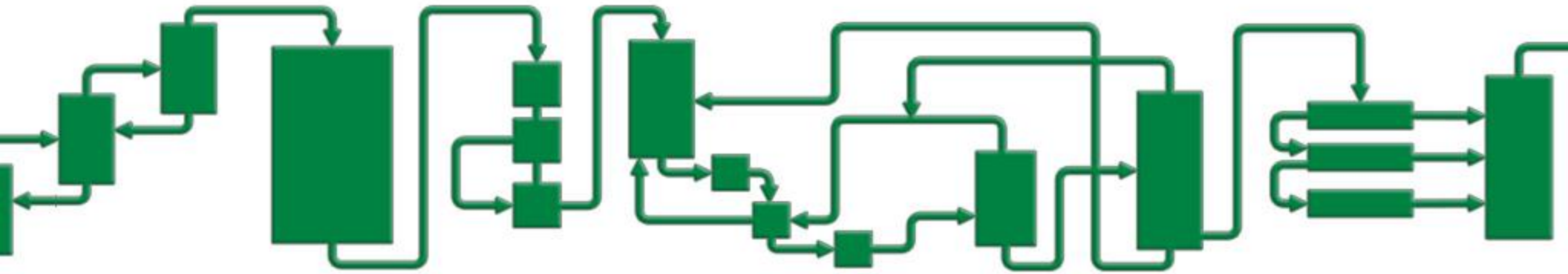

PI in steam methane reforming

PIN meeting June 2017

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Process Technologies

Agenda

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- Steam methane reforming background
  - Flowsheet
  - Reactions
- Catalyst design
  - Catalyst development
  - Historic shapes
- Other PI opportunities
  - Pre-reforming in hydrogen production
  - Pre-reforming in other applications

Hydrogen production flowsheet

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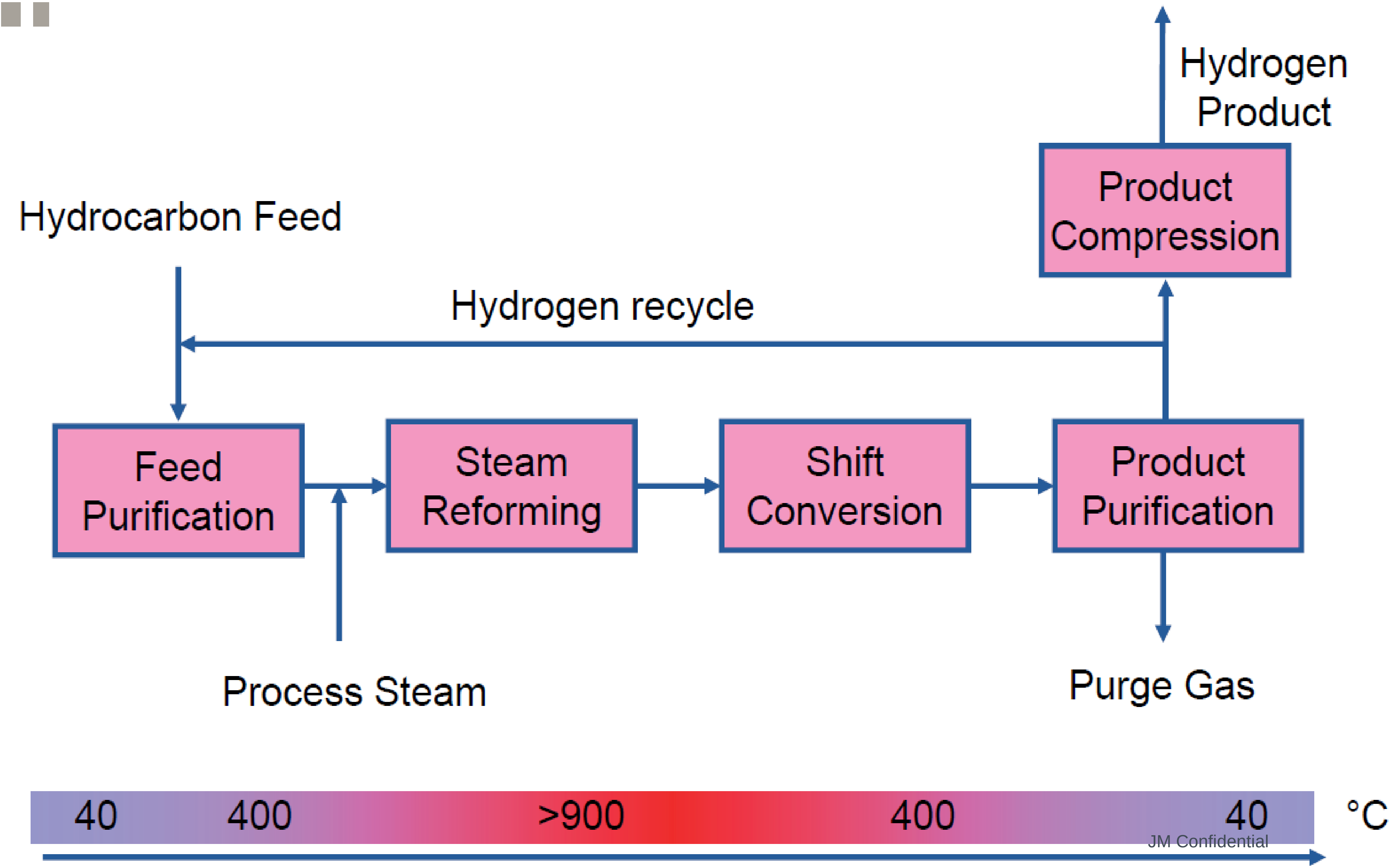

