JM

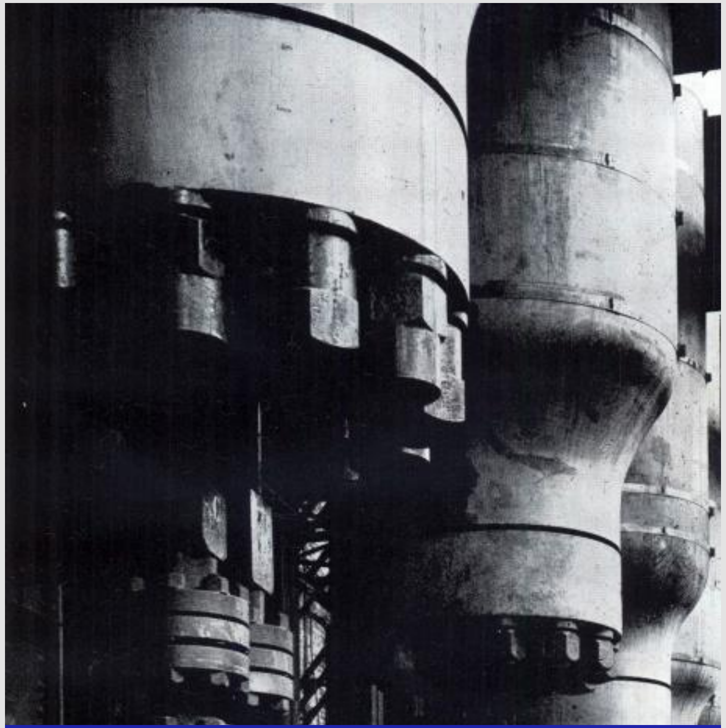
Johnson Matthey
Inspiring science, enhancing life

Americas hydrogen and syngas technical training seminar

Ammonia synthesis

George Sneed

Technology and catalyst development



Historic HP Converters

Fused Fe-ammonia synthesis catalyst

Ammonia synthesis

Consider $3H_2 + N_2 \rightarrow 2NH_3$ at 400-500°C (750-932°F), 200 bar (2900 psi)

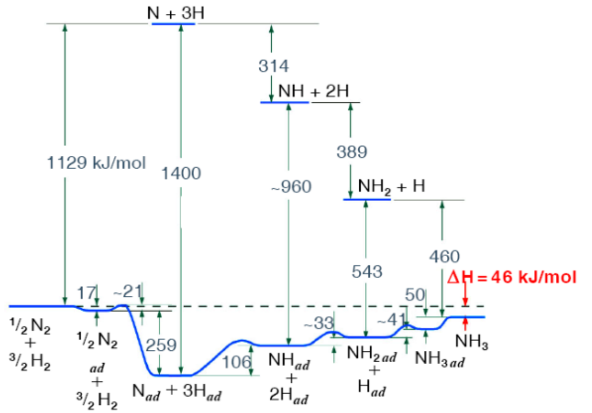
$$N_2 \rightleftharpoons N_{2ad} \rightleftharpoons 2N_{ad}$$

$$H_2 \rightleftharpoons 2H_{ad}$$

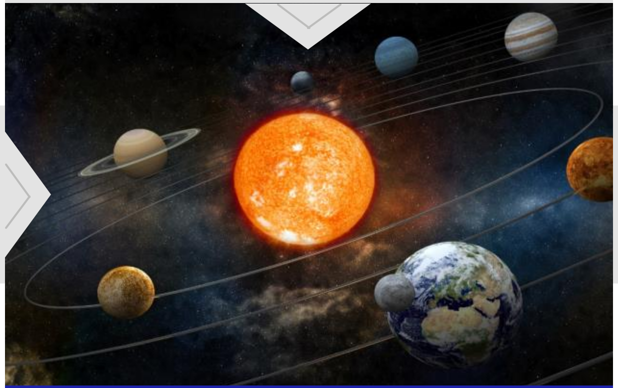
$$N_{ad} + H_{ad} \rightleftharpoons NH_{ad}$$

$$NH_{ad} + H_{ad} \rightleftharpoons NH_{2ad}$$

$$NH_2 + H_{ad} \rightleftharpoons NH_{3ad} \rightleftharpoons NH_3$$



	No catalyst	Catalyst
Reactor size	Big as the solar system	150m³
Daily NH_3 make	A?	B?



Ammonia synthesis

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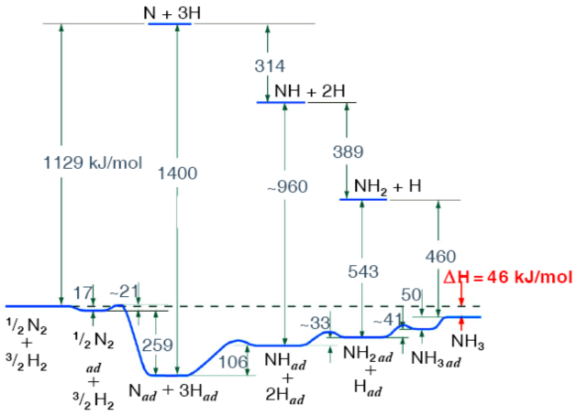
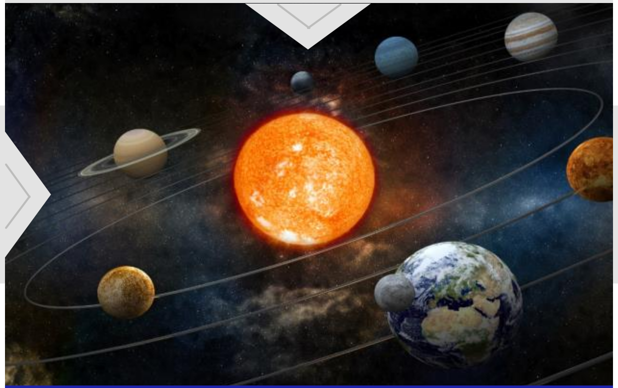
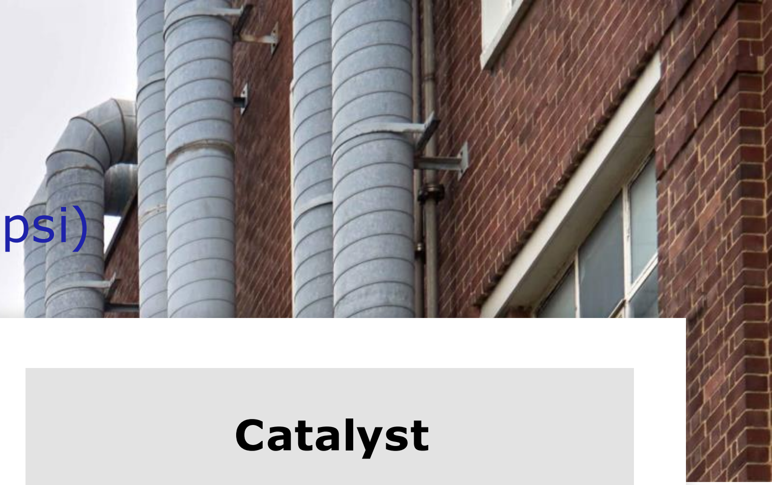


	No catalyst	Catalyst
Reactor size	Big as the solar system	150m³
Daily NH_3 make	**0.1 g**	**3,500 tpd**

