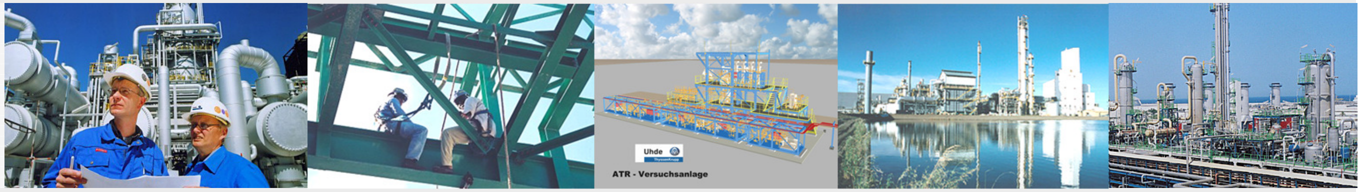

Autothermal reforming: a flexible syngas route with future potential

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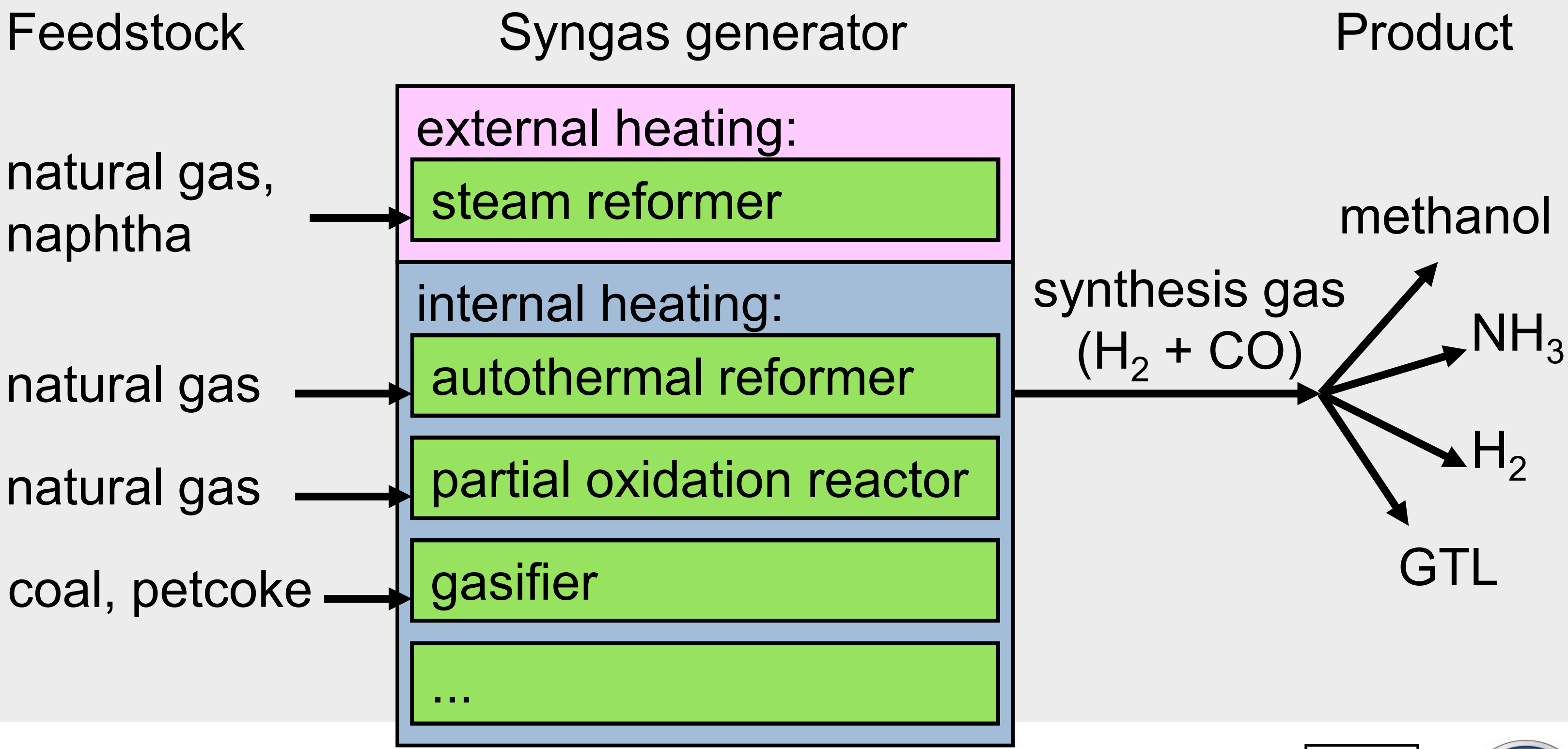
Synthesis gas and its generation

