Johnson Matthey
Inspiring science, enhancing life

Ammonia Cracking: Design and Safety Considerations

Ammonia Energy Conference, Phoenix, November 2002

John Pach

Our strategy: Catalysing the net zero transition for our customers

Automotive

1.8-3.0m

new sales of fuel cell heavy duty and light duty vehicles in 2030

Chemicals

c.30%

decrease in emission intensity by 2030 to reach net zero path in chemicals production

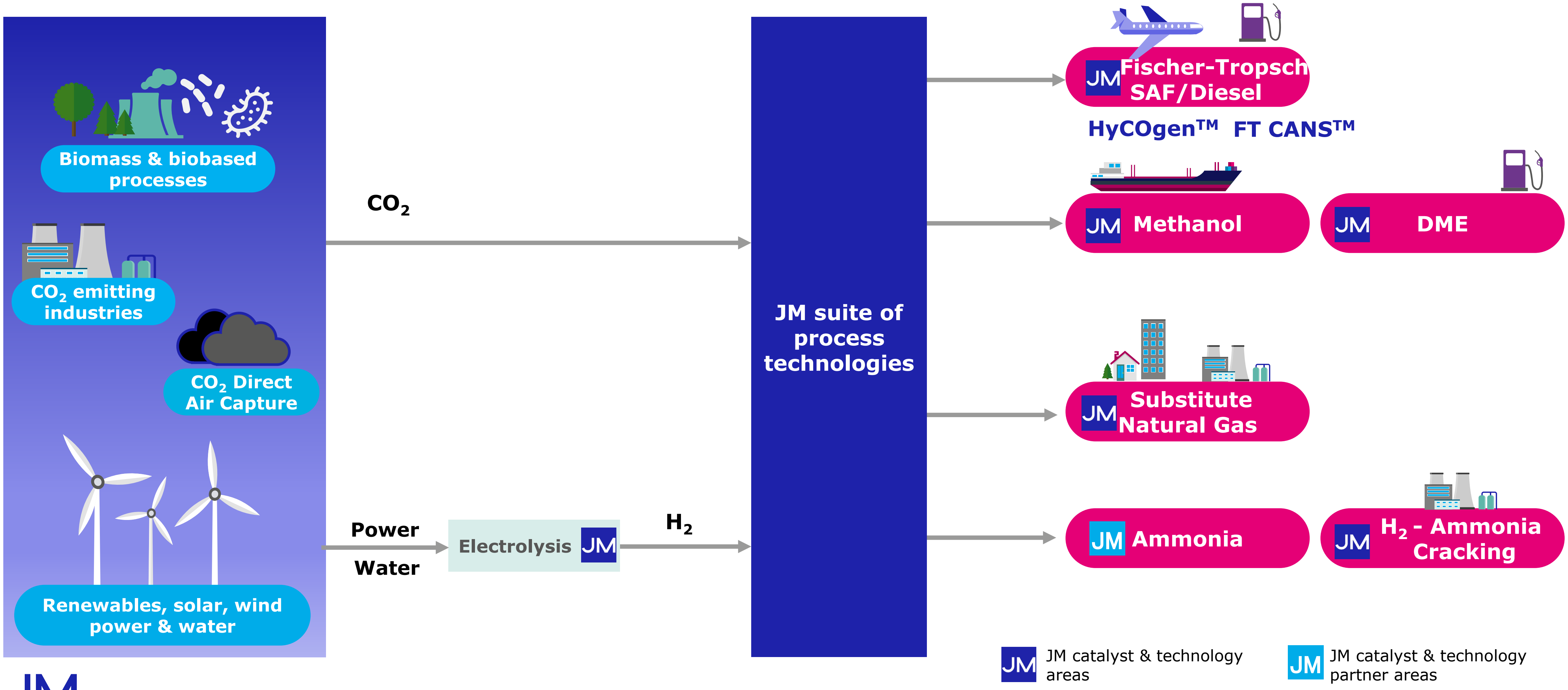
Energy

7 to 9x

increase in sustainable fuels demand by 2040

Enabling production of sustainable fuels

Aviation, marine and land-based energy systems



Arbitrage in wind and solar energy

Interest in green hydrogen as renewable fuel but;

- Low energy density
- Inefficient to store/transport in large amounts

Ammonia has great potential as hydrogen transport vector

- Higher energy density
- Existing infrastructure/expertise in storage and transport

Ammonia can be used directly as a fuel or cracked to form hydrogen at point of use

- Optimal flowsheet must consider:
- Process conditions to favour equilibrium
- Efficient delivery of energy to maintain temperature throughout reactor
- Effective utilisation of waste heat whilst remaining robust to trips
- Emission control technology
- Combination of process engineering & catalyst knowhow is key to maximising the flowsheet efficiency

- New technologies are required … or are they?

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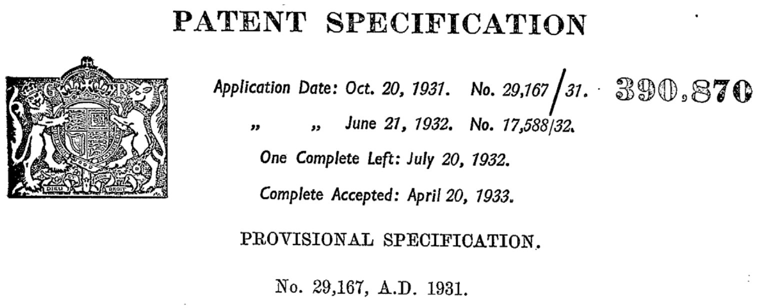
JM and ammonia cracking

Nearly 100 years of ammonia cracking heritage

- Early patent applications
  - 1931: Nitrogen generator, hydrogen superfluous to requirements
  - 1954: for metallurgical purposes, nickel on alpha alumina, improvement over iron based catalysts
  - 1962: nickel on gamma alumina
- Dedicated crackers used to be deployed on syngas plants for start up & shutdown
  - Like a small primary reformer/fired heater
- Ammonia cracking reaction still deployed on some ammonia plants for start up hydrogen
- Small scale crackers and purification systems are commonplace
- Recent developments
  - High activity PGM catalysts (used in CSIRO’s ammonia to hydrogen fuelling system)
  - Large scale ammonia cracking flowsheets


PATENT SPECIFICATION

Application Date: Oct. 20, 1931. No. 29,167/31. 390,870

„ „ June 21, 1932. No. 17,588/32.

One Complete Left: July 20, 1932.

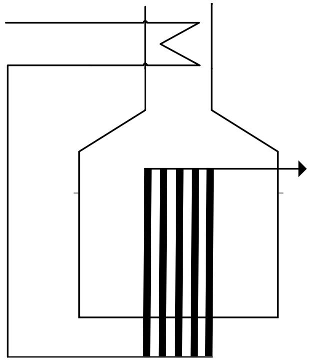
Complete Accepted: April 20, 1933.

PROVISIONAL SPECIFICATION.

No. 29,167, A.D. 1931.

Technology

Cracking



Plant Operator

Separation

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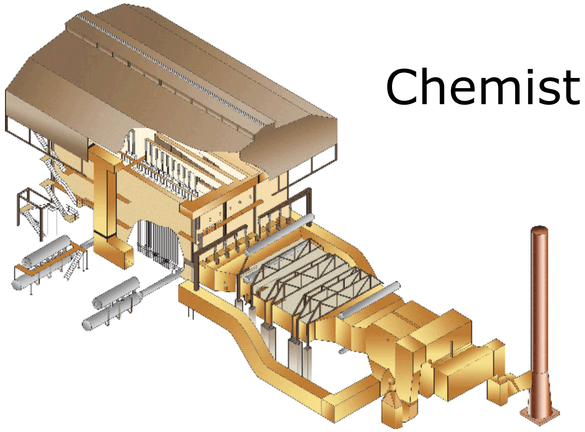
Reaction characteristics

Similar to conventional hydrogen production

	Ammonia Cracking	Steam Reforming
Endothermicity	$2NH_3 = 3H_2 + N_2 \qquad \Delta H = 35\frac{MJ}{kmol\ H_2}$	$CH_4 + H_2O = 3H_2 + CO \qquad \Delta H = 69\frac{MJ}{kmol\ H_2}$ $CO + H_2O = H_2 + CO_2 \qquad \Delta H = -41\frac{MJ}{kmol\ H_2}$ With steam diluent, similar to ammonia cracking
Pressure	To ~80 bar	To ~50 bar
Exit Temperature	700 – 900ºC	800 – 900ºC
Side reactions	None	Many
Feedstock	Synthetic feedstock, consistent quality	Natural feedstock, variable quality