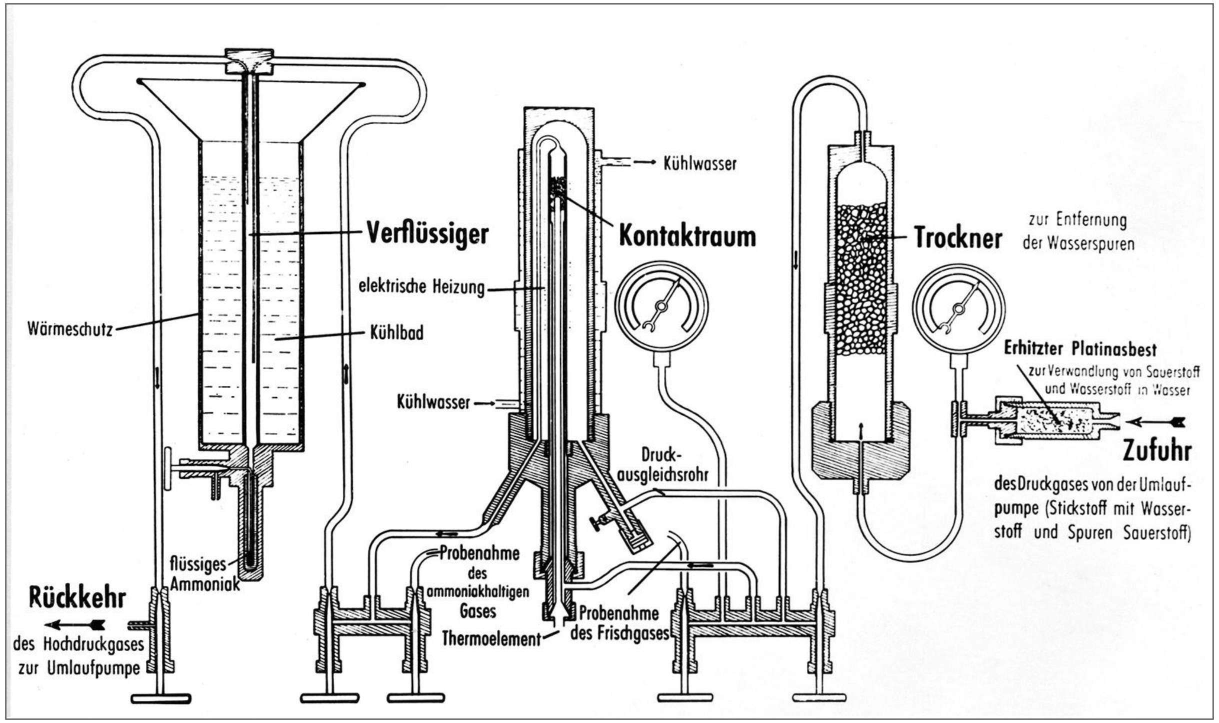


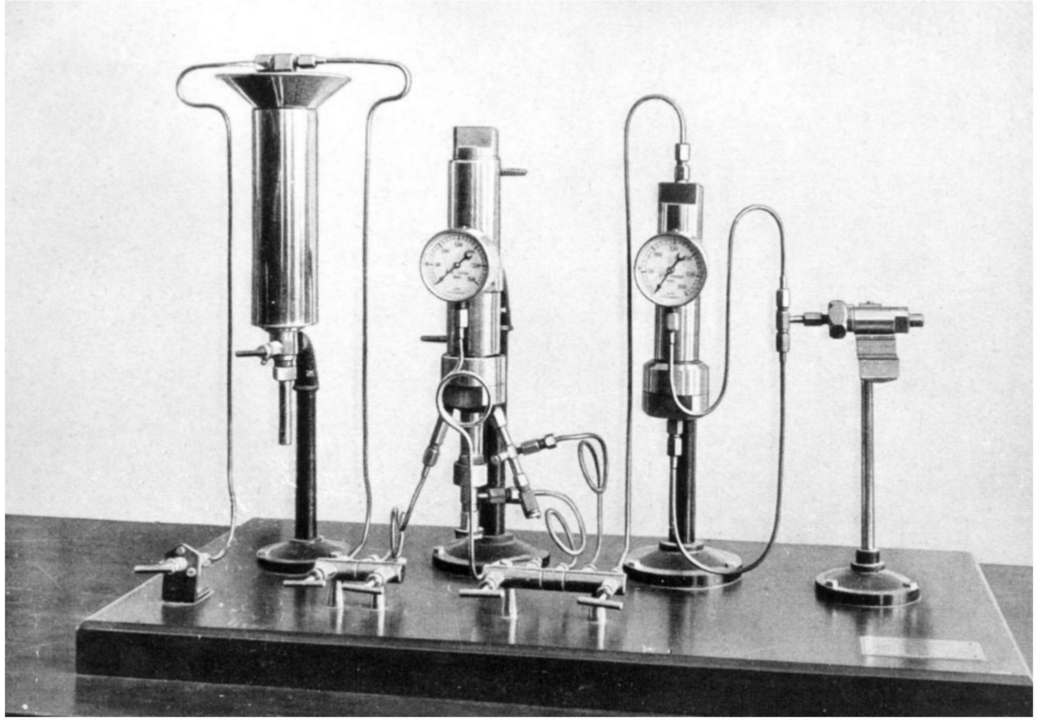


Catalyst Handbook 2nd Edition M V Twigg, Catalyst Activity Page25

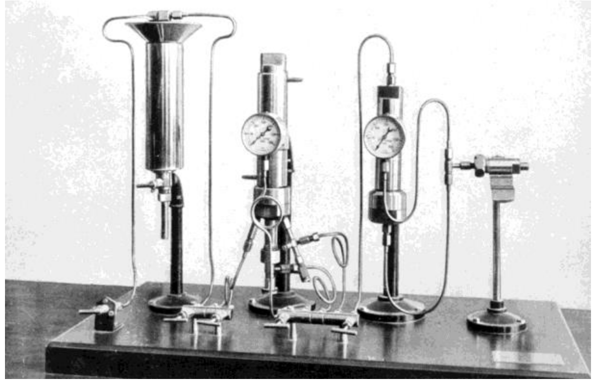
First continuous ammonia process (1909)

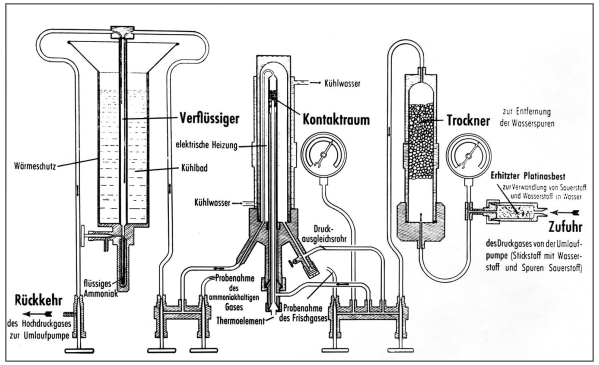
Process was and remains a loop





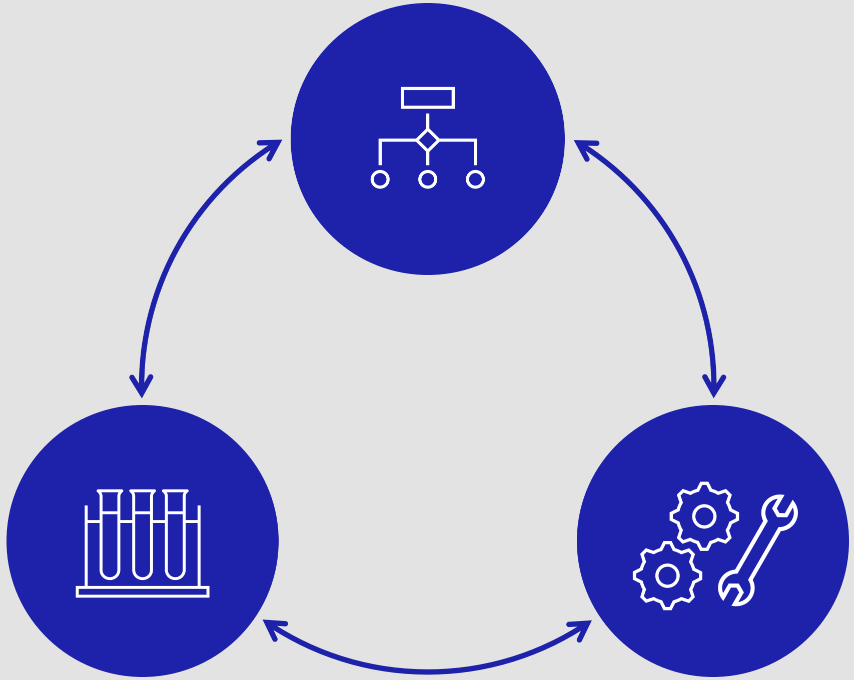
Teamwork – a mix of skills





1908 Laboratory scale
1913 Production scale

Haber
Process design



Mittasch
Catalyst chemistry

Bosch
Mechanical design

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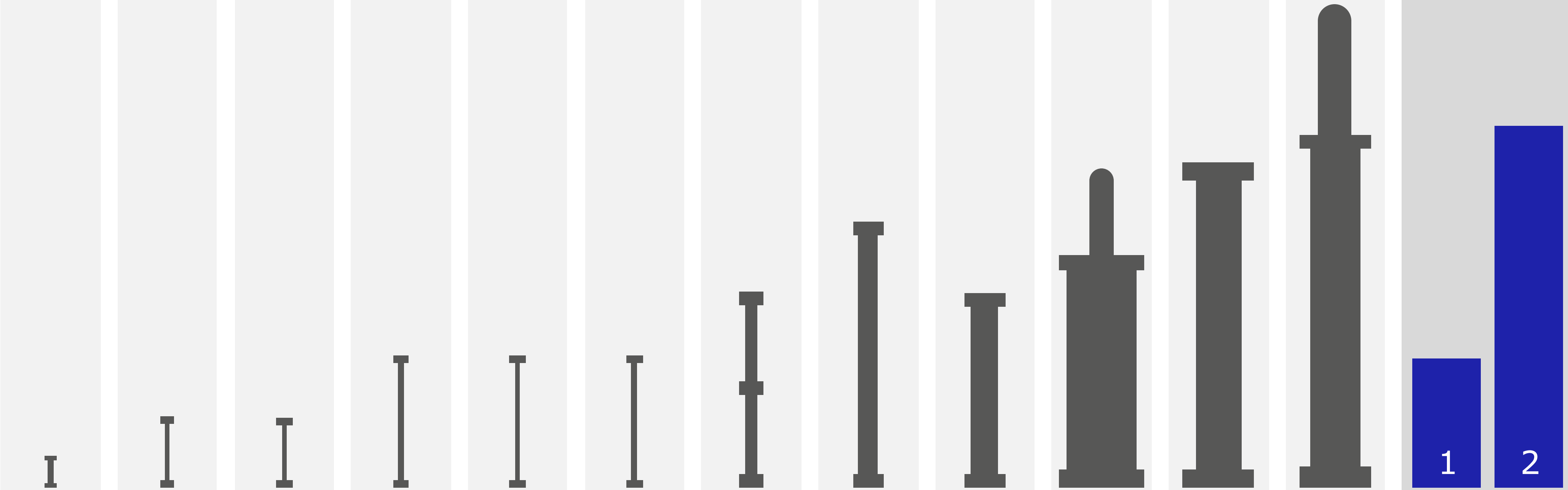
Reactor development – ammonia synthesis

Economies of scale



Year	1910	1911	1912	1913	1913	1914	1915	1940*	1956	1963	1969	1972**	2023
Diameter (mm)	90	90	160	200	300	500	800	1000	1200	2900	2000	2400	2900
Height (m)	1.8	4	4	8	8	8	12	18	12	22	22	34	8 and 24
Pressure (bar)					200		300		300	150	350	210	230
Capacity (mtpd)					3,6-4,8		85		195	910	1200	1580	3500

Ammonia chemistry

Reaction: (exothermic)

$$3H_2 + N_2 \longleftrightarrow 2NH_3$$

$$\Delta H_{298} = -46 \text{ kJ/mol } NH_3$$

Favoured by:

High pressure

Capex, opex

Low temperature

Kinetics vs equilibrium

Low inlet ammonia concentration

Low inert levels - Ar, CH_4, He, etc.