- Gas mixture of H_2 and CO
- Basis for important processes such as synthesis of ammonia, methanol, ...
- Syngas generation:



Synthesis gas and its generation

Main chemical reactions for synthesis gas generation by autothermal reforming of CH_4:

- Steam reforming of CH_4:

  $CH_4 + H_2O \rightarrow CO + 3\ H_2$ $\Delta H_R = +206$ kJ/mol endothermal

- Partial oxidation:

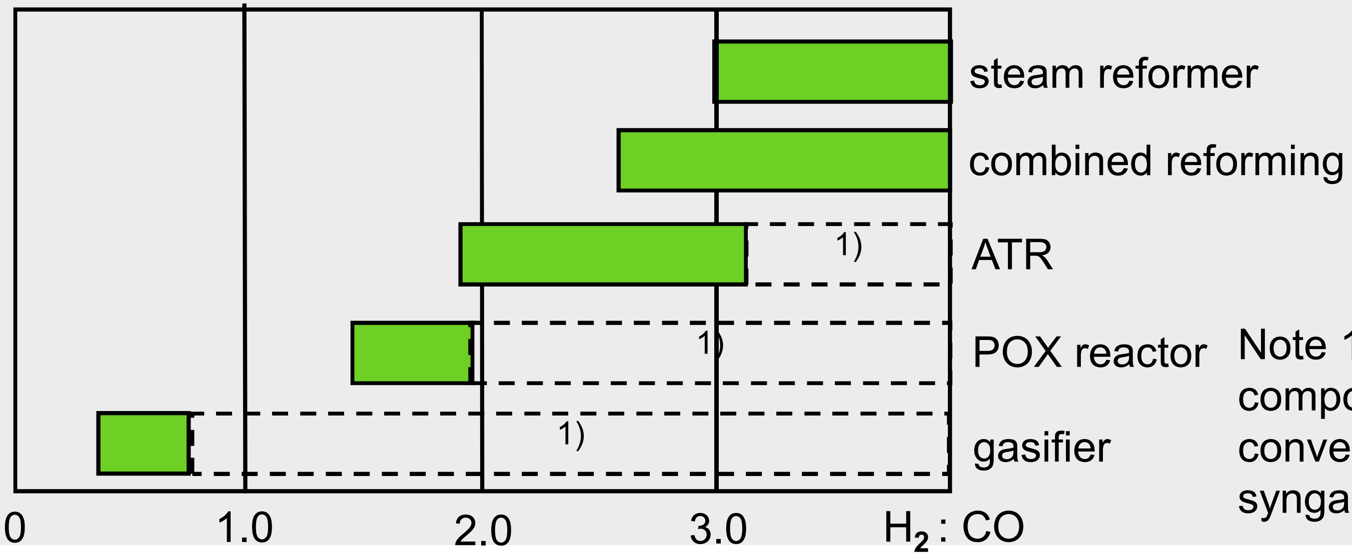
  $CH_4 + \frac{1}{2}\ O_2 \rightarrow CO + 2\ H_2$ $\Delta H_R = -35$ kJ/mol exothermal

Synthesis gas composition

Synthesis gas composition requirements (outlet reformer):

- ammonia: $(H_2 + CO) / N_2 \approx 3.0$
- methanol: $(H_2 - CO_2) / (CO + CO_2) \approx 2.0$
- hydrogen: H_2 = max.
- gas to liquids: $H_2 / CO \approx 2.0$