The steam methane reformer

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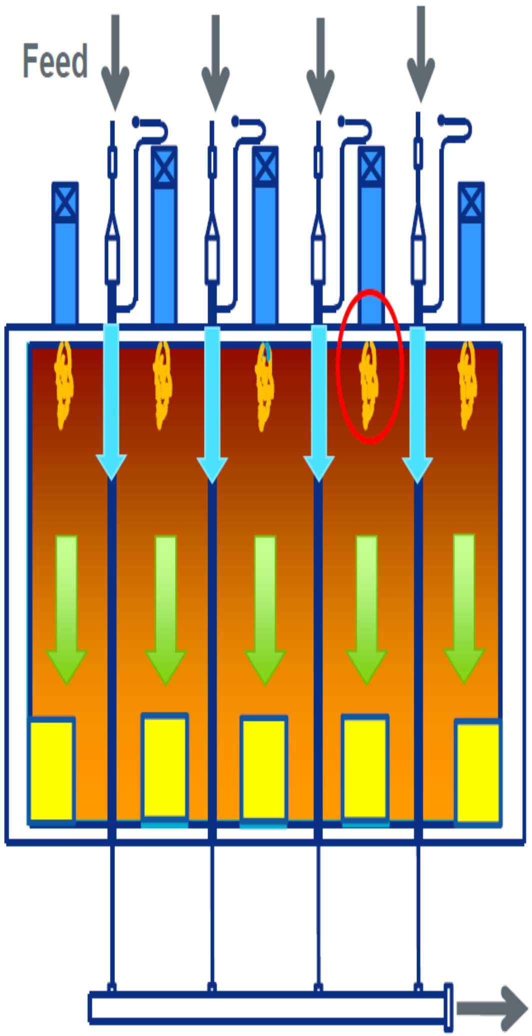

Reaction Stoichiometry and Thermodynamics

- Methane reforming
  - Simple stoichiometry
  - Water gas shift reaction occurs, quickly, in parallel
  - Overall process is strongly endothermic

Steam reforming:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H_{298} = +49.3\text{kcal/gmole}$$

Water gas shift:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_{298} = -9.8\text{kcal/gmole}$$

Reaction Stoichiometry and Thermodynamics

Pressure

$$F_{[CH_4]} = \frac{F_{[CO]}\ F_{[H_2]}^{\ 3}}{K_{ms}\ F_{[H_2O]}}$$

Steam Concentration

$$F_{[CH_4]} = \frac{F_{[CO]}\ F_{[H_2]}^{\ 3}\ P_{tot}^{\ 2}}{K_{ms}\ F_{[H_2O]}}$$

Temperature

$$F_{[CH_4]} = \frac{F_{[CO]}\ F_{[H_2]}^{\ 3}\ P_{tot}^{\ 2}}{K_{ms}\ F_{[H_2O]}}$$