Effect of temperature

At low temperature:

Rate of reaction is slow
(kinetic limit)

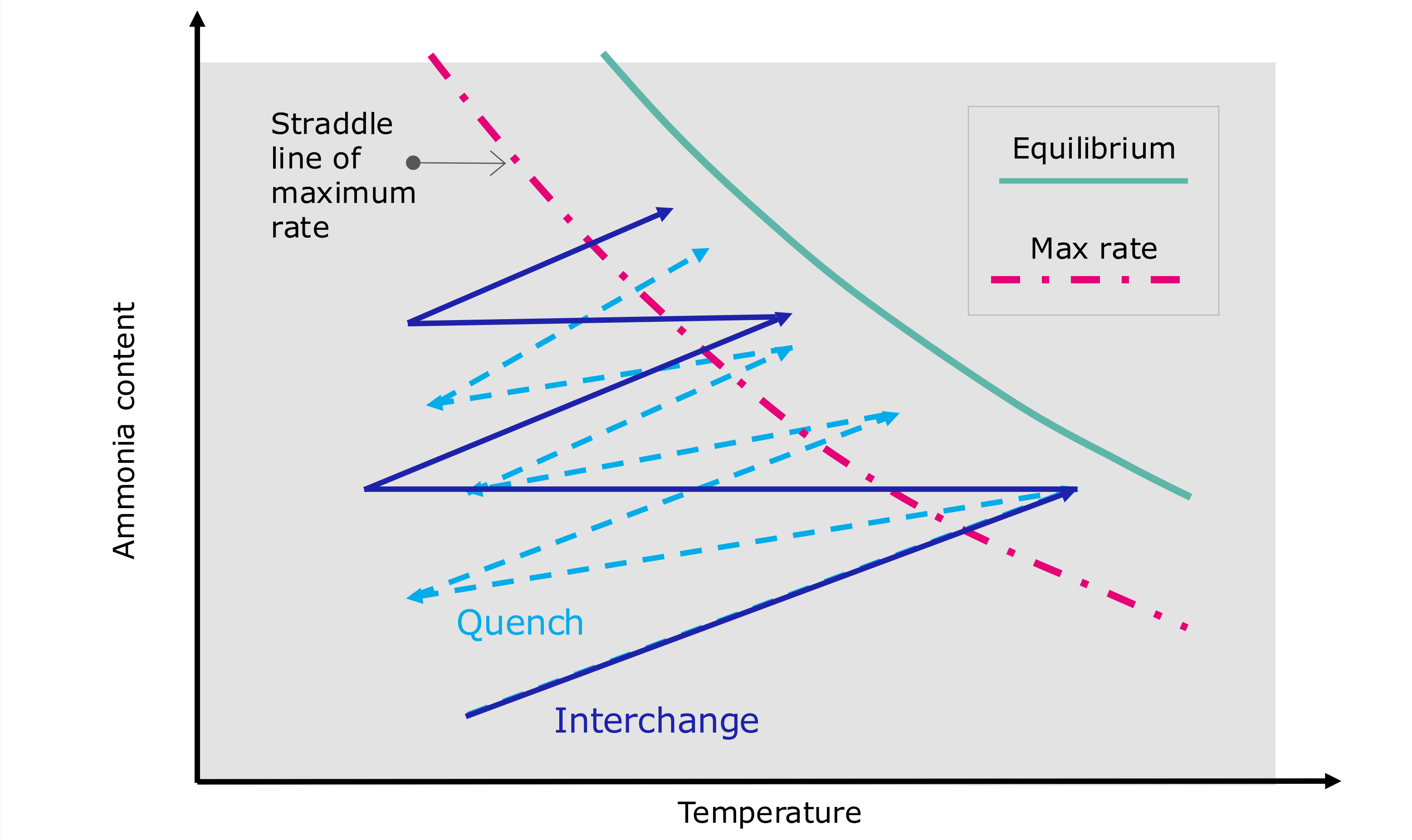
At high temperature:

Rate of reaction is slow
(equilibrium limit)

Hence:

Rate of reaction passes through a maximum as temperature increases

Converters – ammonia synthesis reactors



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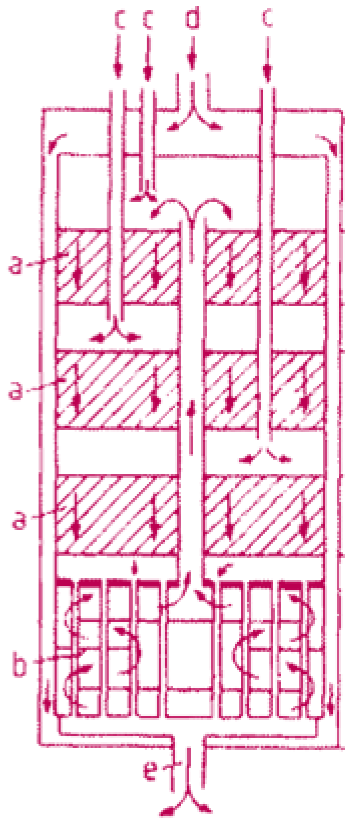
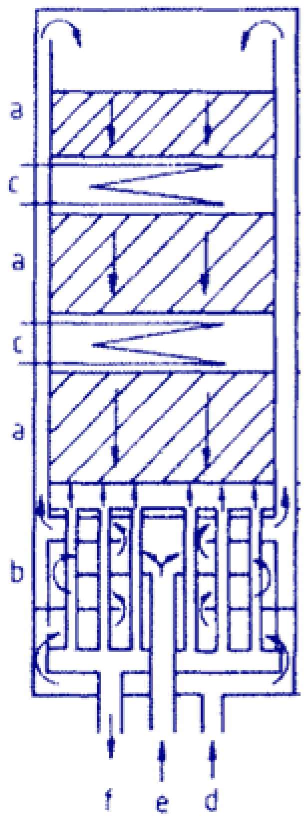
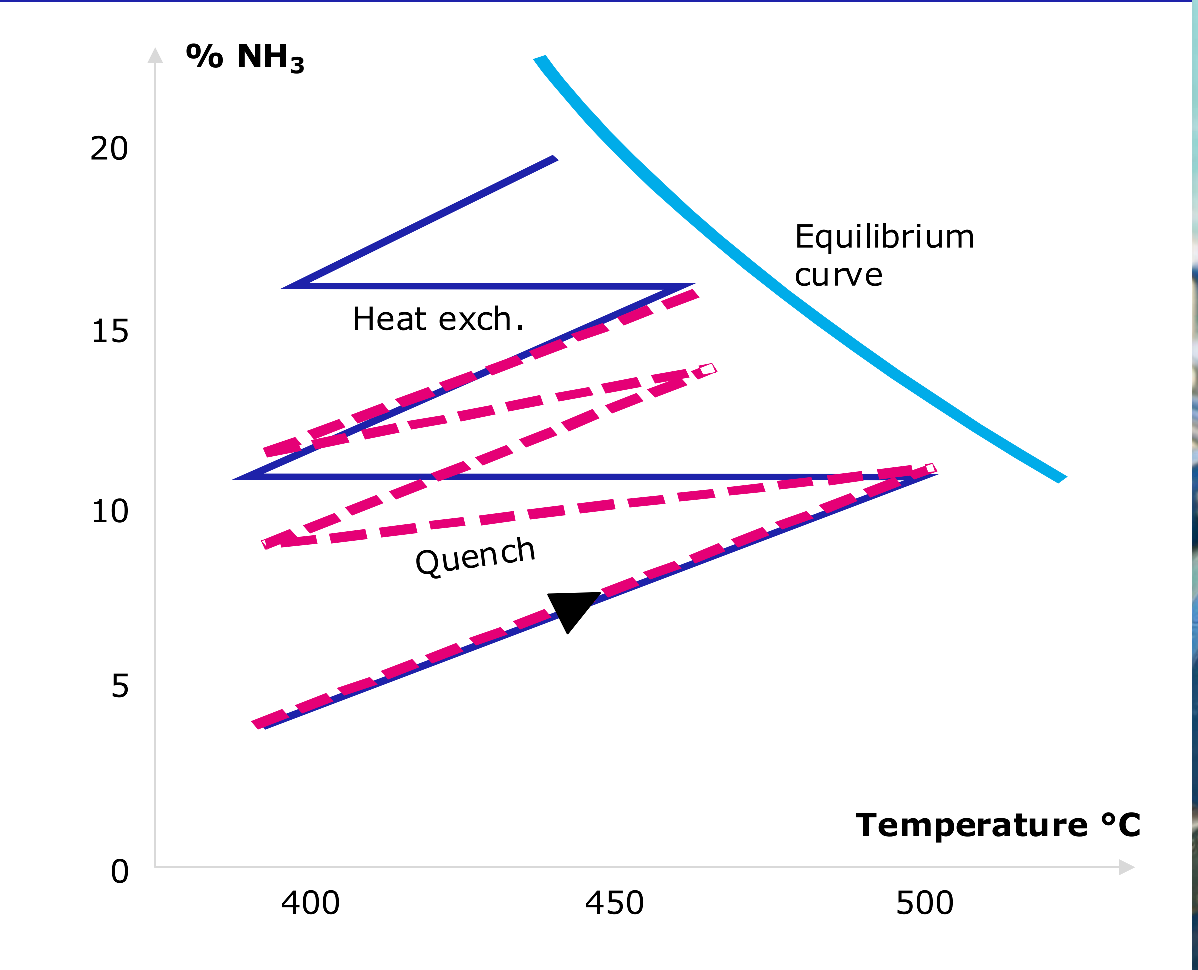
Reactor development – ammonia synthesis