Composition ranges provided:



Note 1) possible gas compositions via CO conversion of the syngas

Application of autothermal reforming

Autothermal reforming already established for syngas production:

- stand-alone ATR for GTL plants
- ATR combined with conventional tubular primary reformer for NH_3 and methanol plants:
  - NH_3: ATR used as secondary reformer on pre-reformed gas
  - methanol: mixture of pre-reformed gas and natural gas

"mild" conditions by:
- high steam ratio
- H_2 at inlet

$\Rightarrow$ low risk of soot formation

Idea: use ATR as <u>only</u> reforming reactor, delete costly tubular primary reformer.

Risk: soot formation in ATR with no pre-reformed gas

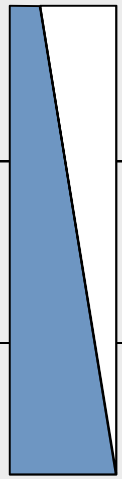
Research needed (especially experimental) prior to commercialisation

Flowsheet options for ATR based NH_3 plant

Different oxidator compositions possible

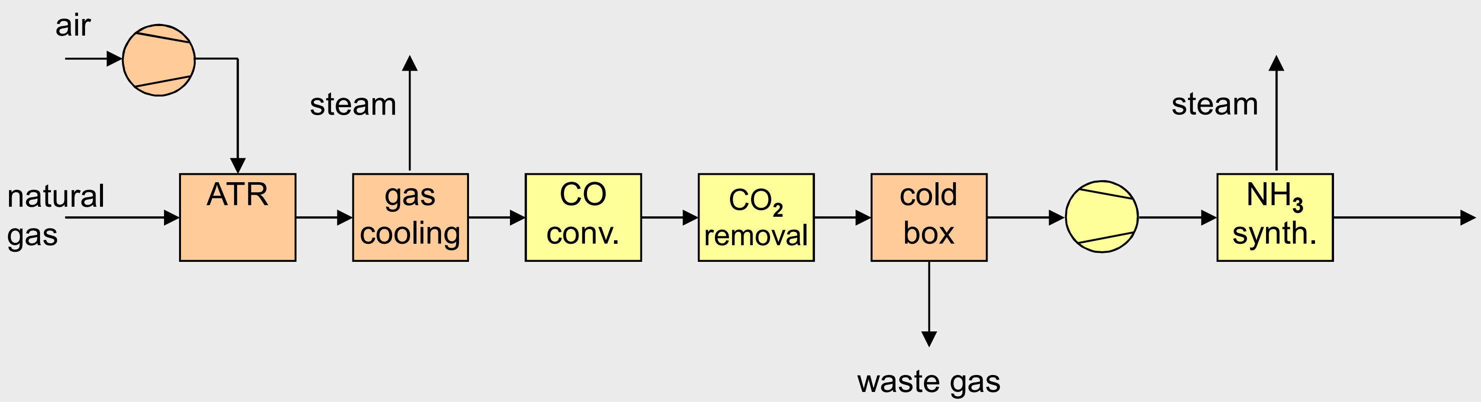
⇒ different flowsheets for syngas generation of an NH_3 plant possible

Oxidator	Oxygen demand	Nitrogen content compared to demand of NH_3 synthesis
plain air (21 % O_2)	defined by heat demand of the reforming reaction	too high
enriched air		matching
pure O_2		too low



