems
  - not much space under the Pt/Rh/Pd gauzes + no support for bulk catalyst



Note: The grate ater removing the gauzes

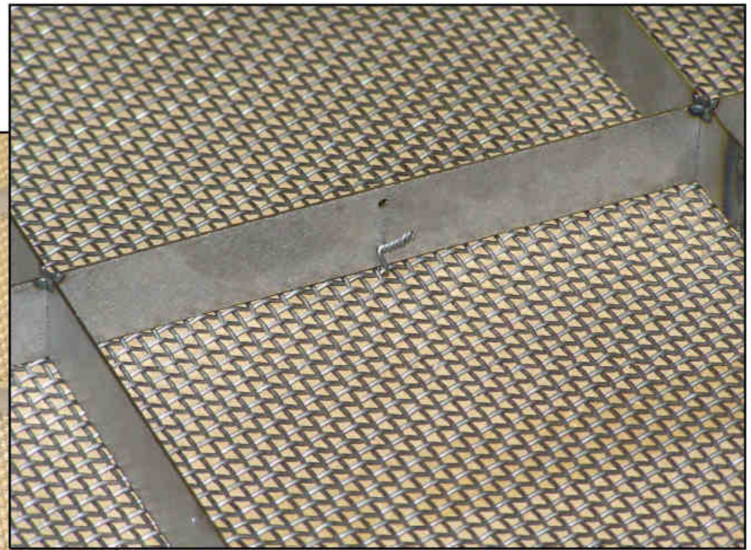
Secondary catalysts for older reactors

- Older reactors do not have baskets, but steel grates ⇒ problems
  - not much space under the Pt/Rh/Pd gauzes + no support for bulk catalyst
  - Catalyst in cartridges (height only 15–25 mm)
  - N_2O emissions reduction by 30–45% only



2 Secondary catalysts for older reactors

- Why is the efficiency of cartridges only ca. half compared to the bulk cat.?
  - ▶ thin catalyst layers (15–25 mm) well visible in the photos:



Final reduction catalyst (tertiary)

- Differences with the secondary catalyst
  - catalytic reduction of N_2O by reaction with a reducing agent
  - combination into a 2-stage process: $DeNO_x$ + DeN_2O
  - very high N_2O removal efficiency: 98–99%
  - construction of the special reactor before the expansion turbine necessary
  - operating temperature 340– 600℃ → necessity to reheat the gas

very high capital costs!

Principle of tertiary catalysts

- The most widespread system EnviNOx® by ThysenKrupp Uhde company
  - It uses catalysts on the basis of Fe-zeolite: EnviCat®–N_2O & EnviCat®–NO_x
  - 2 variants of the system:

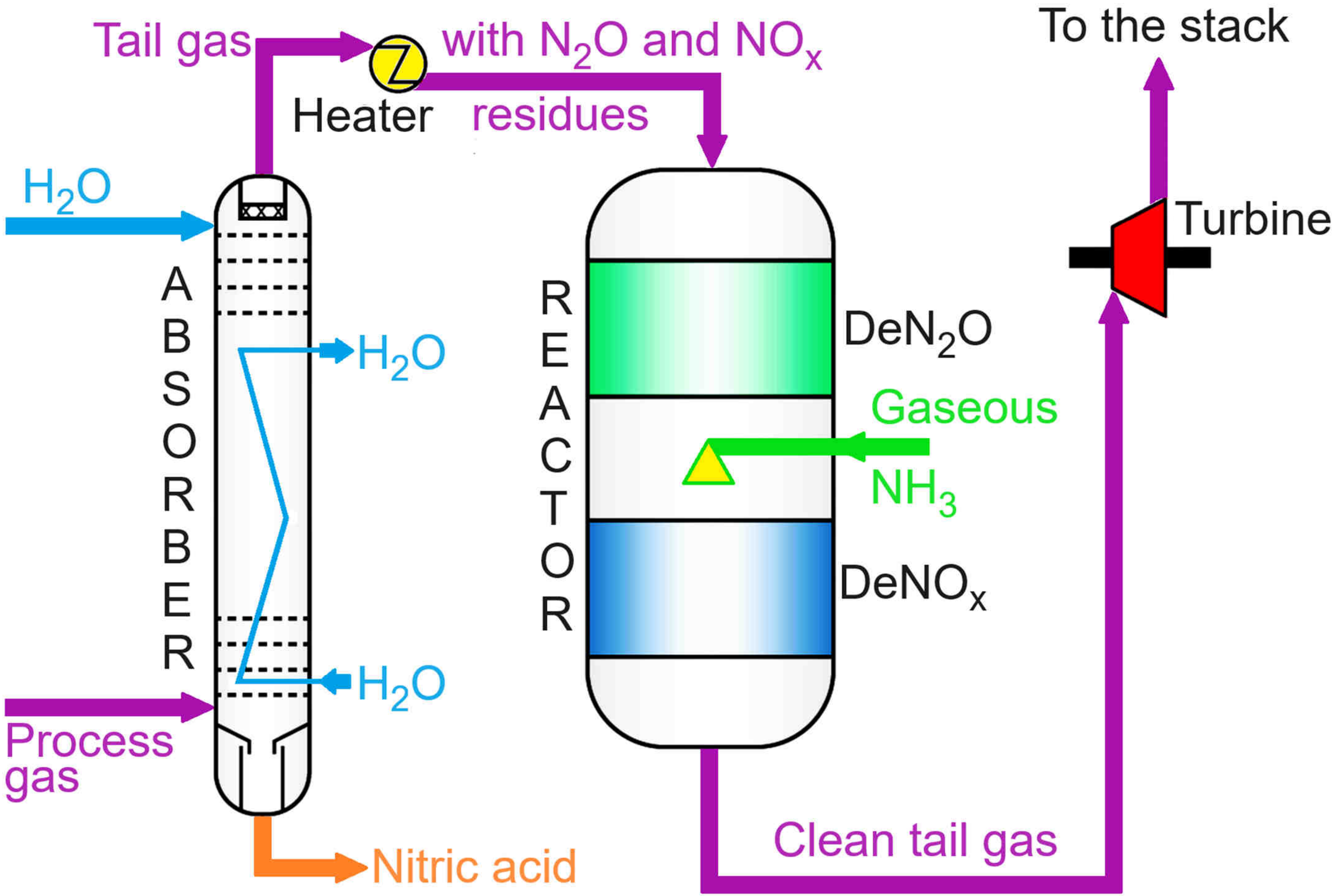
    (a) only NH_3 as a reagent

    (b) propane or methane and NH_3 as reagents

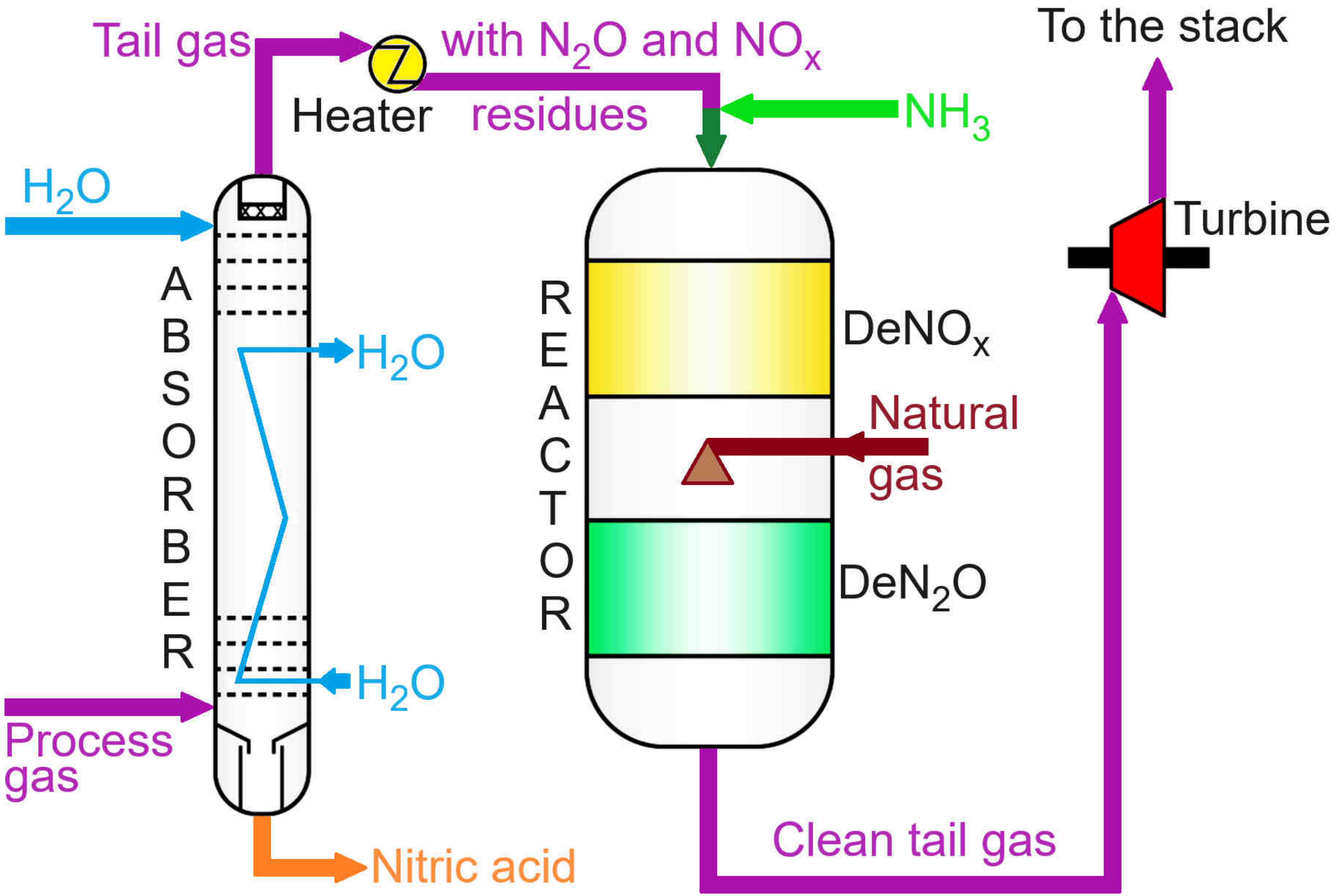
  - In the case (a): first stage = decomposition of N_2O without reagent
    second stage = reduction of NO and NO_2 with ammonia to N_2

  - In the case (b): first stage = reduction of NO and NO_2 with ammonia
    second stage = reduction of N_2O with hydrocarbons to N_2 + CO_2

EnviNOx® using NH_3 only



EnviNOx® using NH_3 and C_xH_y



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