Quench



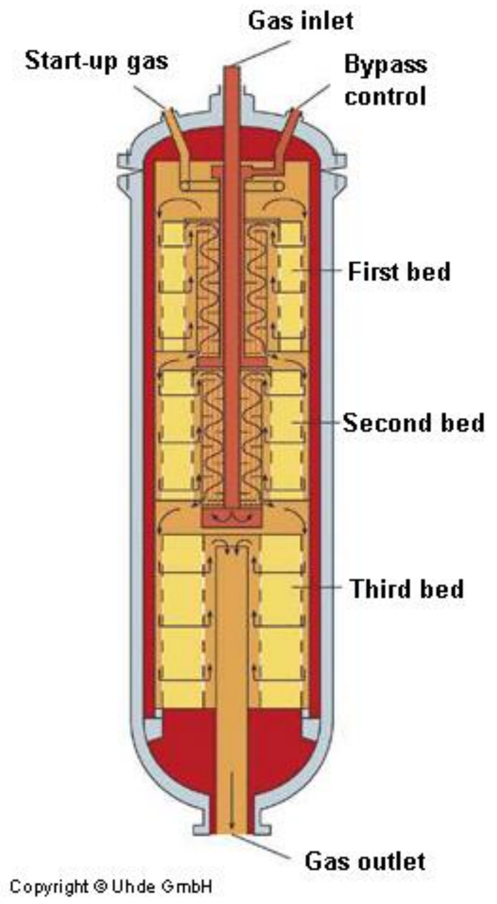
Heat exchange





Max Appl, IFA Technical Conference, September 25.-26., 1997, Sevilla, Spain

Reactor development - ammonia synthesis



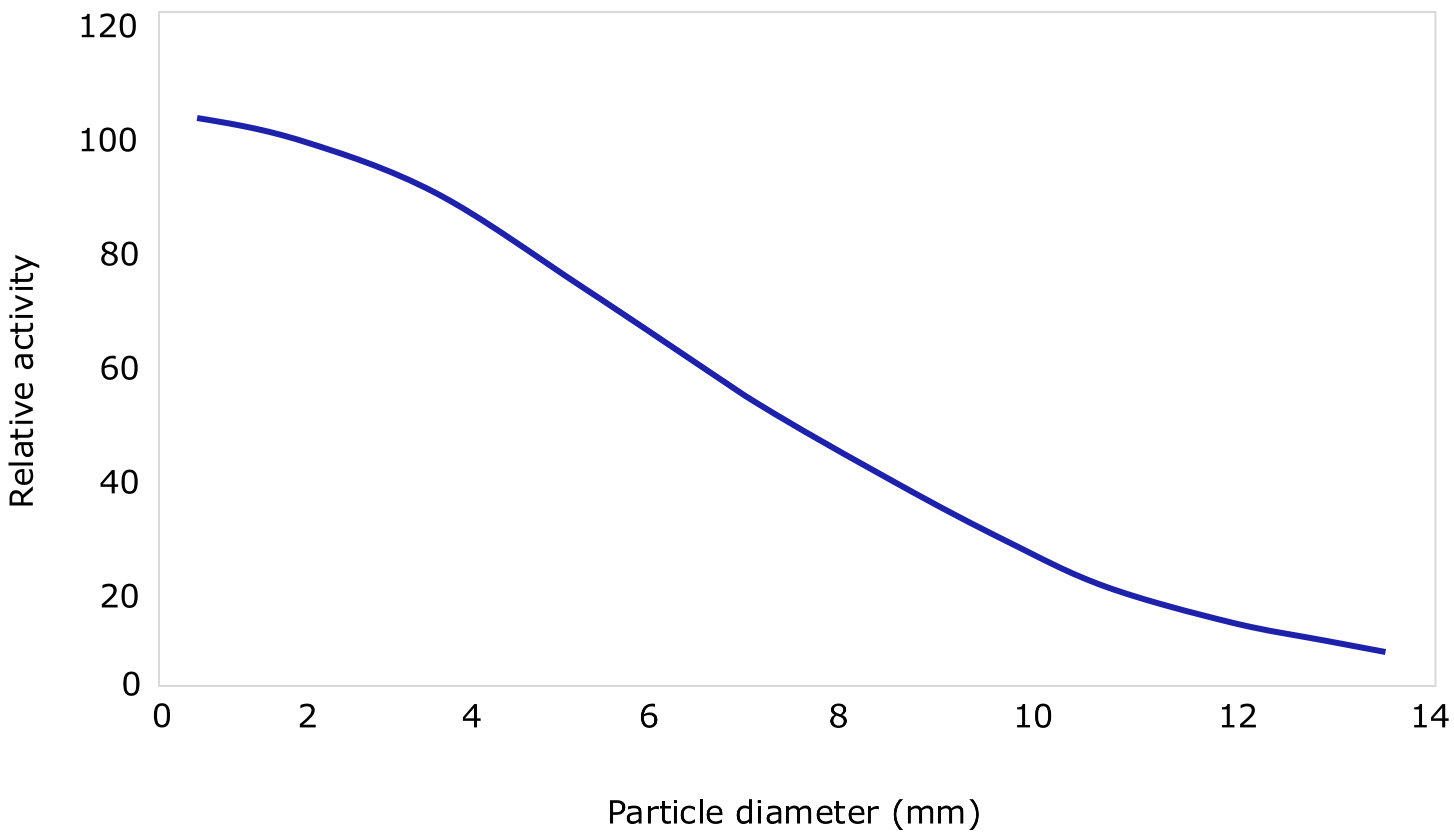
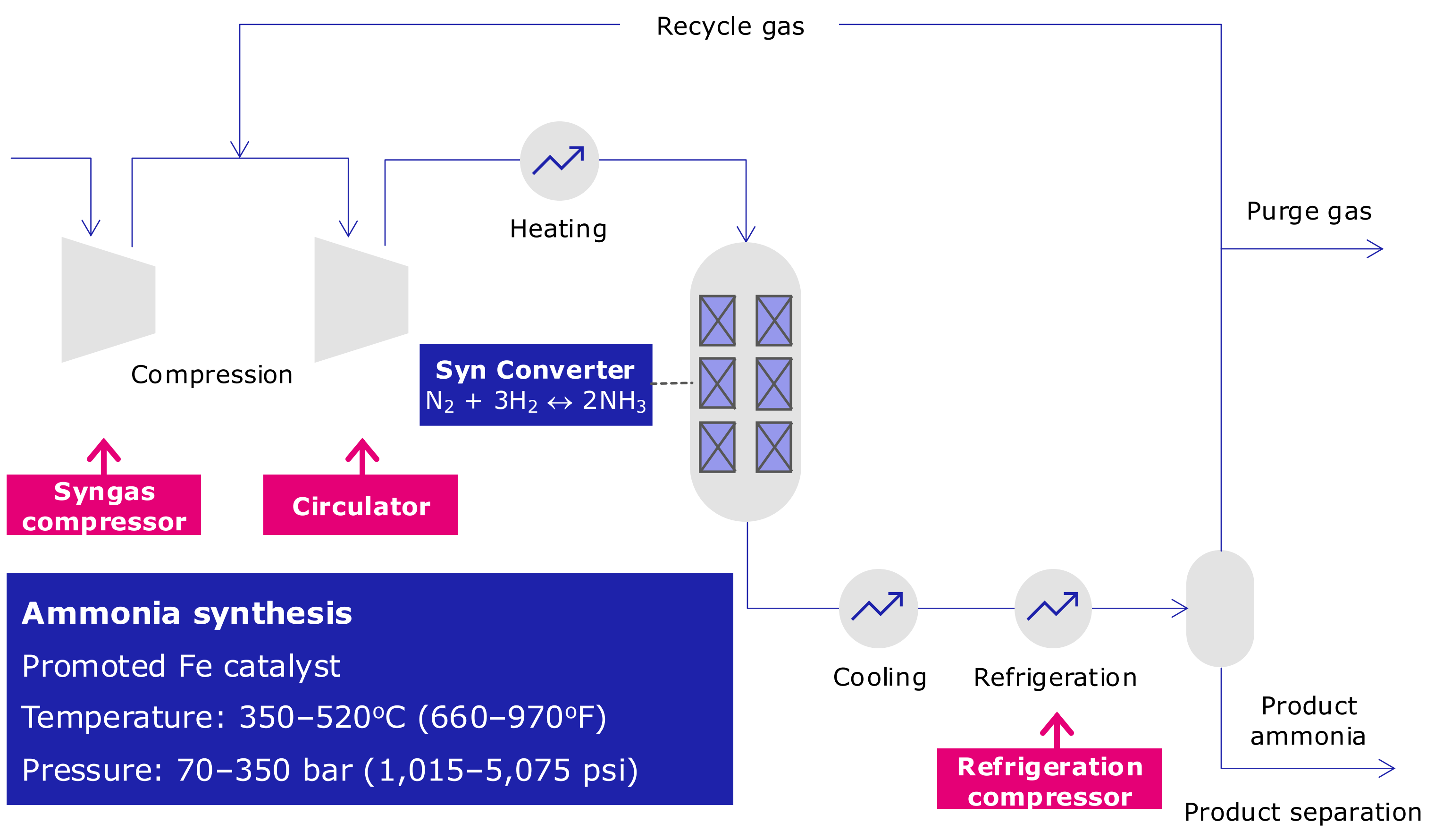