Flowsheet options for ATR based NH_3 plant

Option 1: Plain air as oxidator



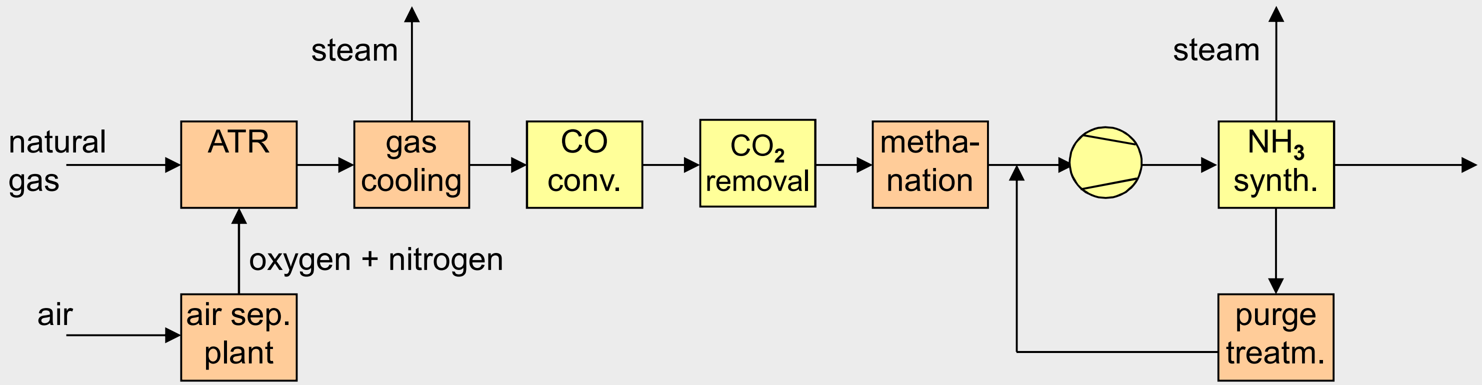
Gas composition: large N_2 surplus in syngas

Consequence: either cryogenic unit to remove N_2
or large purge gas stream

Size: largest flowrates and equipment sizes in front end

Flowsheet options for ATR based NH_3 plant

Option 2: Oxygen enriched air as oxidator



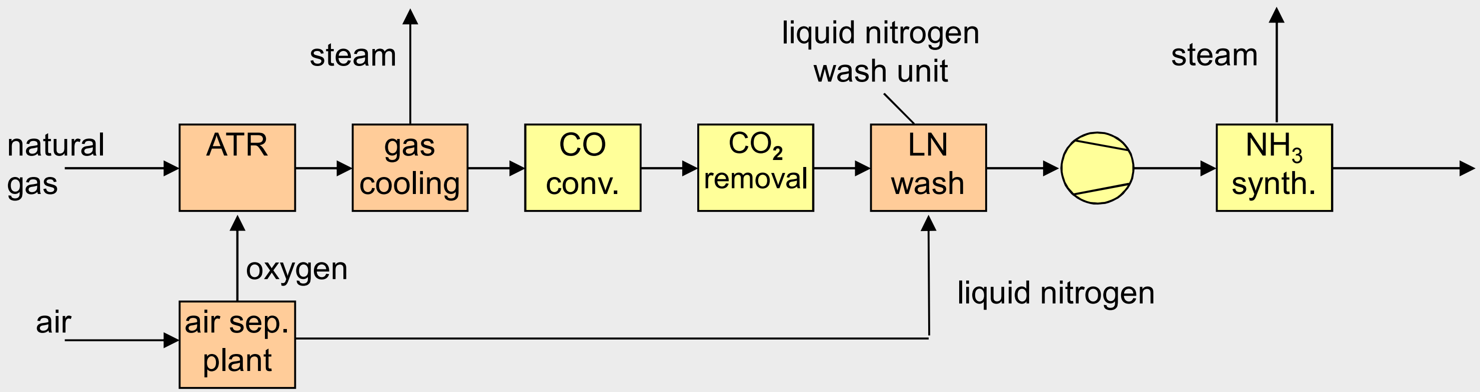
Gas composition: correct amount of N_2 for NH_3 synthesis

Consequence: need air separation unit

Size: medium

Flowsheet options for ATR based NH_3 plant

Option 3: Pure oxygen as oxidator



Gas composition: no N_2 in syngas

Consequence: N_2 to be added at the end of the front end (for example by liquid nitrogen wash unit)
large air separation unit needed

Size: smallest flowrates and equipment sizes in front end

Flowsheet options for ATR based NH_3 plant

Economic comparison between 3 options

- Operating cost:
  Similar (similar energy consumption)

- Investment cost:
  Option 3 (pure oxygen) seems to be most expensive:
  – large air separation unit
  – nitrogen wash unit