- Similar heat transfer & heat management challenges to steam reforming

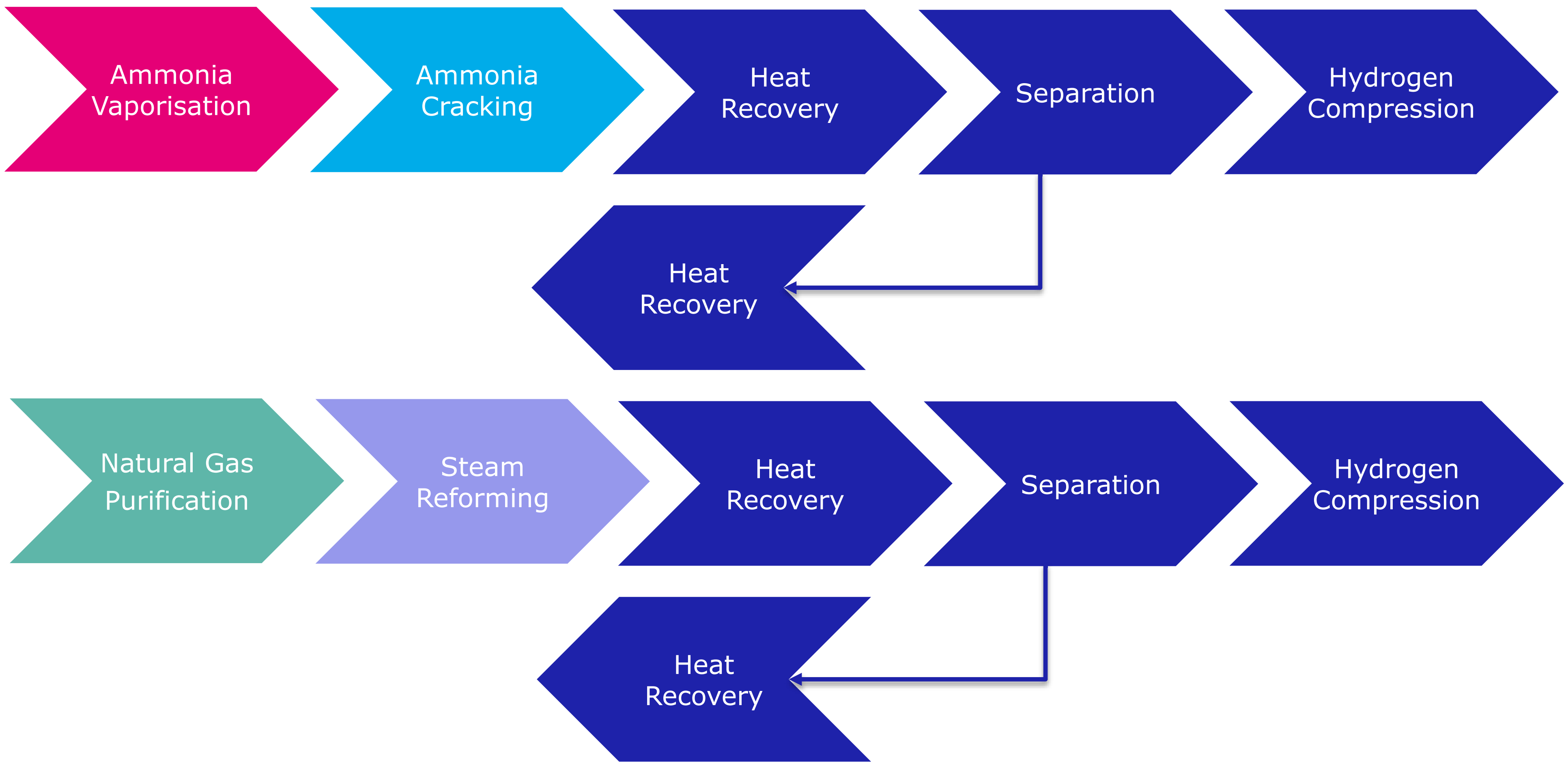


Chemistry

Heat management

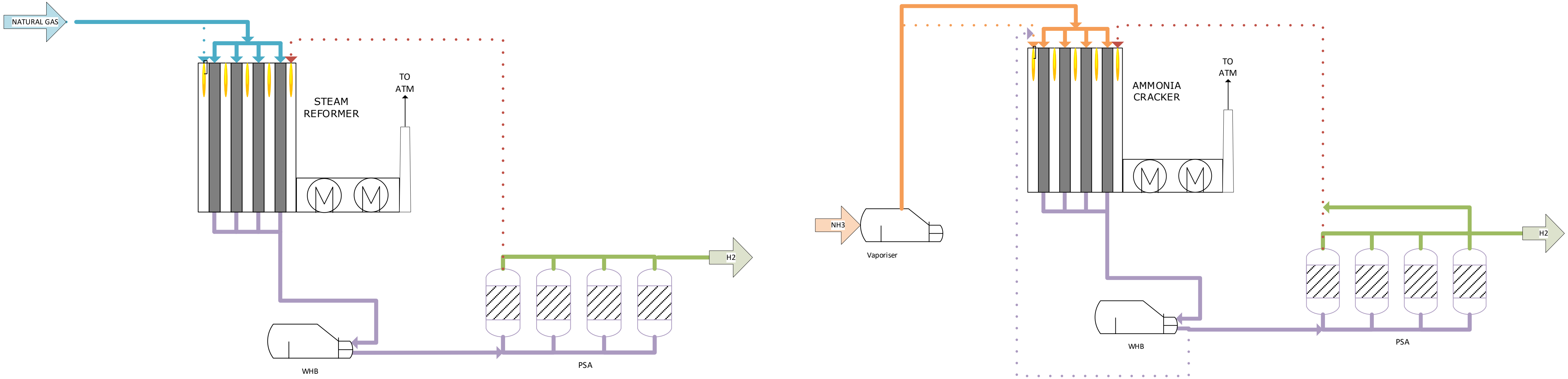
Block diagram

Similar reaction characteristics, similar process flow diagram



EHS Considerations

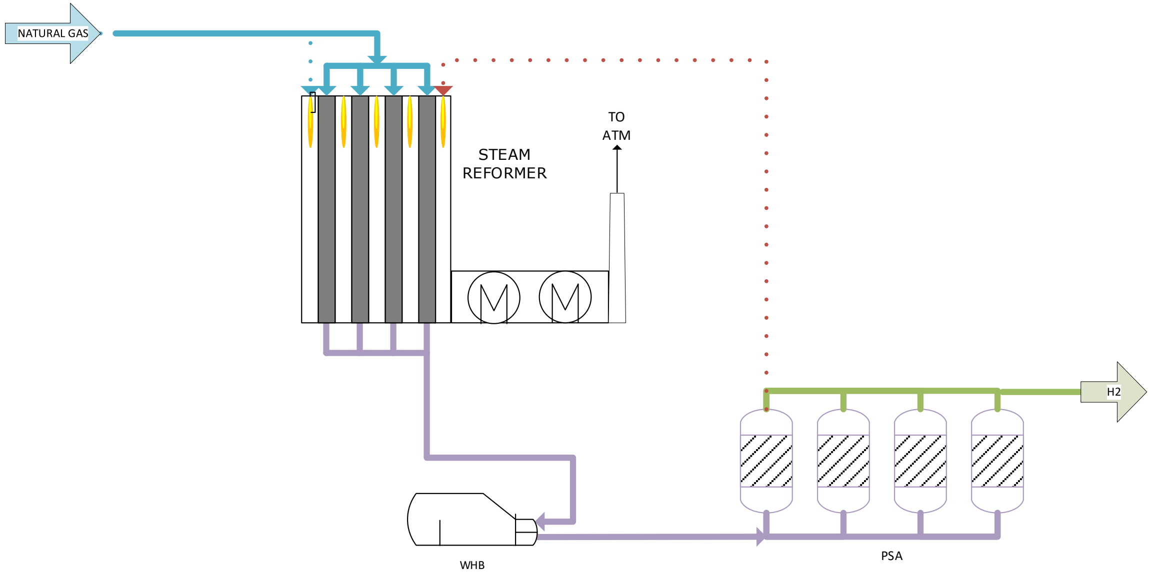
Similar but different