Image: tk Uhde

Synthesis loop



Ammonia synthesis

Promoted Fe catalyst

Temperature: 350–520°C (660–970°F)

Pressure: 70–350 bar (1,015–5,075 psi)

KATALCO™ 35-4	Multi-promoted magnetite
KATALCO™ 35-8	Pre-reduced and stabilized multi-promoted magnetite
KATALCO™ 74-1	Multi-promoted magnetite
KATALCO™ 74-1R	Pre-reduced and stabilized multi-promoted magnetite

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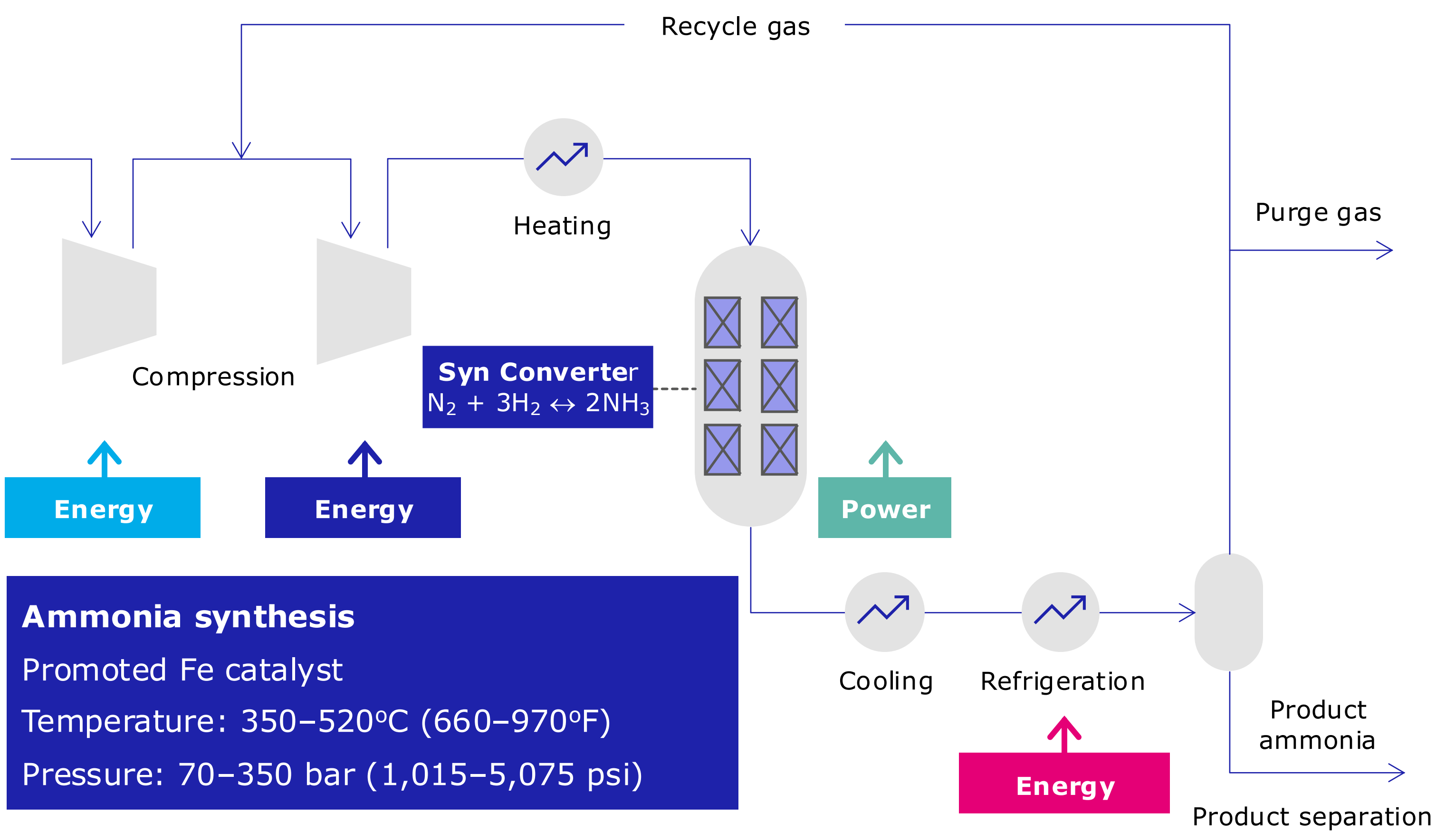
Synthesis loop – energy demand



Ammonia synthesis

Promoted Fe catalyst

Temperature: 350–520°C (660–970°F)

Pressure: 70–350 bar (1,015–5,075 psi)

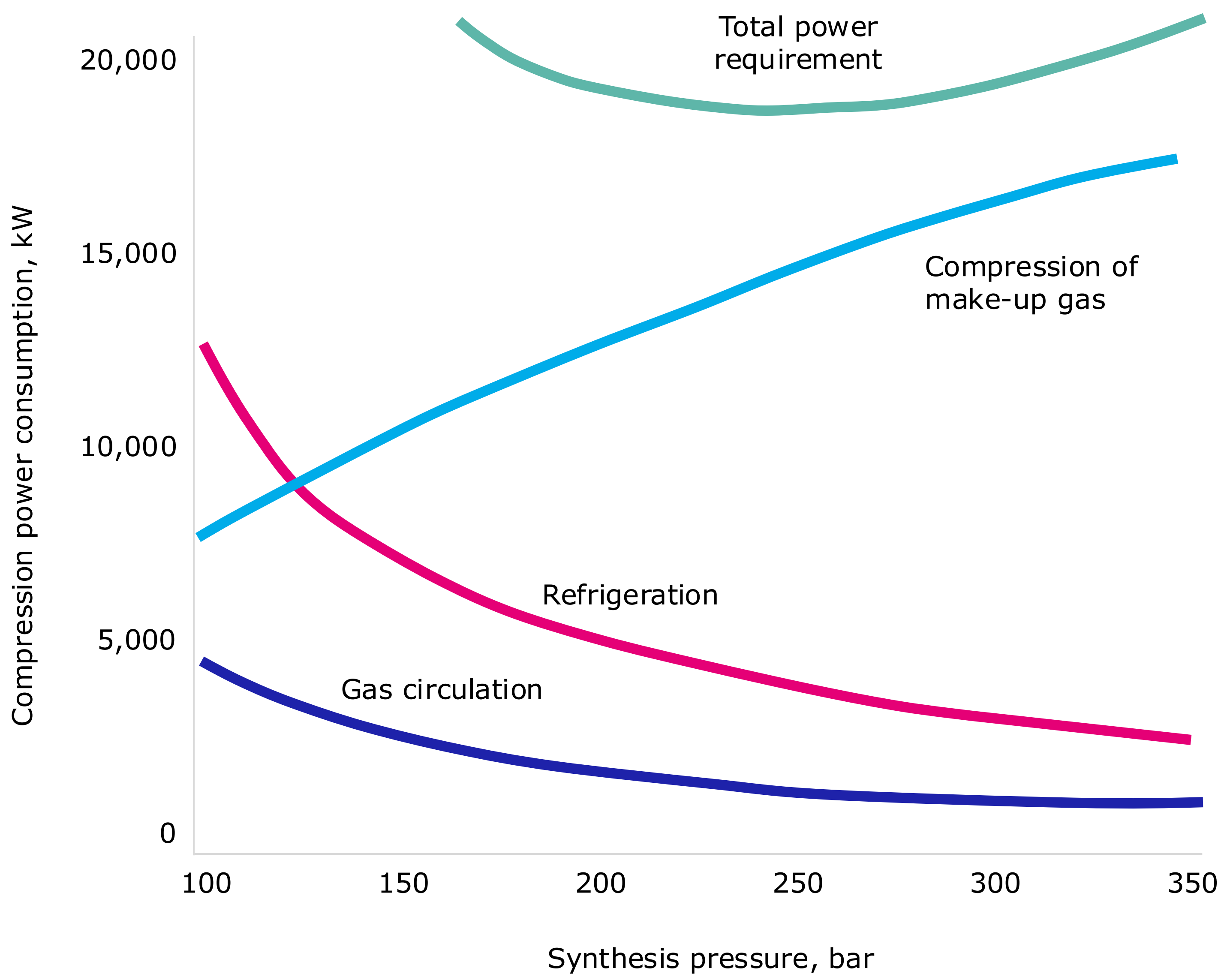
Interactions between:-

- **loop operating pressure**
- **refrigeration level**
- **circulation rate**

Give **total power required** to drive machinery.

Lower pressures require more power for refrigeration and recirculation.