Economic comparison between steam reformer and ATR plant

Operating cost (energy consumption)

steam reformer	ATR
basis	↑ heat of reaction supplied by burning feed gas ⇒ higher feed gas flow ⇒ higher energy demand for preheating
	↓ lower loss from flue gas
	↑ air separation

Overall:

↑ + 6 % cost for option “enriched air”
+ 10 % cost for option “pure oxygen”

Economic comparison between steam reformer and ATR plant

Investment cost

judgement difficult because no purely on ATR based NH_3 plant built so far

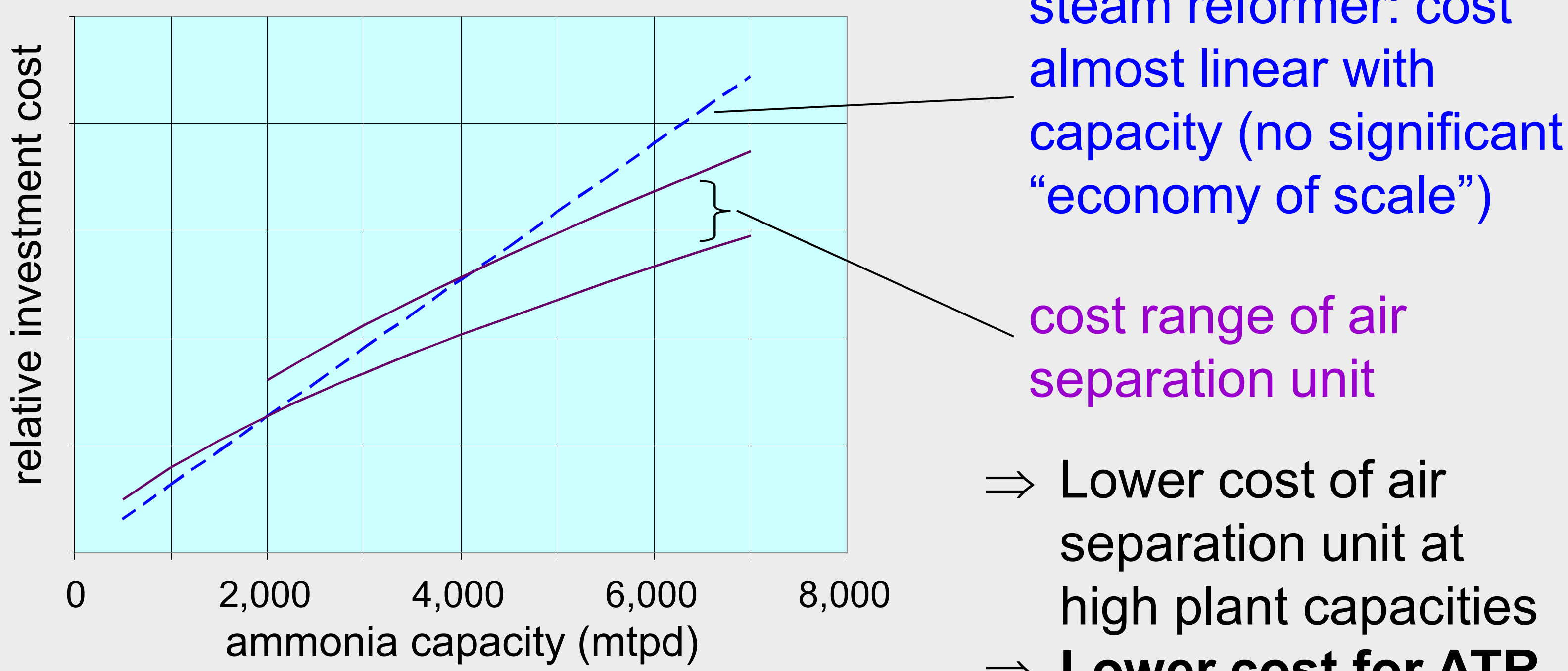
steam reformer	ATR
basis	↑ air separation; ↓ no steam reformer — biggest contributors
	~ ATR similar to secondary reformer
	↑ liquid nitrogen wash unit (option "pure oxygen")
	↓ no H_2 recovery unit (option "pure oxygen")