Process Variable	Change	Exit CH_4	Notes
Pressure	Increase ↑	↑	Plant economics dictate higher pressures (20 bar)
Steam/Carbon Ratio	Increase ↑	↓	Often dictated by plant design (3 - 5)
Temperature	Increase ↑	↓	Limited by tube metallurgy

Catalyst Design Features

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- Key design features
  - Activity
    - To achieve close to equilibrium conversion as possible to maximise H_2 make
  - Pressure drop
    - Multi-tubular reactor (steam reformer) needs features to minimise pressure drop
  - Stability
    - Predictable and long catalyst lives

Catalyst Design – Activity

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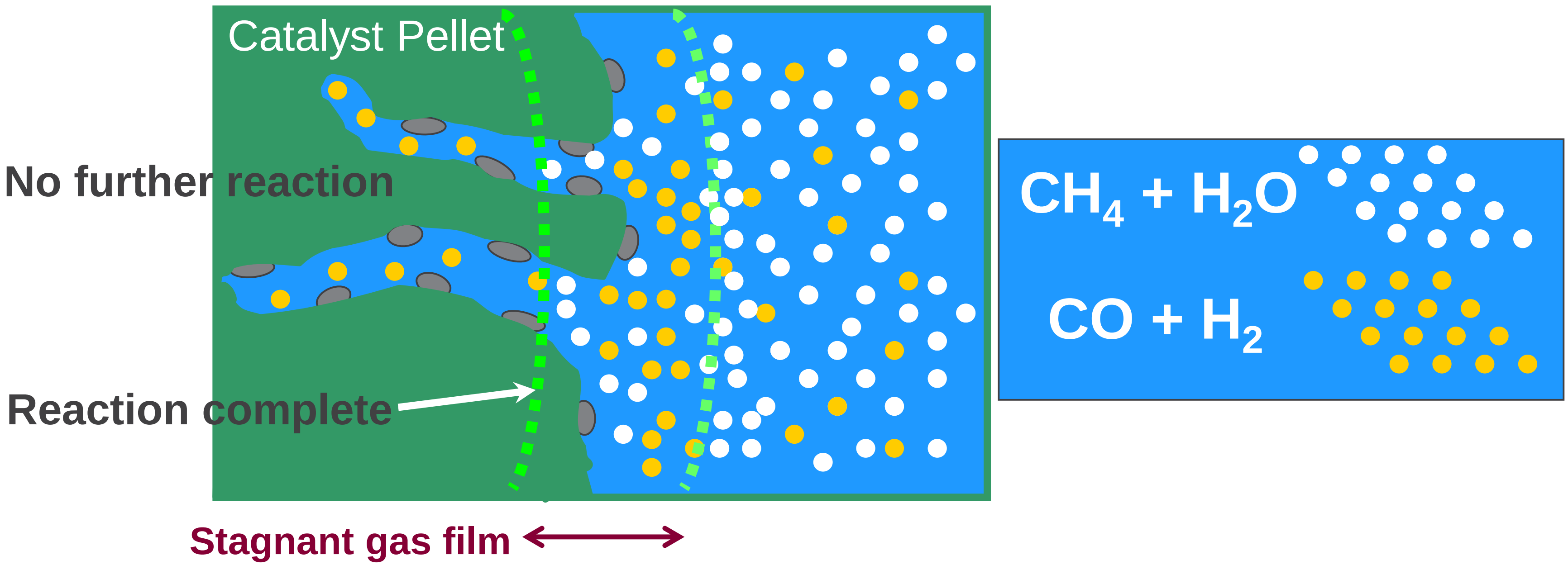
- Activity proportional to geometric surface area (GSA = tablet surface area per unit volume of catalyst bed)
  - Diffusion through gas film – slow
  - Reaction at catalyst surface – very fast



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The early days of steam reforming 1930s - 1940s

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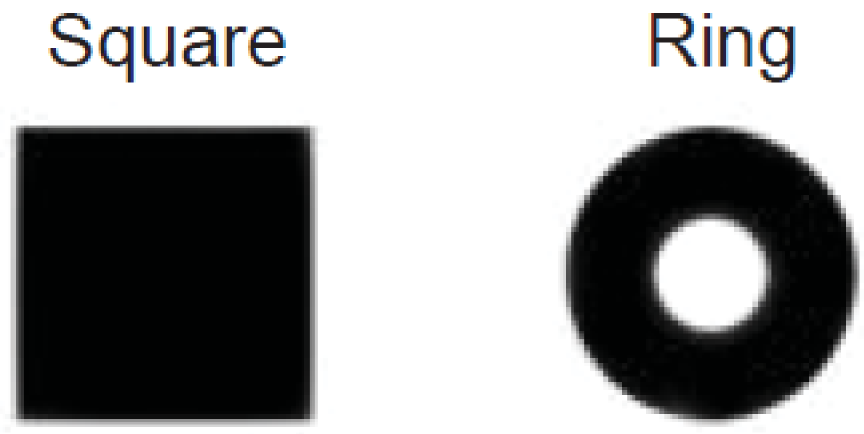