Catalyst Handbook Figure 8.10 , Power required 1000 stpd plant



Typically loop designs
130 - 220 bar
(1,900 - 3,200psi)

Catalyst Handbook Figure 8.10 , Power required 1000 stpd plant

Optimum conditions – swings and roundabouts…

Pressure

Increased pressure gives:

- Increased ammonia content
- Increased compressor power
- Reduced circulator power
- Reduced refrigeration power
- Non-linear effect on capex

Flat optimum, most plants between
130 bar and 220 bar (1,900 – 3,190 psi)

Temperature

Catchpot removes ammonia from the loop

Lower catchpot temperature

- More ammonia removed per pass
- Less ammonia recycled to converter
- More ammonia made in the converter

But

Increased refrigeration duty

No impact on overall conversion

Moisture

Moisture poisons ammonia synthesis catalyst

Moisture comes from

H_2O	
$O_2 + 2H_2 \rightarrow 2H_2O$	Rarely present
$CO + 3H_2 \rightarrow CH_4 + H_2O$	Remove by methanation
$CO_2 + 4H_2O \rightarrow CH_4 + 2H_2O$	Remove by methanation

Water removed as follows…

Before the loop

- Syn Gas Driers
- Ammonia Wash

In the loop

Add make-up gas before the catchpot / refrigeration system and let water leave with the ammonia product stream

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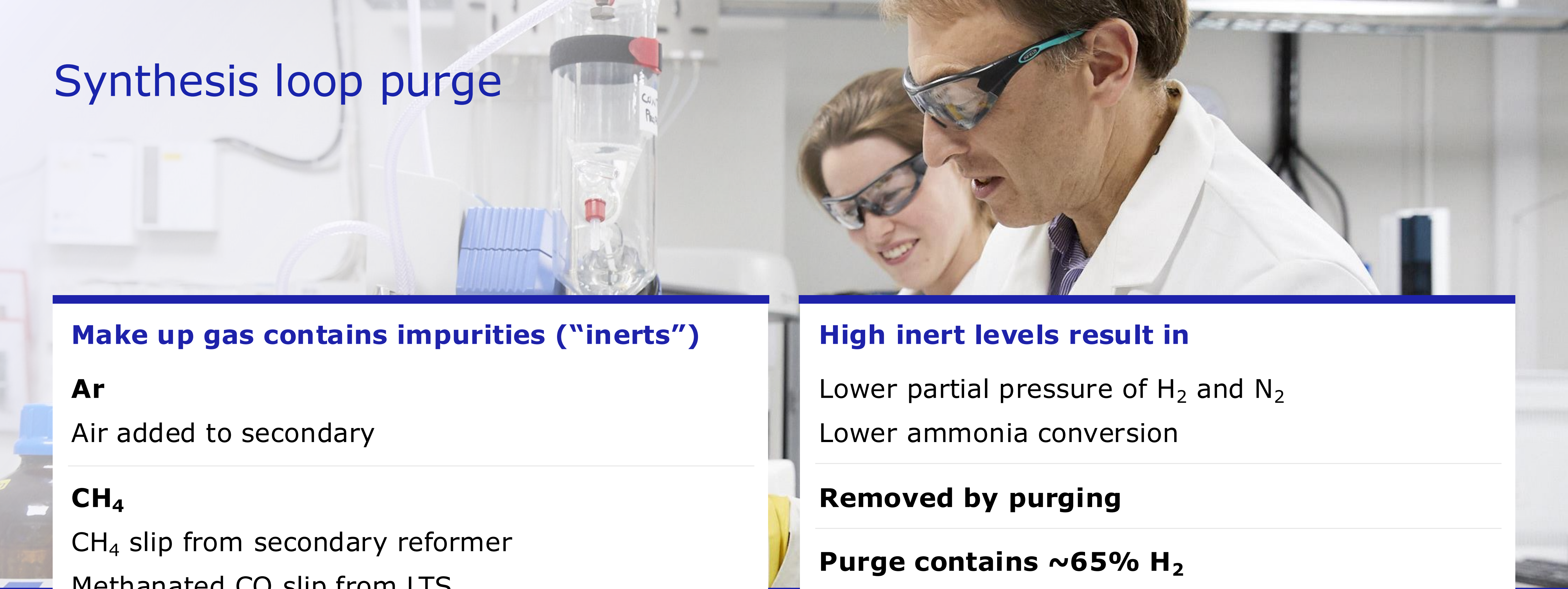
Synthesis loop purge



Make up gas contains impurities ("inerts")

Ar

Air added to secondary

CH_4

CH_4 slip from secondary reformer

Methanated CO slip from LTS

Methanated CO_2 slip from CO_2 removal unit

Sometimes He

Natural gas

High inert levels result in

Lower partial pressure of H_2 and N_2

Lower ammonia conversion

Removed by purging

Purge contains ~65% H_2

High inerts in MUG

→ High purge

→ Loss of hydrogen

→ Less ammonia

H_2 recovery

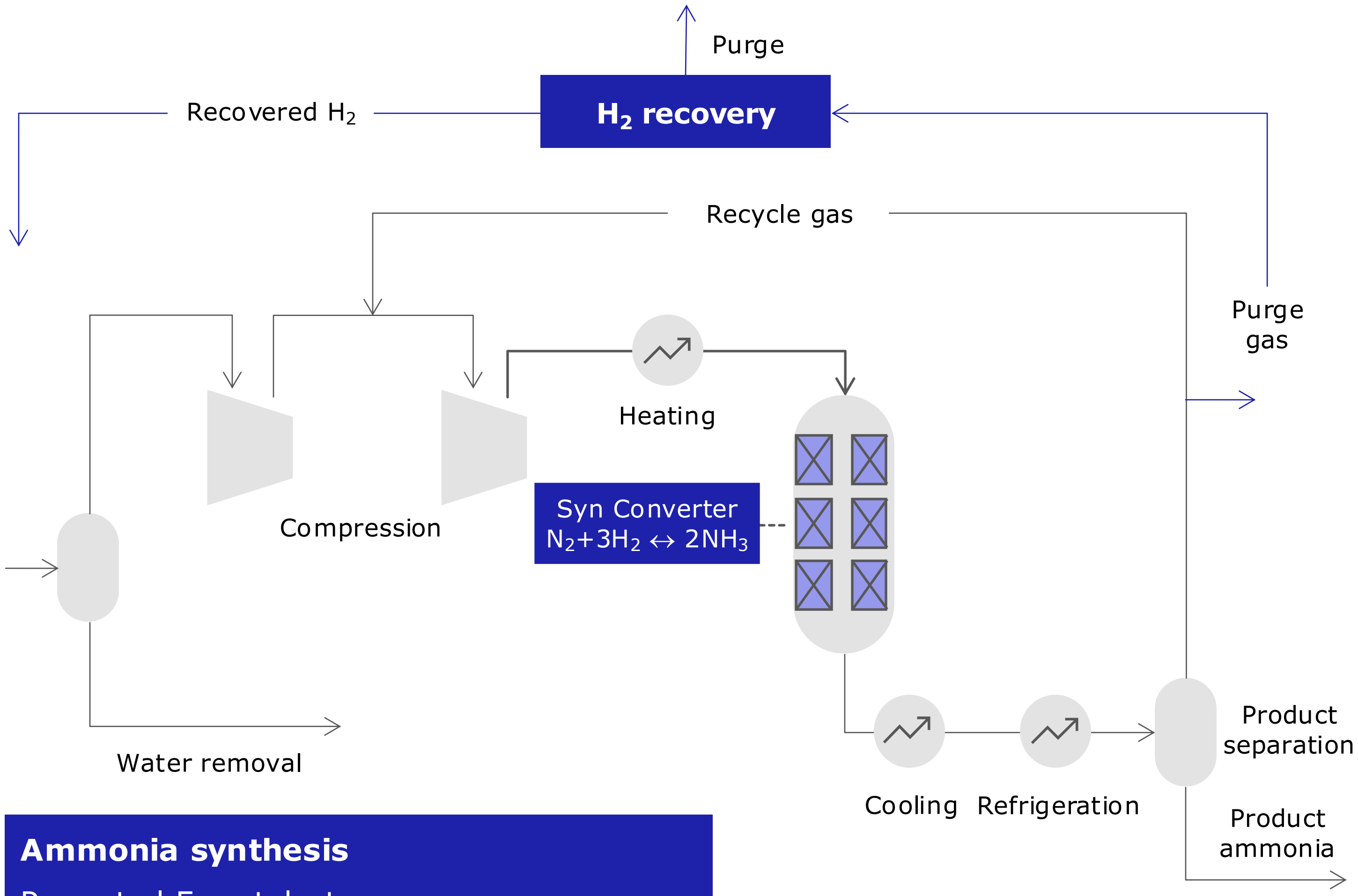
Most plants recover H_2 from the loop purge

- Cryogenic
- Membrane
- PSA (less common)

Overall performance is similar, typically 90% H_2 recovery at 90% purity

Overall loop H_2 conversion to NH_3 increases from about 92% to 98%

MUG H / N ratio changes from 3.0 to approx. 2.85, and returns to 3.0 after H_2 addition



Ammonia synthesis

Promoted Fe catalyst

Temperature: 350–520°C (660–970°F)

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Activity decreases with time

As catalyst activity decreases...