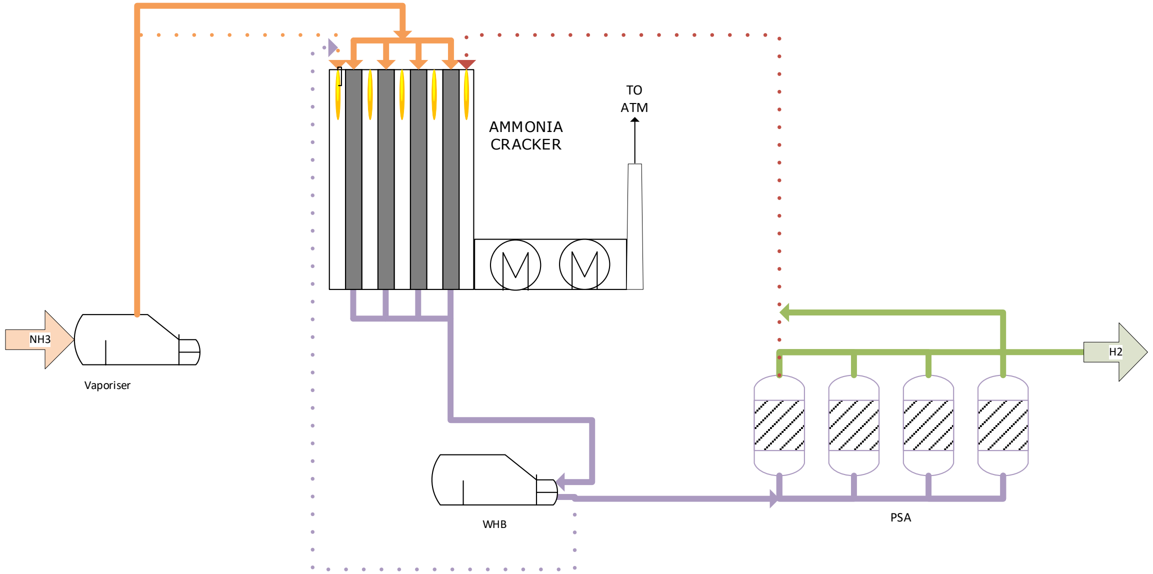
EHS Considerations

Similar but different

Flammable gas

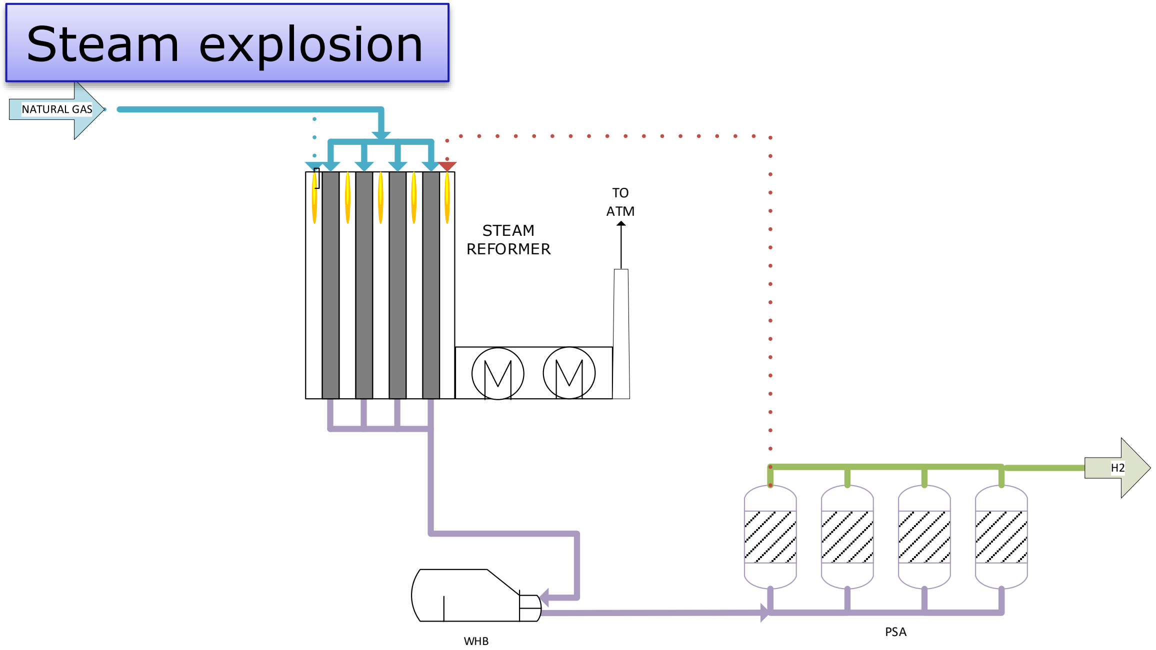


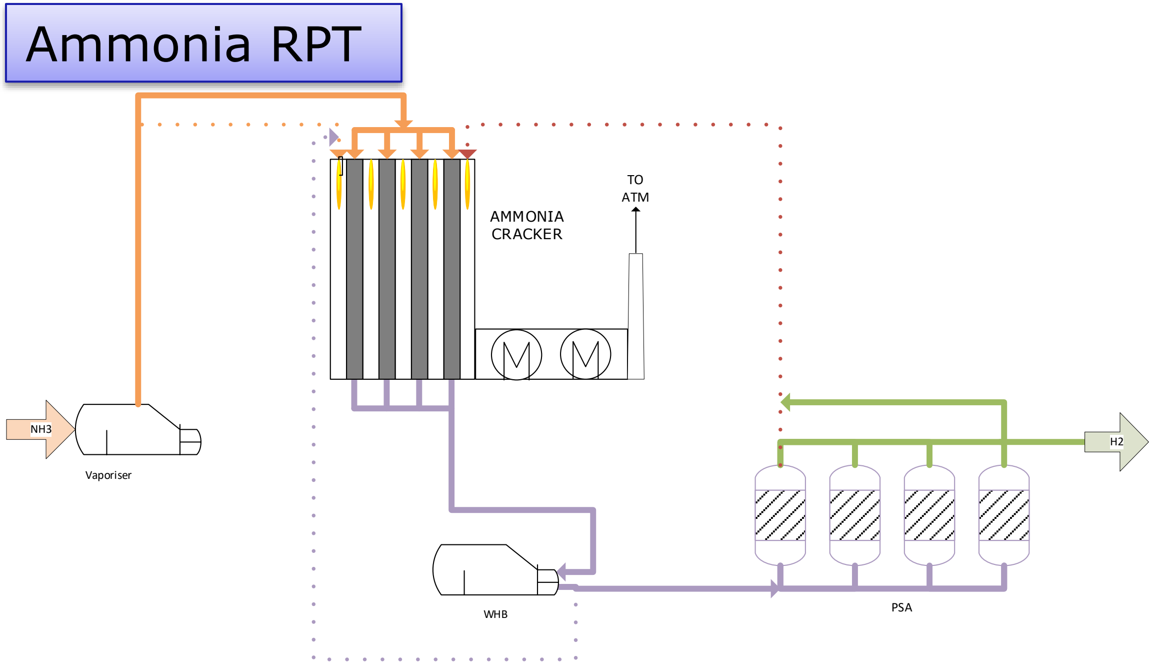
Toxic liquid



EHS Considerations

Similar but different

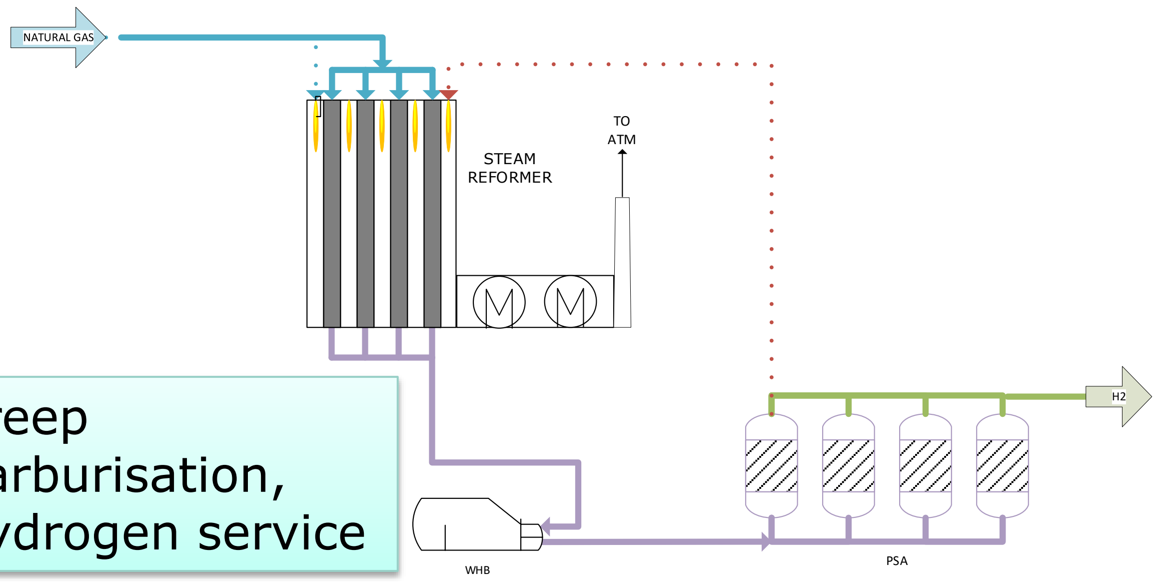




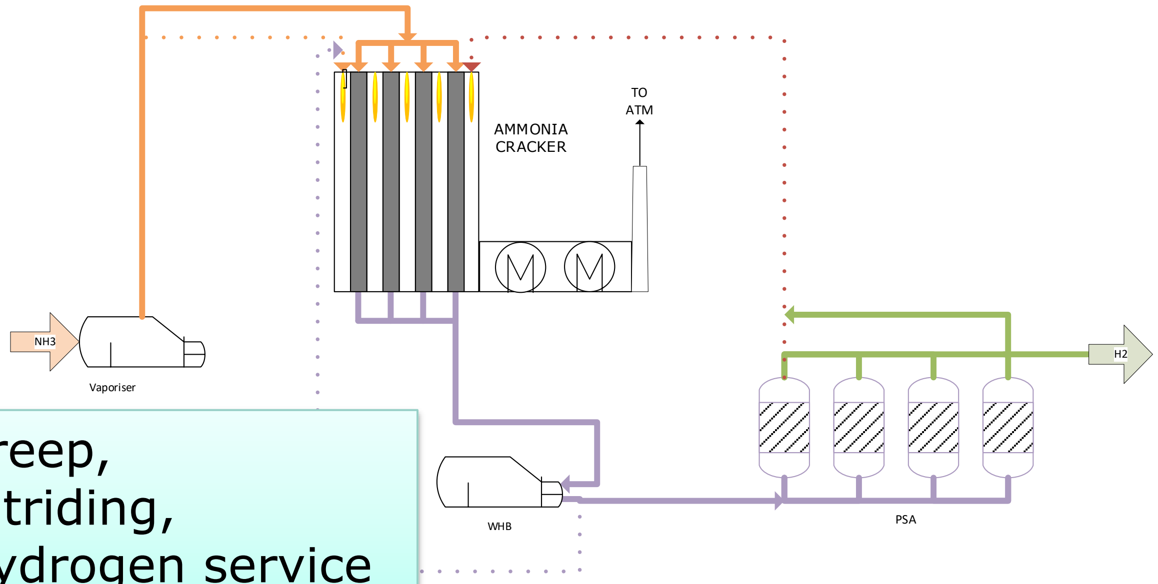
RPT = Rapid Phase Transition

EHS Considerations