	1930s	1940s
Cross section	Square	Ring
Form	Cube	Cylindrical pellets
Relative Activity	1.00	1.32
Relative pressure drop	1.00	0.47

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The next development – 4 holes 1980s – 2000s

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	1980s	2000s
Cross section	4 – hole	QUADRALOBE™
Form	Cylindrical pellets	Cylindrical pellets
Relative Activity	1.64	2.00
Relative pressure drop	0.62	0.43

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Current development 2014

CATACEL$_{JM}$ SSR^{TM}

Cross section	CATACEL$_{JM}$SSR^{TM}
Form	Cylindrical foil supported structure
Relative Activity	3.00
Relative pressure drop	0.34

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Other opportunities for PI

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- Pre-reforming as an option to treat different feedstocks
- What is the aim of a pre-reformer?

  "To react hydrocarbon feed with steam over a high nickel catalyst to give a methane rich product suitable for further downstream reforming"
- Chemistry – 3 main reactions occur – all to equilibrium
  - Steam / methane reaction
    - Endothermic
  - Water / gas shift reaction
    - Exothermic
  - Methanation
    - Exothermic

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Flow Scheme – Pre-Reformer Installation

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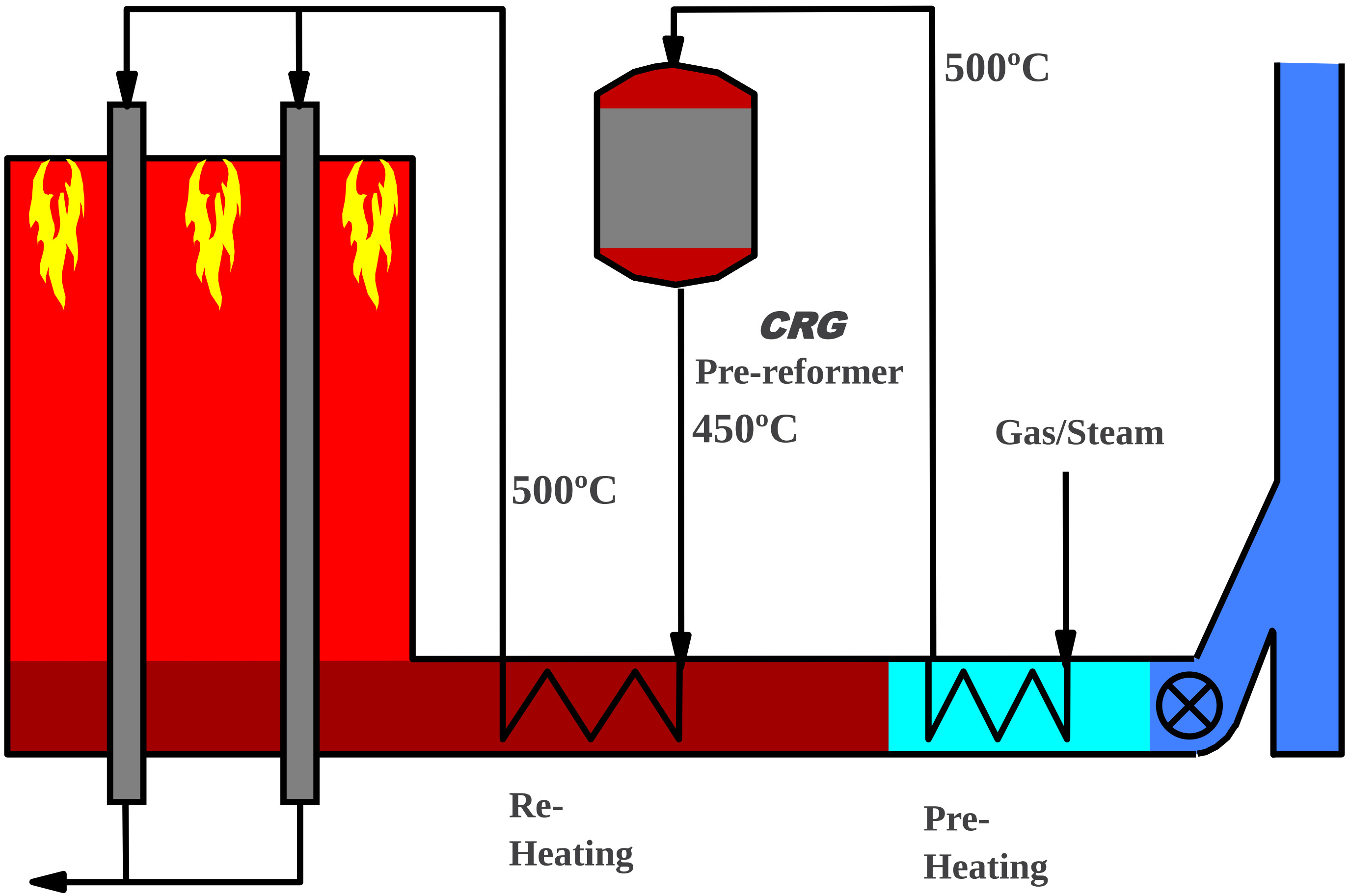