Loop pressure increases

- Efficiency reduced
- No effect on throughput

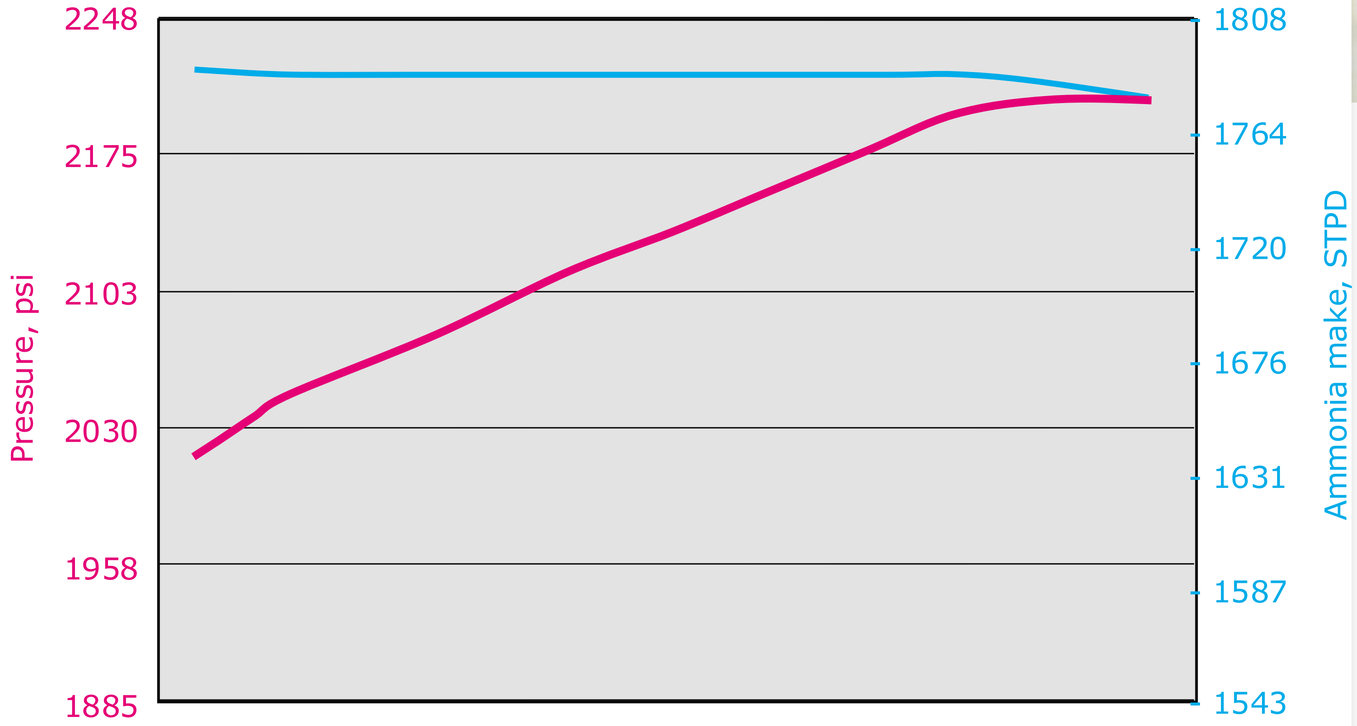
Throughput affected when loop limit encountered

- E.g., relief valve setting

Converter can become more difficult to restart and more sensitive to plant upsets

Efficiency loss , typically

- 0.1-0.2GJ/te
- 0.095-0.19mmBTU/te



Years on line	0	1	2	3	4	5	6	7	8	9	10
Pressure, psi	2016	2049	2082	2092	2116	2134	2153	2175	2197	2204	2204
NH_3 make (STPD)	1788	1786	1786	1786	1786	1786	1786	1786	1786	1784	1777

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Formulation

Magnetite (Fe_3O_4) precursor

Controlled reduction

Pre-reduction or in situ reduction

Oxygen is removed from the crystal lattice without shrinkage

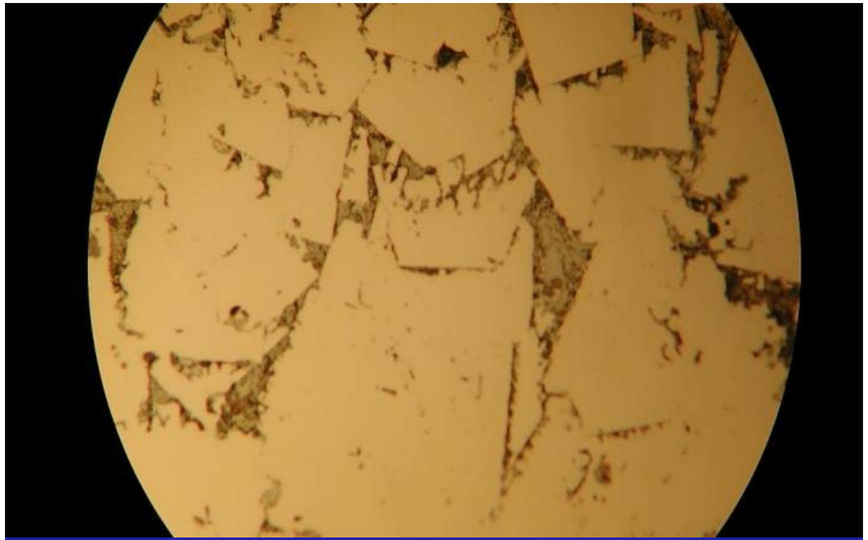
Produces extremely porous metallic iron structure

Key to achieving a high activity catalyst

Promoters boost catalyst performance

Effect of promoters and stabilisers

Promoter	Effect
Al_2O_3	Stabilises the internal surface
MgO	Increases the thermal stability
SiO_2	Stabilises activity in presence of oxygen compounds during normal operation and reduction
K_2O	Increases intrinsic activity of Fe particles
CaO	Protects the K promoter against neutralisation and increases the stability against poisoning by sulphur
CoO	Increases intrinsic activity **KATALCO** 74-1



Need to balance activity, reduction speed and lifetime

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Ammonia synthesis

KATALCO 74-1

Uniquely Co-promoted

Most active Fe-catalyst

Largest plants use it

Lowest pressure commercial reference

Has replaced high activity Ruthenium catalyst

Achieved lives of >20 years

Ammonia synthesis

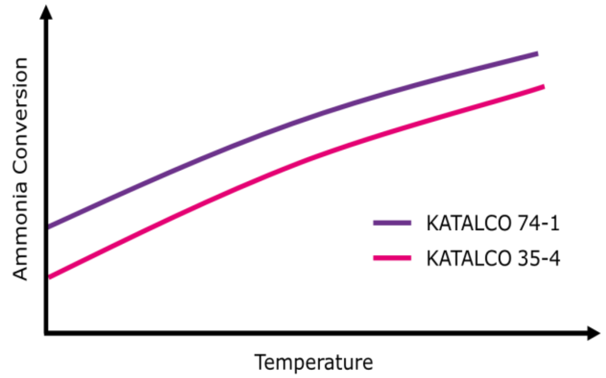
KATALCO 74-1

Unique cobalt promotion

Increases activity

Increases reaction rates

High stability



$N_2 \rightleftharpoons N_{2ad} \rightleftharpoons 2N_{ad}$ RDS → faster

$H_2 \rightleftharpoons 2H_{ad}$

$N_{ad} + H_{ad} \rightleftharpoons NH_{ad}$

$NH_{ad} + H_{ad} \rightleftharpoons NH_{2ad}$

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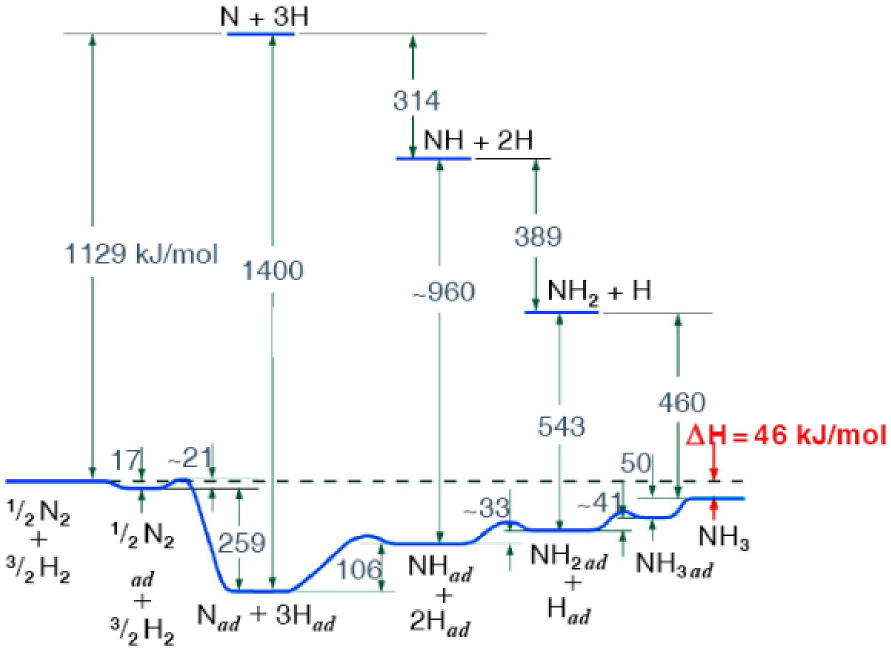
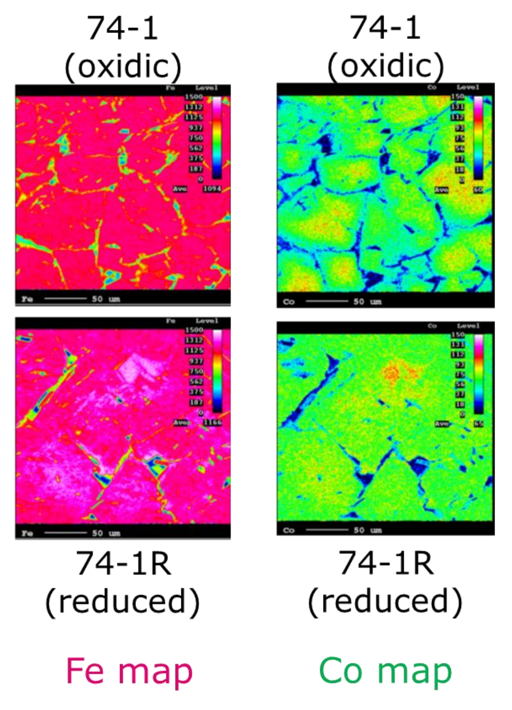