Overall:
+ / – ??? ⇒ evaluation on next slide

Economic comparison between steam reformer and ATR plant

Investment cost

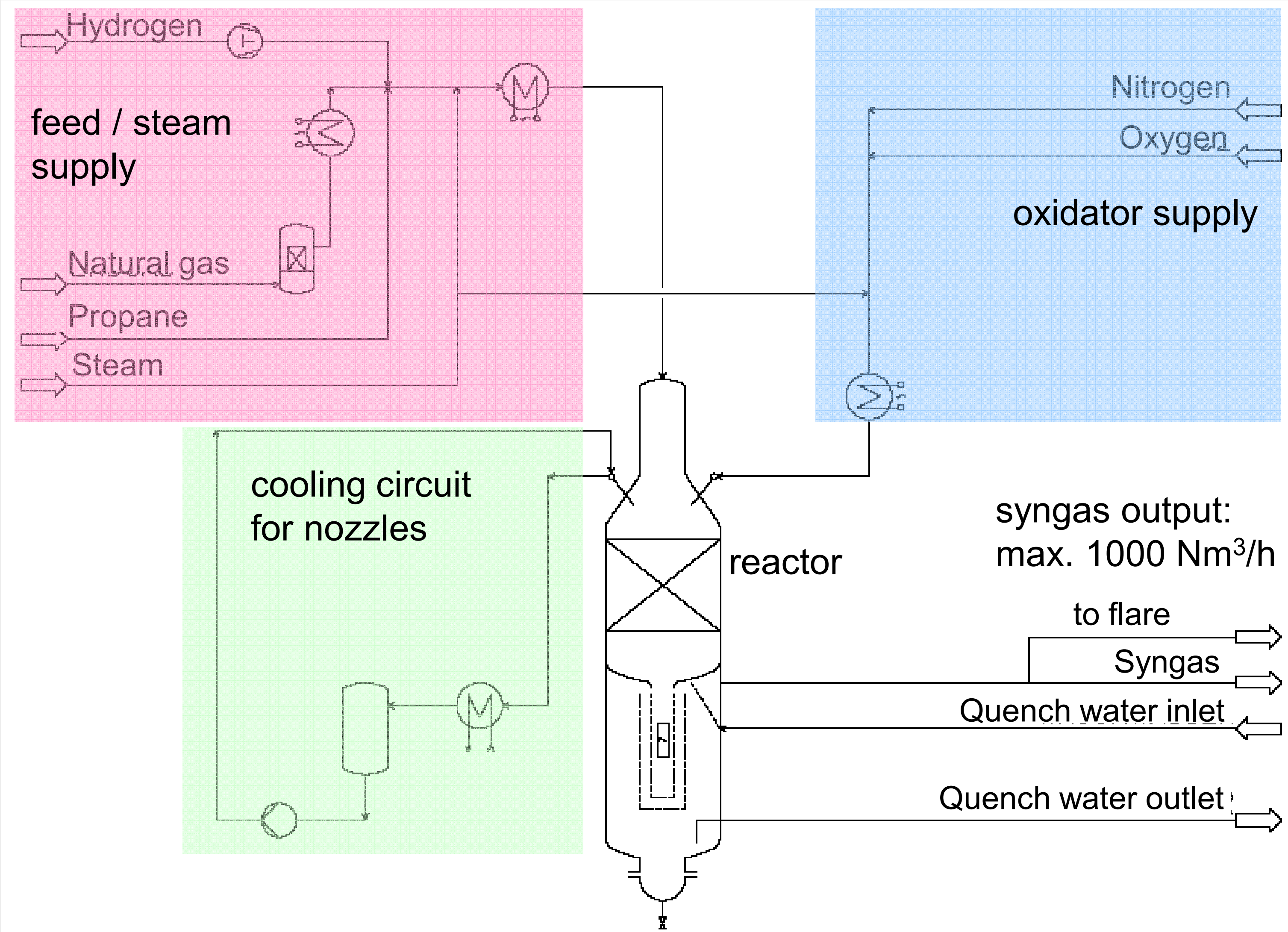
Most significant effect comes from cost relation of air separation and steam reformer



⇒ Lower cost of air separation unit at high plant capacities

⇒ **Lower cost for ATR**

Uhde's ATR test facility – process flow diagram



Uhde's ATR test facility

Aus Datenschutzgründen wurde das automatische Herunterladen dieses Bilds von PowerPoint gesperrt.