Similar but different



Creep
Carburisation,
Hydrogen service

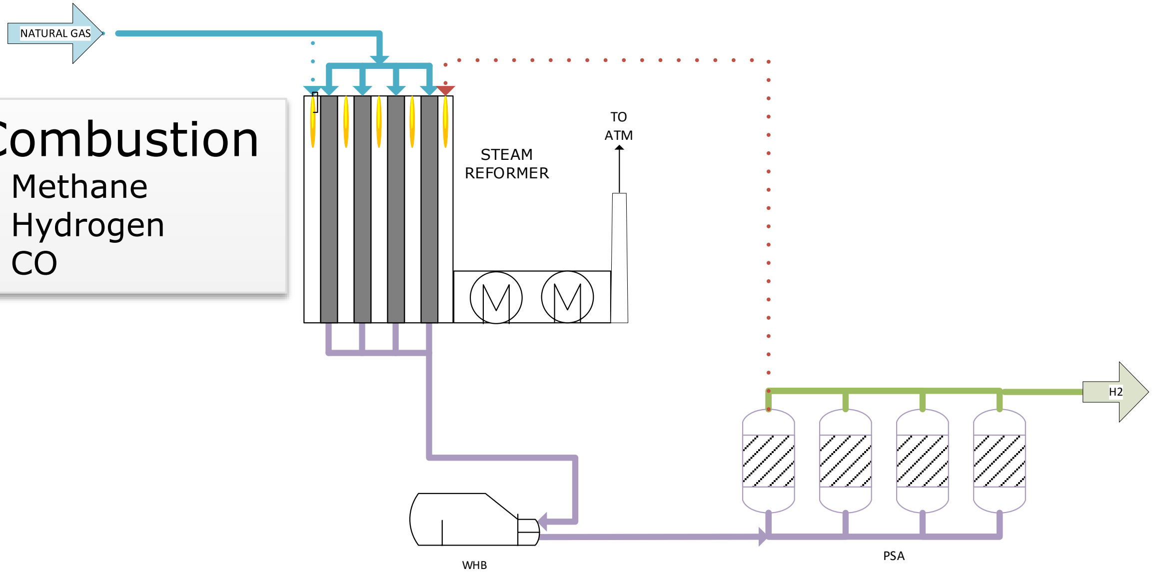


Creep,
Nitriding,
Hydrogen service

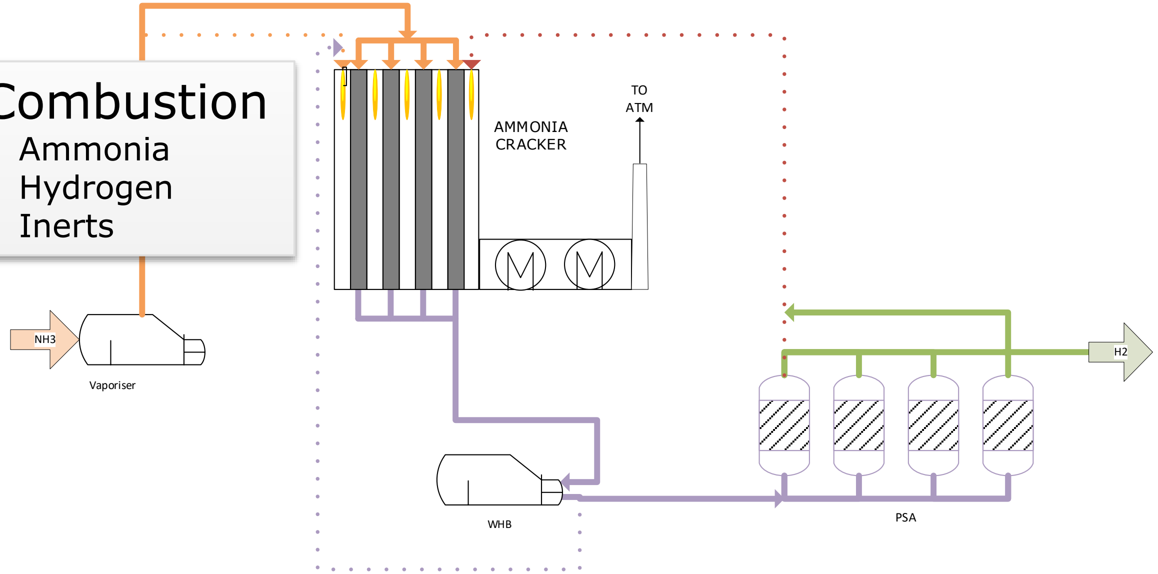
EHS Considerations

Similar but different

Combustion
- Methane
- Hydrogen
- CO



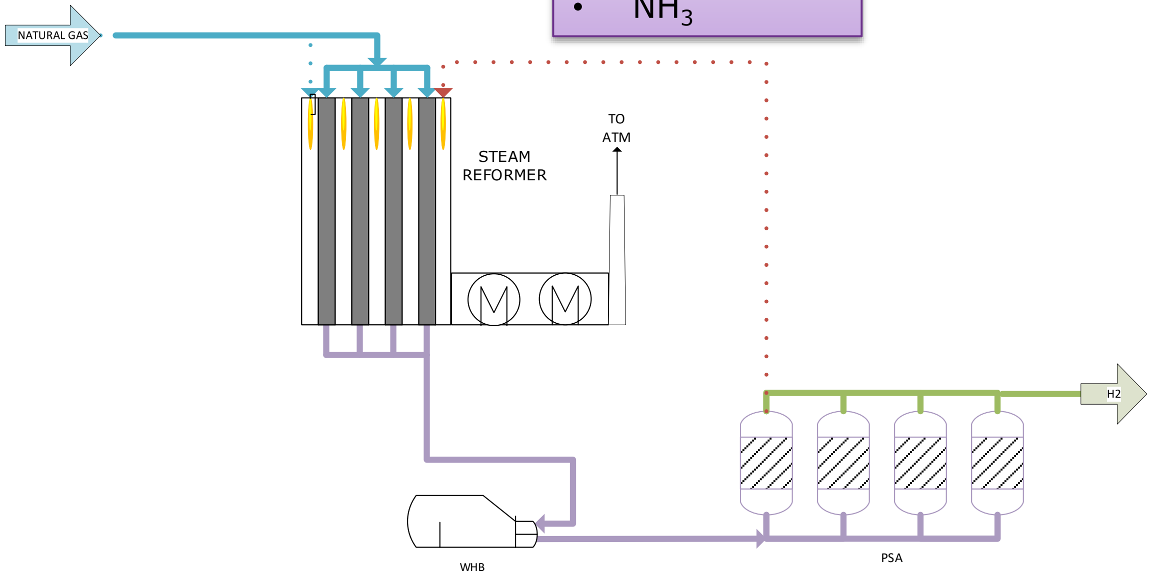
Combustion
- Ammonia
- Hydrogen
- Inerts