KATALCO 74-1 Koch Fort Dodge low pressure reference

Recent North American reference

14 Jun 2023 09:00

thyssenkrupp Uhde and Johnson Matthey increase ammonia synthesis capacity at Koch Fertilizer facility

Koch Fertilizer facility, Fort Dodge, Iowa (USA)

For this revamp to increase capacity a key challenge was the **very low** ammonia synthesis **operating pressure** of **only 960 psig / 66 barg** for the ammonia synthesis converter

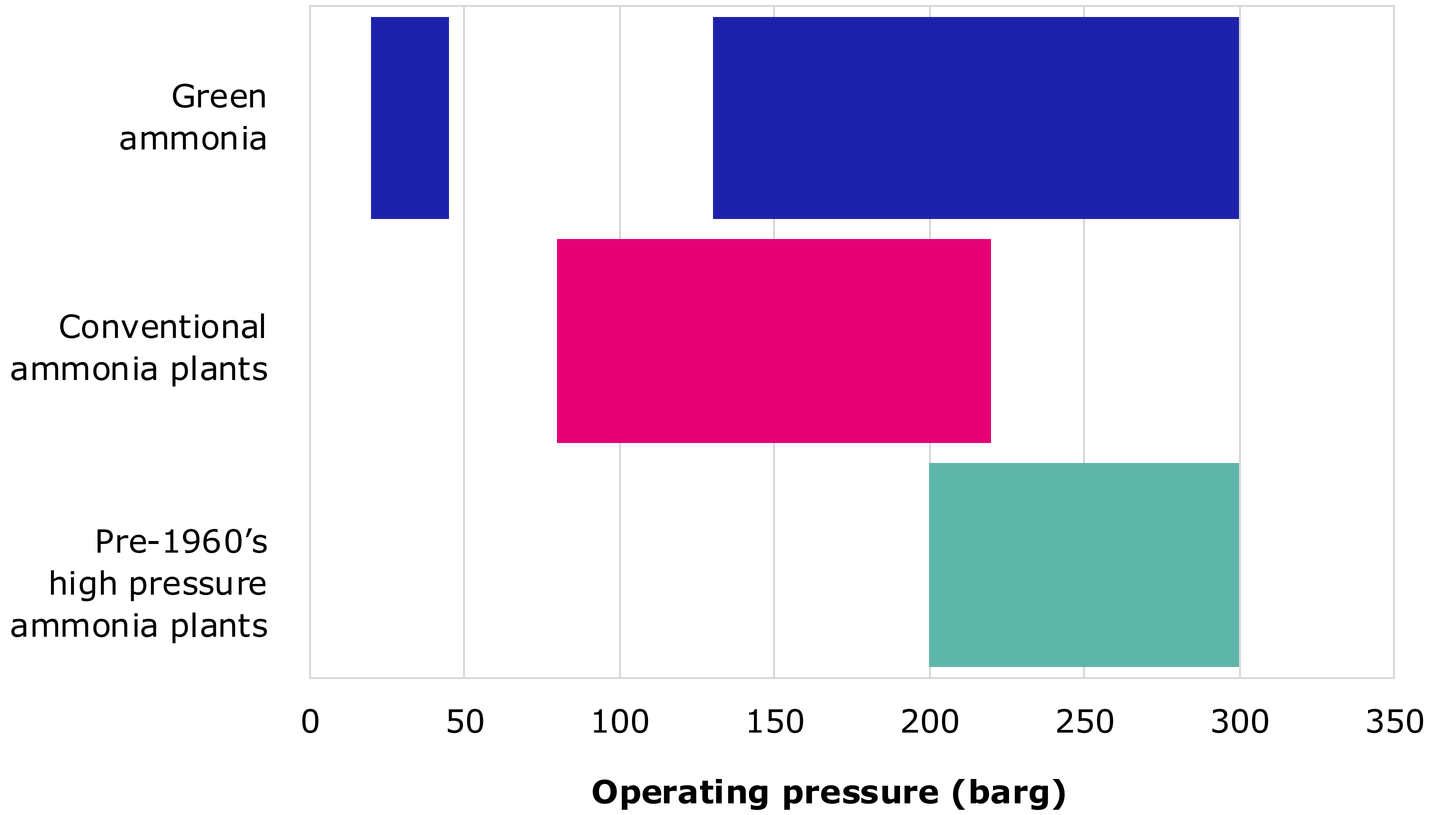
Solved by combining high-performance catalyst **KATALCO** 74-1 with an adapted novel process design from thyssenkrupp Uhde

This joint solution has enabled the increased ammonia synthesis capacity

https://www.thyssenkrupp-uhde.com/en/media/press-releases/press-detail/thyssenkrupp-uhde-and-johnson-matthey-increase-ammonia-synthesis-capacity-at-koch-fertilizer-facility-225744

Green ammonia technologies in development

Operating pressure ranges for synthesis loops



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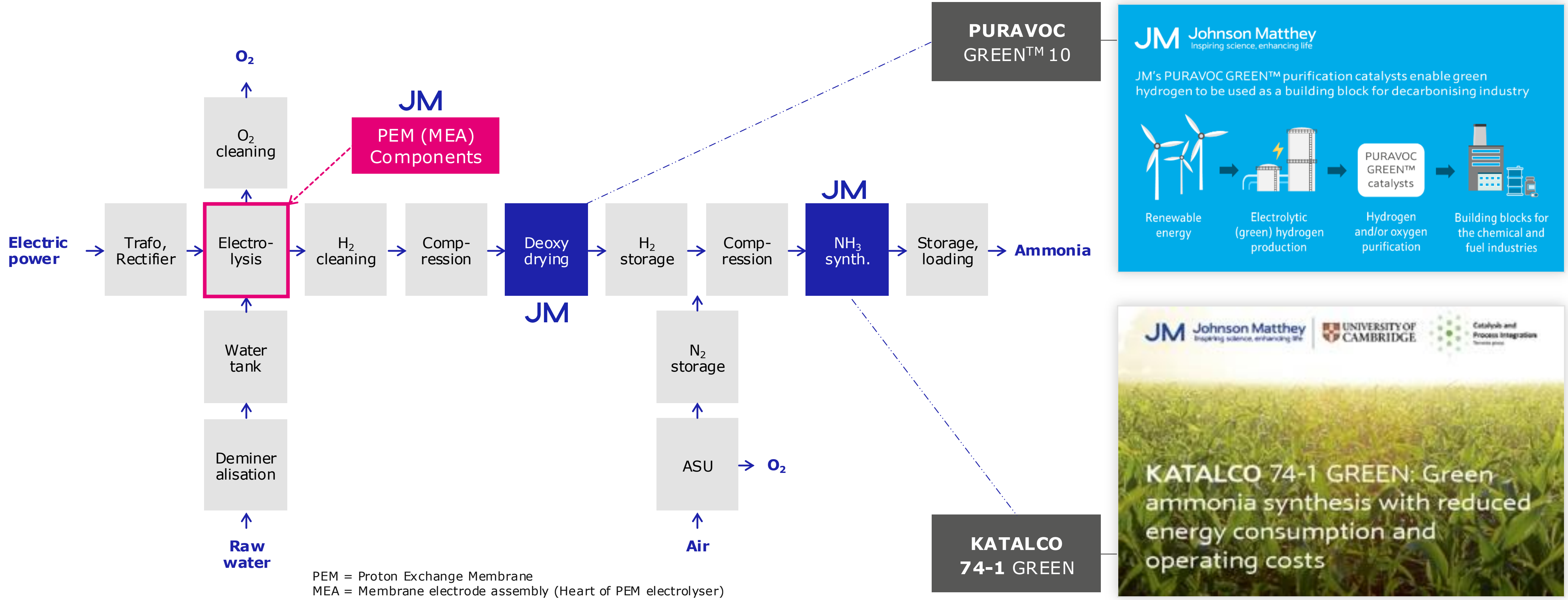
JM GREEN ammonia products



PEM = Proton Exchange Membrane
MEA = Membrane electrode assembly (Heart of PEM electrolyser)

Catalyst reduction basics

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Catalyst reduction and pre-reduction

Conversion of magnetite to active iron

Promoters migrate and protect against sintering

Oxygen removed with no change in crystal size

Surface area increases from 0.02 to ~18m^2g^{-1} providing active sites

Reduction water and recycled water are poisons

Reduction with H_2

No ammonia

All heat from start-up heater → Slow

Circulator design

Reduction with syngas

Ammonia formed → reduction liquor

Heat of reaction → fast

Making product whilst still reducing

T > 350°C

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

Pre-reduced catalyst

How long does catalyst reduction take?

A good crew can reduce a charge of synthesis catalyst in 4–5 days	Often times it takes 10 days	Some examples >20 days

Pre-reduced catalyst

- 1-2 days for reduction
- 2x the cost

Usual compromise is

- One bed of pre-reduced
- All other beds are oxidic

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Ammonia synthesis summary

Topics of interest	Comment
Key variables	• Inlet temperature • Exit temperature • PD
Good performance indicators	• Profile • Loop pressure • Exit ammonia conc
Common issues	• Mechanical issue with cartridge • $CO/CO_2/H_2O$ poisoning
End of life criteria	• Loop pressure • Mechanical issue with cartridge • Replace with better cartridge
Optimisation	• Inlet bed temperatures

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