Uhde's ATR test facility

- 2007 – 2009: Installation of test facility in Russia in an existing chemical complex – advantage: all utilities and manpower available
- June 2009: first ignition

Highlights:

- Critical parameter: soot formation at low steam-to-carbon ratio of the feed gas
- Sampling nozzles for soot detection in quench water and in gas
- Analysis equipment for soot detection with detection limit at 1 to 3 ppm
- When soot formation detected: change operating conditions to soot-free in order to get the soot again out of the system.

Test programme for the ATR

Outlet gas requirements:

- composition (e.g. $[CO + H_2] / N_2 \approx 3.0$ or $H_2 : CO \approx 2.0$; no soot)

Design parameters:

- combustion zone geometry, nozzles etc.
- combustion zone gas residence time
- inlet velocity feed/steam mixture
- inlet velocity oxidator
- space velocity catalyst bed

Operating parameters:

- steam-to-carbon ratio
- combustion zone temperature (by oxygen-to-carbon ratio)
- oxidator composition

Can be varied by operation of the test facility

Target of the optimisation:

- highest CH_4 conversion
- minimum oxygen consumption

Test programme for the ATR

Variation of parameters:

Parameter	Unit	Lower limit	Upper limit
feedstock higher hydrocarbon content	%	2	14
N_2 content oxidator	%	0	55
operating pressure	bar	20	30
steam-to-carbon ratio	–	0.5	3.0
combustion zone shape	–	A	B
rel. gas residence time comb. zone	%	50	100
combustion zone temperature	°C	1150	1250

Operational results from the ATR test facility (1)

Operation without catalyst

Parameter	Unit	Operating point A: NH_3 syngas, enriched air	Operating point B: NH_3 syngas, pure oxygen	Operating point C: FT syngas
Feed CH_4 **content**	% mole	89.2	82.9	88.7
Feed C_{2+} **content**	% mole	7.1	14.5	7.4
Oxidator N_2 content	% mole	42.1	5.0	5.0
Steam-to-carbon ratio	–	3.0	2.0	0.7
Outlet temp. ox. zone	°C	1200	1250	1238
Oxygen-to-carbon ratio	–	0.85	0.74	0.60
Syngas pressure	bar abs	28.0	28.0	28.0
Outlet temp. cat. zone	°C	1086		1100

Operational results from the ATR test facility (2)

Operation with catalyst, p = 28 bar		Operating point		
		A	B	C
Parameter	**Unit**	**NH_3 syngas, enriched air**	**NH_3 syngas, pure oxygen**	**FT syngas**
Feed CH_4 **content**	% mole	91.9	91.3	96.9
Feed C_{2+} **content**	% mole	4.0	4.8	1.9
Oxidator N_2 content	% mole	48.9	5.0	5.0
Steam-to-carbon ratio	–	2.7	3.0	0.62
Outlet temp. ox. zone	°C	1200	1200	1210
Oxygen-to-carbon ratio	–	0.76	0.71	0.68
Outlet temp. cat. zone	°C	920	908	1024
Outlet CH_4 content	% mole	0.13	0.32	0.55

Summary

- Autothermal reformers well established in combination with other syngas generators like tubular reformers (“conventional concept”)
- Cost advantage of conventional concept vs. stand-alone ATR shrinking at higher plant capacity
- Research work triggered by less experience with stand-alone ATR
- Uhde’s test facility built and in operation
- Operating data used to identify best design and to tune the design tools for commercial applications
- Uhde will be ready to offer an ATR for NH_3 and other applications in the near future

Summary

Thank you for your attention!

Questions please!