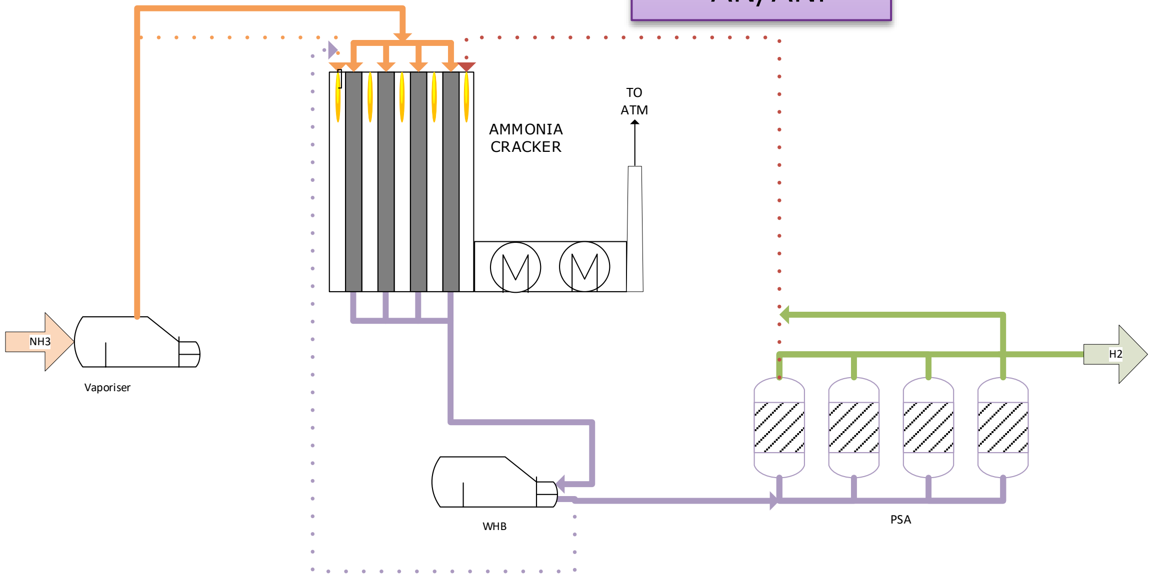
EHS Considerations

Similar but different

Effluents
- NO_x
- CO
- CO_2
- NH_3

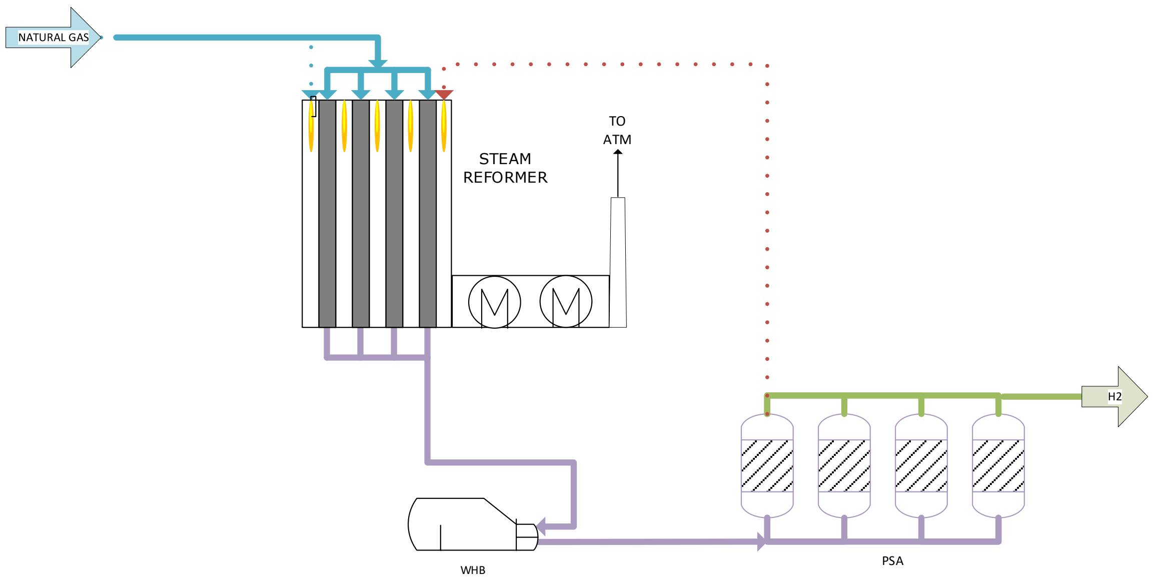


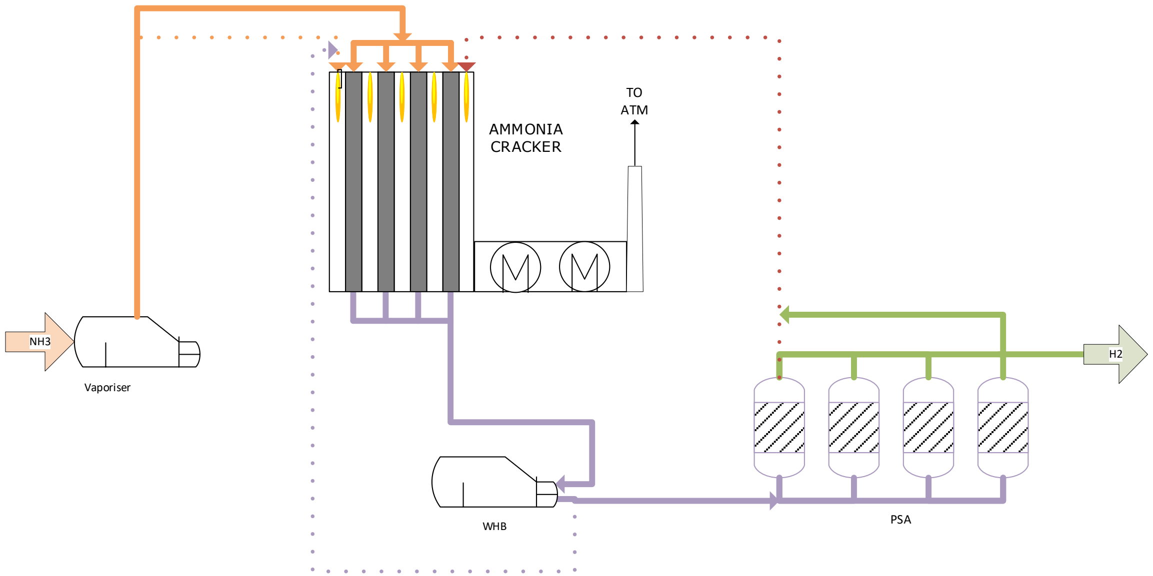
Effluents
- NO_x
- N_2O
- NH_3
- AN/ANi



EHS Considerations

Similar but different



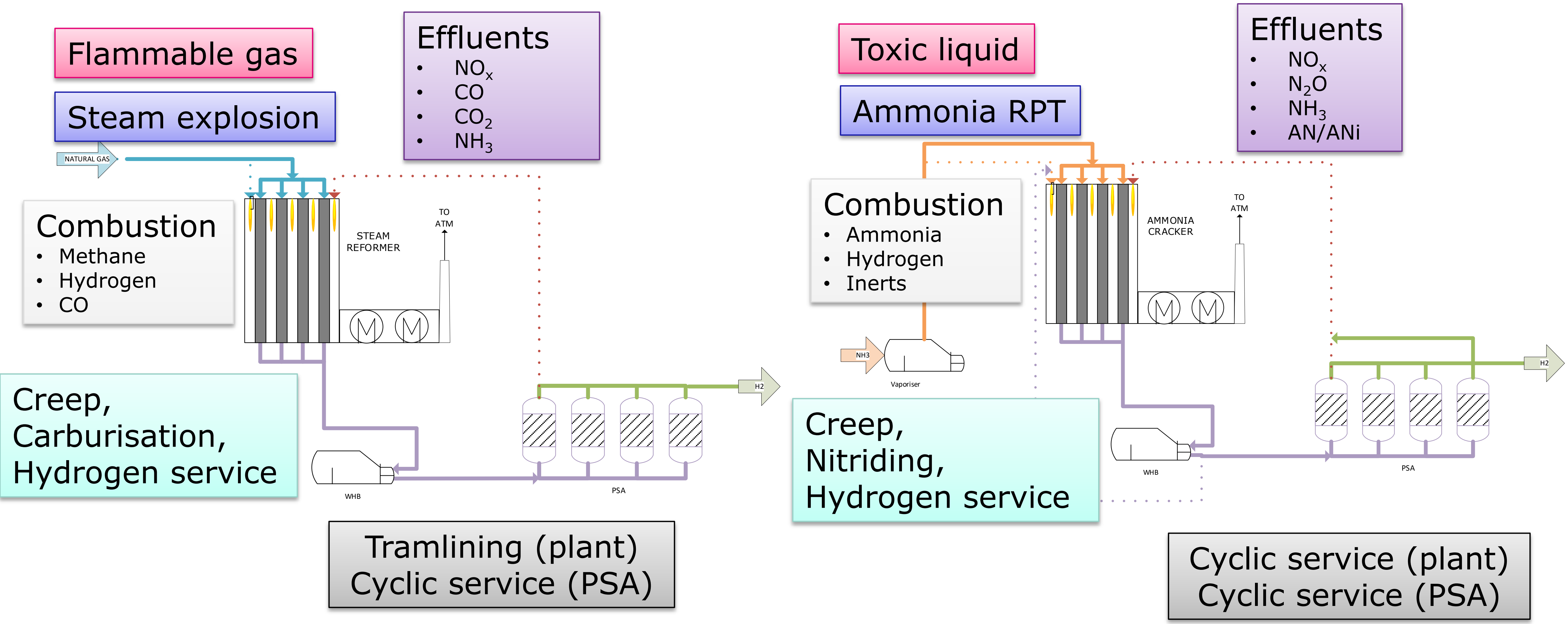


Tramlining (plant)
Cyclic service (PSA)

Cyclic service (plant)
Cyclic service (PSA)

EHS Considerations

Similar but different



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Challenges of Scale Up

From kilos to thousands of tons (of NH_3) per day

Scale Up Expertise

Catalyst Science

Process Safety

Heat transfer knowhow

Catalyst Science

Core capabilities

Materials
- PGM and base metal materials
- Wet and physical synthetic methods

Formulation
- Colloid science
- Rheology
- Polymers
- Statistics and automation

Core Engineering
- Reaction kinetics
- Reaction hazards
- Process analysis and control
- Process data analytics

SMART Manufacturing
- Extrusion
- Spray drying
- Solids Engineering
- Modelling to support manufacturing
- Industry 4.0

Electrochemical Transformations
- Low and high T electrolysis
- Flowsheeting and technoeconomic assessments
- Electrosynthesis

Statistical Thinking
- Design of experiments
- Data Analytics
- Build JM community of statistical thinkers

Physical and Chemical Modelling
- Atomistic and coarse grains simulation of material properties
- High performance computing
- Mechanical and materials engineering

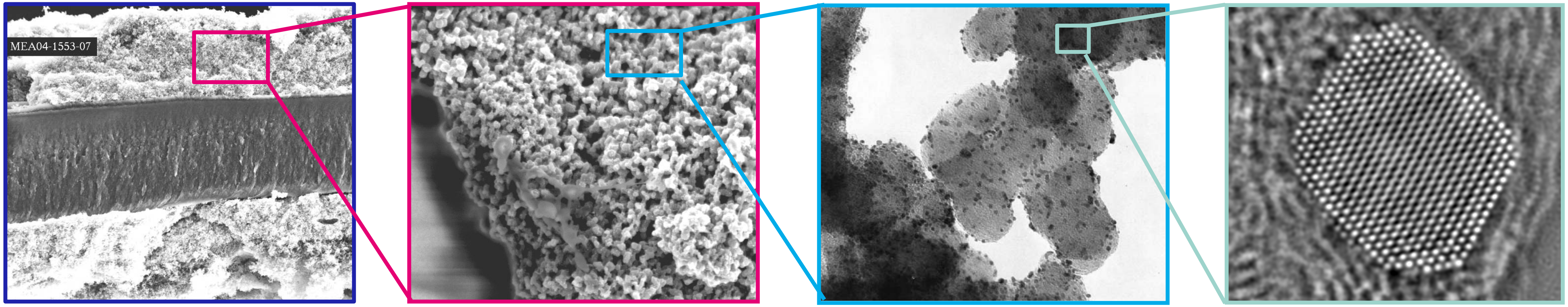
PGMs as Critical Materials
- PGM award scheme
- Safe handling and sensitisation
- Technologies for responsible sourcing
- Refining solutions

Alternative Activation
- Plasma for process activation
- Plasma for material treatment
- Advanced thermal processing
- Microwave processing

Advanced Characterisation
- Microscopy
- Spectroscopy
- Surface science
- Assay

Catalyst Science

Access to and expertise in these techniques allows us catalyst optimisation across all scales



Catalyst-coated Membrane

Catalyst Layer

Catalyst on support

Atomic-resolution catalyst

- Better catalysis means better efficiency and lower cost
- Better catalyst layer design means lower mass transport, higher power and lower cost
- More functionality means more value for JM and our customers