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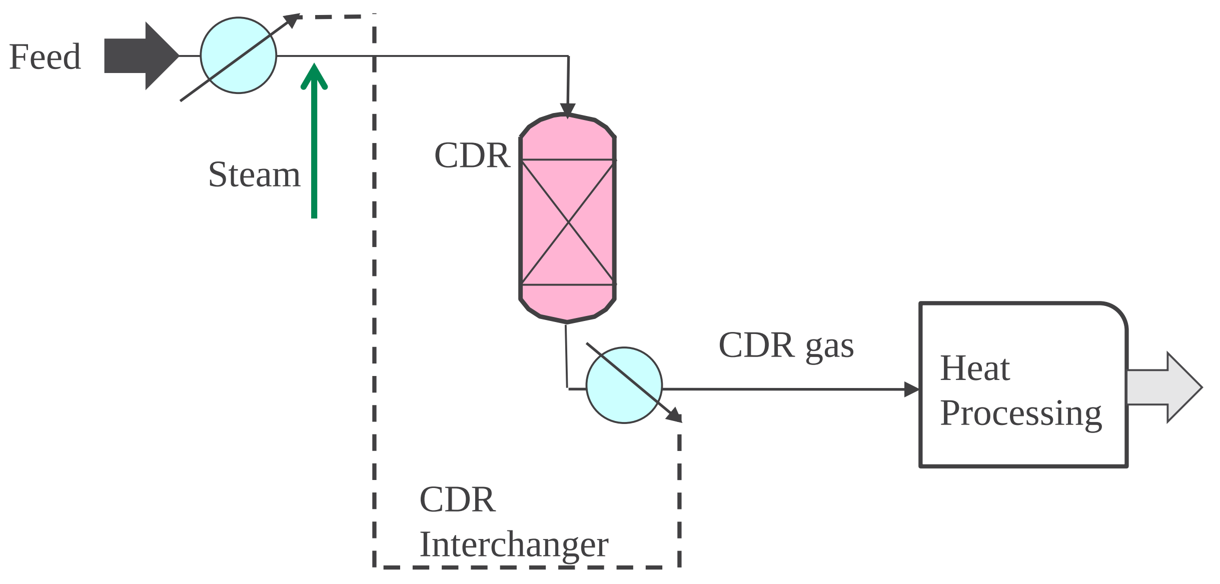
Benefits of a Pre-Reformer

- Increase in plant throughput
- Increased energy efficiency
- Feedstock flexibility
- Reduction in plant CAPEX and OPEX

Other pre-reforming PI opportunities

- Catalytic route to converting higher HCs to methane
  - LNG
  - Associated gas



Summary

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- Steam Methane Reforming is currently the main industrial method for producing hydrogen

- Steam reforming catalyst has undergone a number of developments that have led to process intensification

- Pre-reforming has been another process intensification opportunity in both hydrogen production and in other areas of hydrocarbon processing

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