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Catalyst Science

Product development and scale up with quality assurance at every step

Small scale laboratory samples <100 mL

- Initial Testing
- Key performance parameters assessed

Large scale laboratory samples 1 L

- Longer term testing
- Lifetime testing

Pilot scale preparations

- Key parameters validated
- Data collected for trial

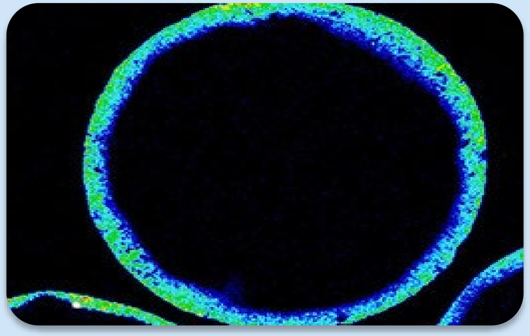
Trial manufacturing batch

- Key parameters validated
- Recipe finalized

Manufacturing campaign

Catalyst Science

A range of catalysts to optimise performance



Low temperature cracking

KATALCO™

27-612

promoted pgm

Continuous development

Multiple chemistries

Multiple operating temperatures

High temperature cracking

KATALCO 27-2

Nickel based

Nearly 100 years operating experience in ammonia cracking applications

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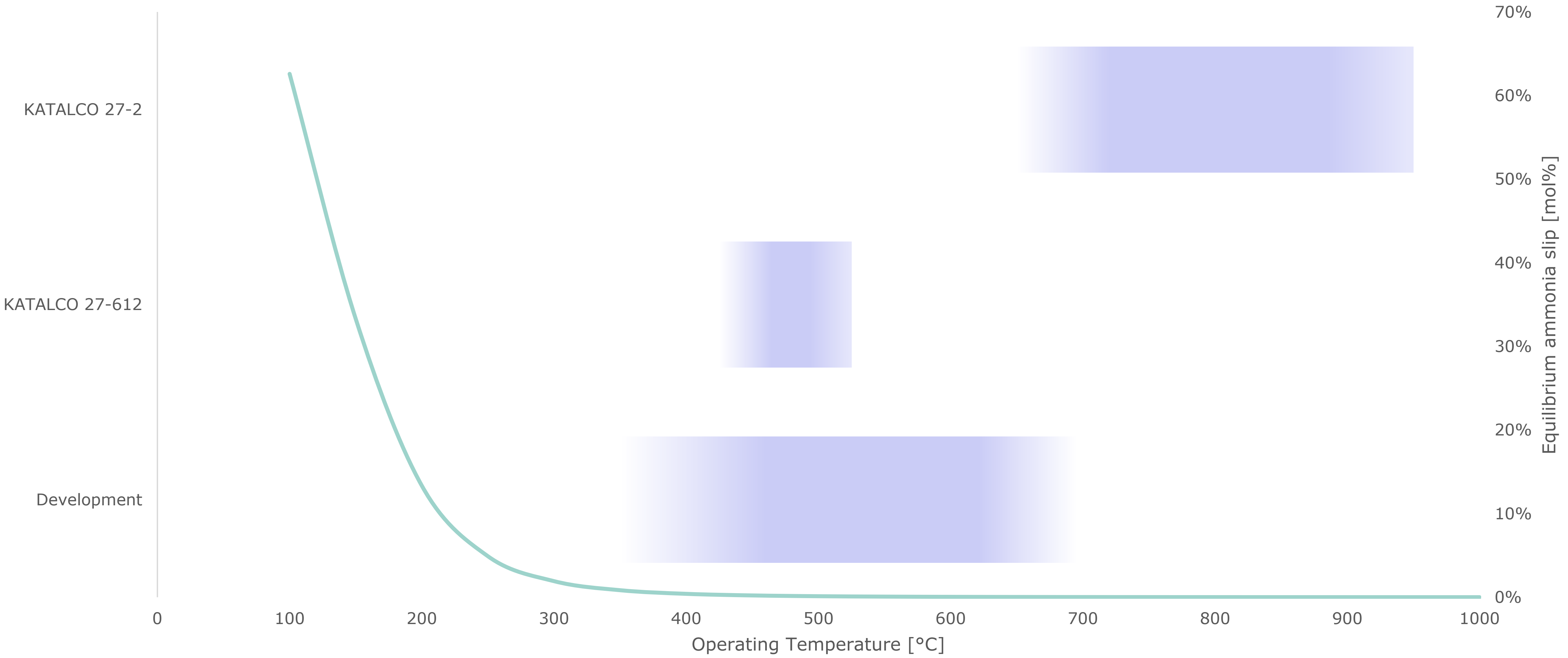
Catalyst Science

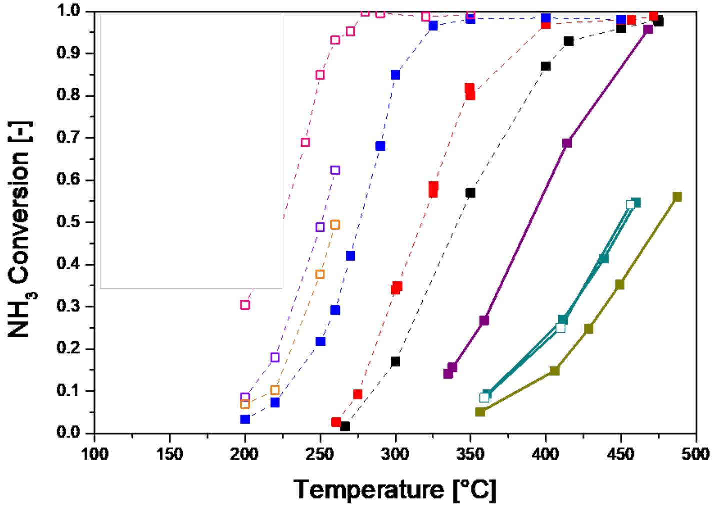
Development products

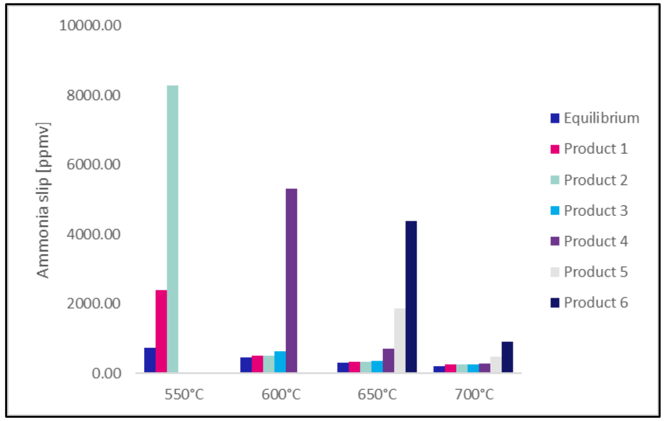


Catalyst Science

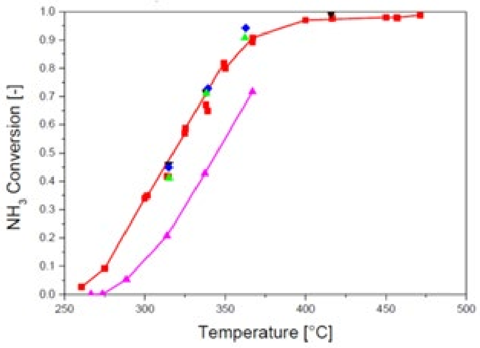
Rigorous testing generates insights for detail design

- Robust results





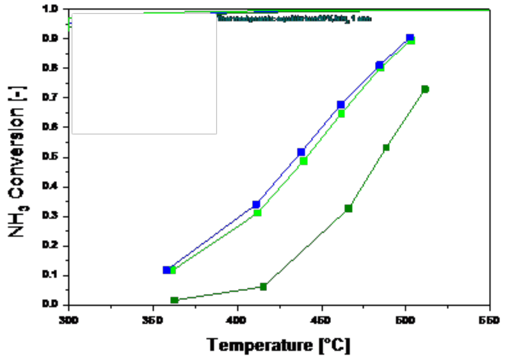
- Activation



- Background reactions

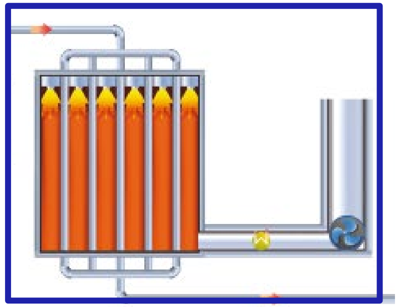
	NH3 conversion [%]	
F_{TOT}	115	320
700 °C	7,4%	5,3%
800 °C	52,9%	48%
850 °C	73,2%	66,0%
$C(NH3)_{in}$ [%]	9,0 %	10,3 %

- Inhibition



Heat Transfer Knowhow

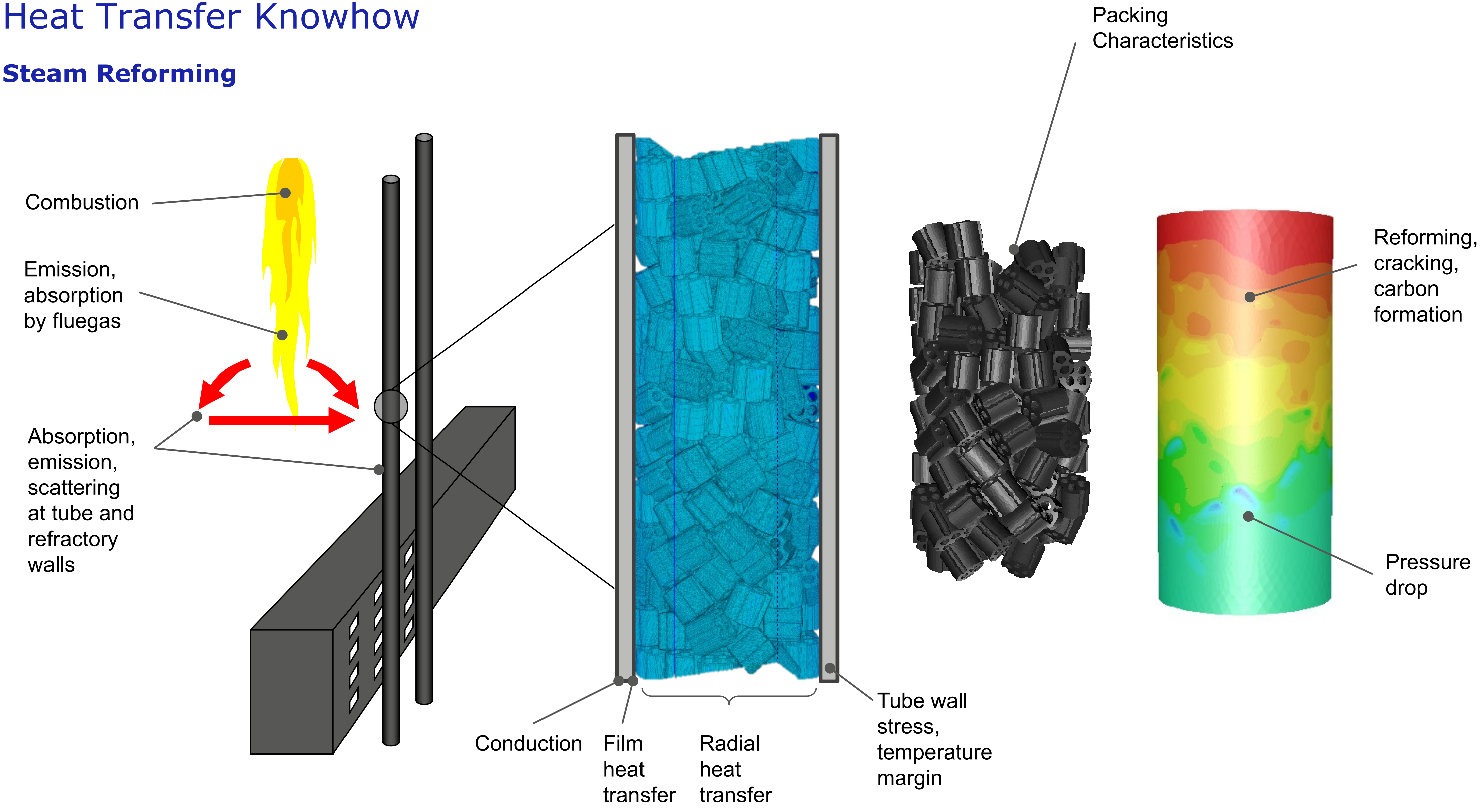
Unrivalled expertise in reformer design



- Leader in large steam reformers
- Heat exchange reforming (GHR)
- Compact reforming
- Catalysts

Heat Transfer Knowhow

Steam Reforming



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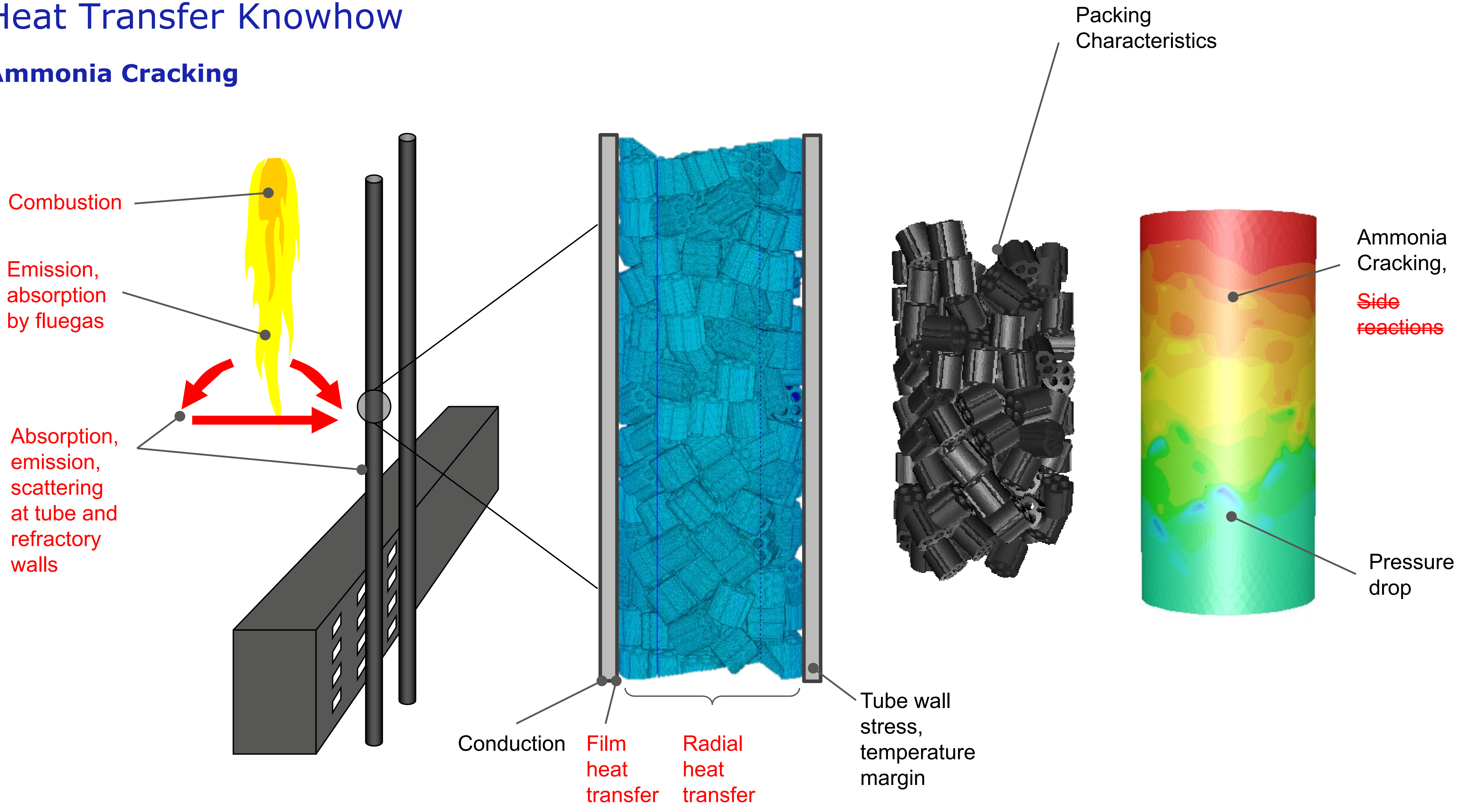
Heat Transfer Knowhow

Ammonia Cracking



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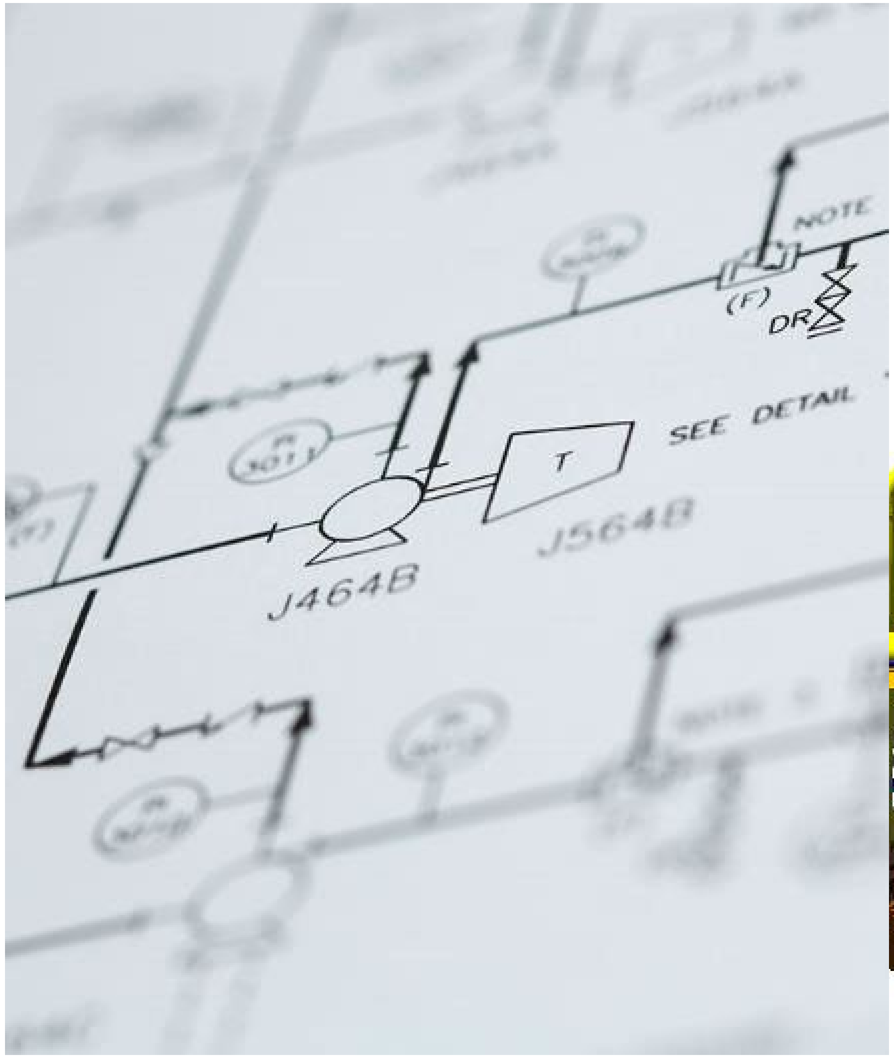
Scale Up Expertise

From concept to reality



Scale Up Expertise

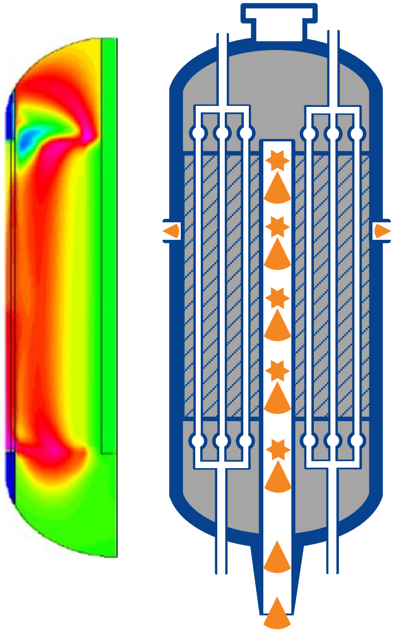
Many examples of successful development & scale up in the fuel and chemical sectors

Technology	Partner	Status
Methanol	-	Licensed technology
Formaldehyde	-	Licensed technology
BuOH Oxo	Dow	Licenced Technology
2EH Oxo	Dow	Licenced Technology
2PH Oxo	Dow	Licenced Technology
Detergent Alcohols Oxo	Dow/Sasol	Licenced Technology
PTA	Dow	Licenced Technology
FT-CANs	BP	Licenced Technology in construction
MEG	Eastman	Licenced Technology in construction
BioFormate Fuels	Virent	Being developed
BioFormate Chemicals	Virent/BP	Being developed

Building on our expertise in syngas, **JM is meeting our customers needs for innovative processes that enable the production of sustainable fuels and chemicals** such as the award-winning FT-CANs process.

Process technology development is a core competency for JM

Process technology development from idea to commercial plant scale-up



Detailed knowledge

Computer modelling confirms aspects such as heat transfer, reaction kinetics and mechanical arrangement.

Fast scale-up

Methanol converter weighing 600 tonnes installed without pilot plant trials

Successful experience with very high scale up factors

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Process Safety

Inherent safety

- Remove or reduce the hazard as far as possible, then control the remaining hazard

  "What you don't have can't leak" *

- Best considered as early as possible in a project
- Similar in principle to "Green Chemistry"
- Generally based on Guidewords, checklist methods can also be used
- An open-minded consideration of all options is essential
  - There are often multiple aspects to consider for each option, it is rarely an easy choice

Idea
- HS0
- HS1

Evaluate
- HS2
- Initial LOPA

Define
- HS3 (HAZOP)
- Final LOPA

Implement
- HS4
- HS5

Operation
- HS6
- PHR

Eliminate

Substitute

Minimise

Moderate

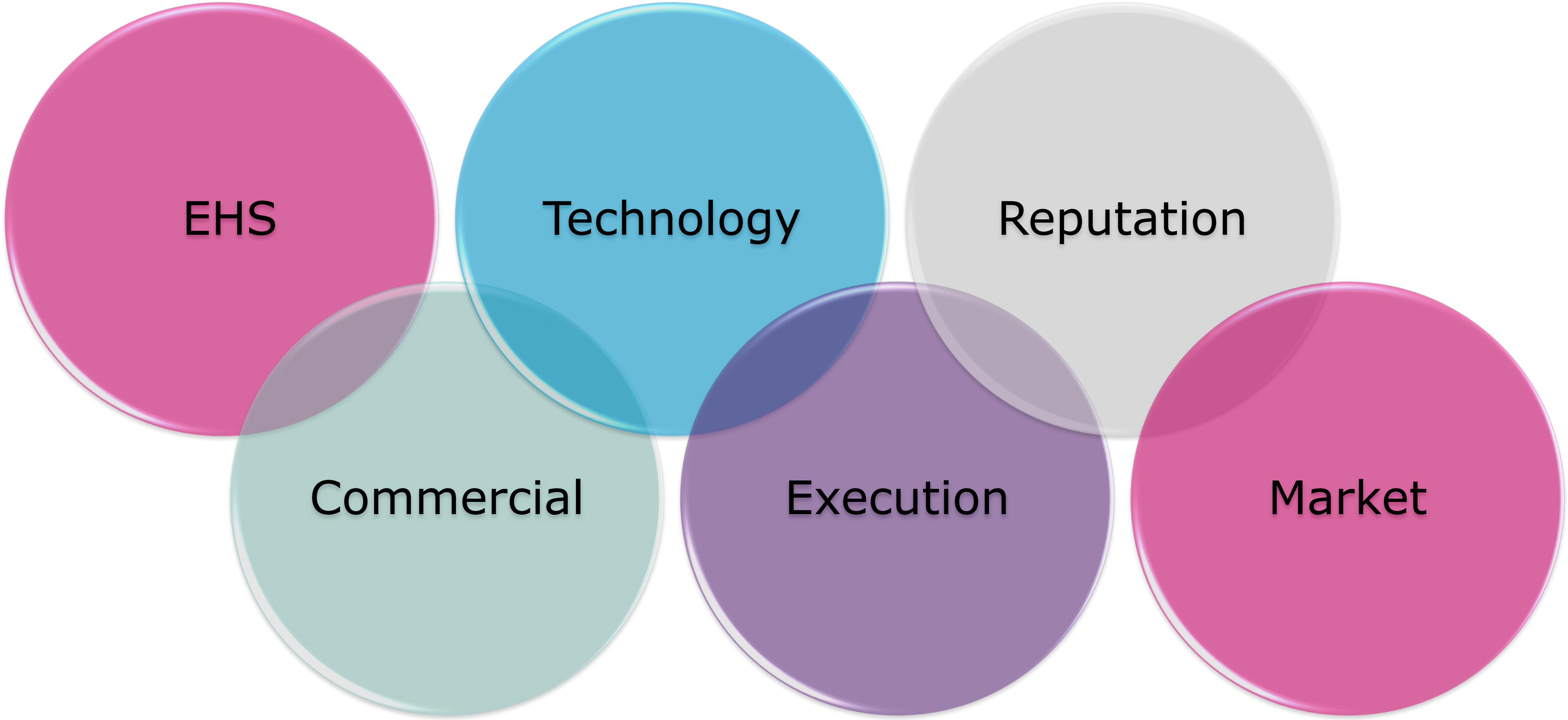
Segregate

Simplify

*Trevor Kletz

Process Safety

Need to consider other types of risk



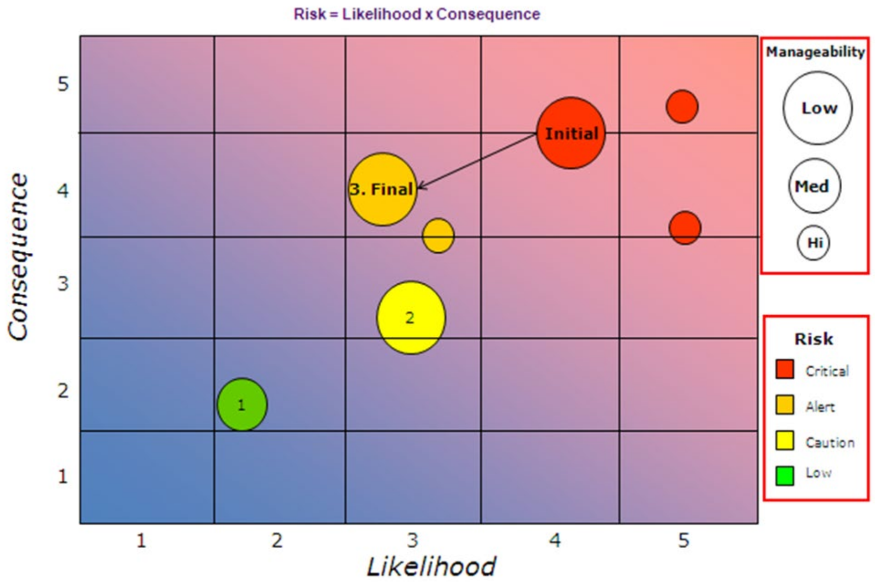
Process Safety / Scale Up

Technology Risk Assessment

For example:

- Experimental basis
  - Can R&T results can be extrapolated to full scale plant?
  - Entire operating range?
    - intentional and fault conditions
- Design Basis
  - Assumptions and methodology
- Operational and EHS learning for similar products / technologies
  - AIChE Ammonia Safety Conference
  - ANNA Conference

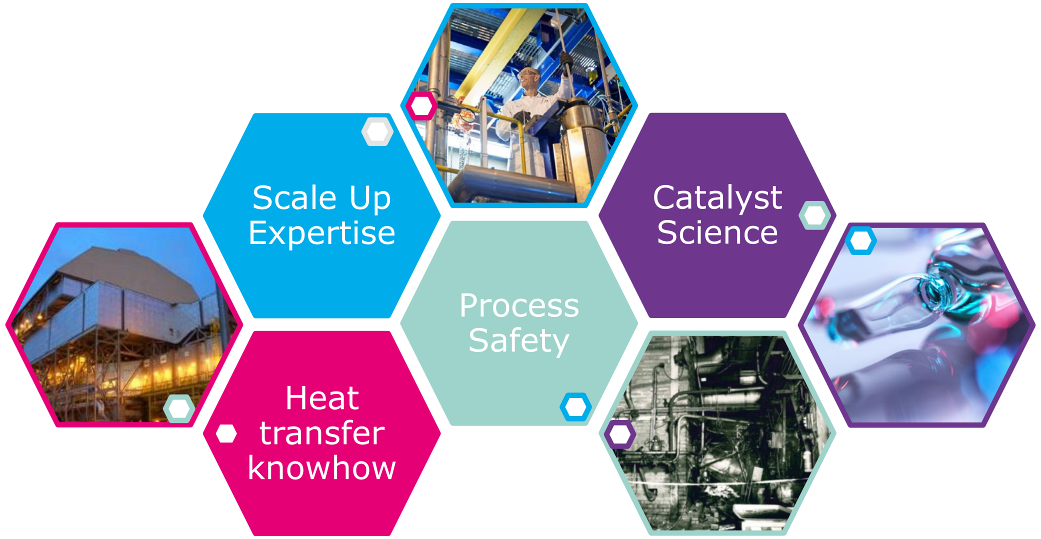
	Likelihood					
Consequence	Remote	Highly Unlikely	Unlikely	Possible	Quite Likely	Likely
Catastrophic						SEVERE
Massive						
Major				HIGH		
Moderate			MEDIUM			
Minor						
Slight	LOW					



Johnson Matthey Ammonia Cracking

Using world class science and technology to deliver solutions to our customers

- **Catalysts**
  - High performance catalysts
  - Investment in new product development



- **Catalysts & Technology**
  - Strong engineering capability
    - Catalyst
    - Utilities
    - Unit operations
  - Integrate engineering and catalyst knowhow to get the best out of both
  - Investment to develop new ammonia cracking technologies
    - Optimised plant efficiency
    - Reliable plant performance
    - Best environmental performance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