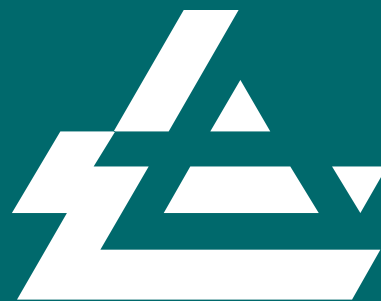


AIR
PRODUCTS





GCEP Energy Workshop



Frances C. Arrillaga Alumni Center, Stanford University

Production of Hydrogen



RJ Allam Air Products



Why Hydrogen?



- **H₂ is an energy vector, is converted to water which has minimal environmental impact.**
- **H₂ is a non-polluting fuel for transportation vehicles and power production**
- **Currently road vehicles emit about the same quantity of CO₂ as power production.**
- **H₂ can be produced from fossil fuels with CO₂ capture and storage or from renewables**

Production of Hydrogen Options

Method	Characteristics
Photolysis	catalytic-water splitting
Electrolysis	water
Power for electrolyser	ambient → high temperature ambient → high pressure
Thermal splitting	water
\equiv^m conc as function of temp	high temperature freeze equilibrium
Fossil fuel Conversion	Heat, water, oxygen, catalytic
Far Future	Non fossil fuel alternatives based on sunlight, renewables and nuclear
Present	Fossil fuels

Carbon Containing Fuels

Coal

Lignite → Anthracite

Natural gas

Refined Hydrocarbons

Ethane → Fuel Oil

Heavy refinery waste

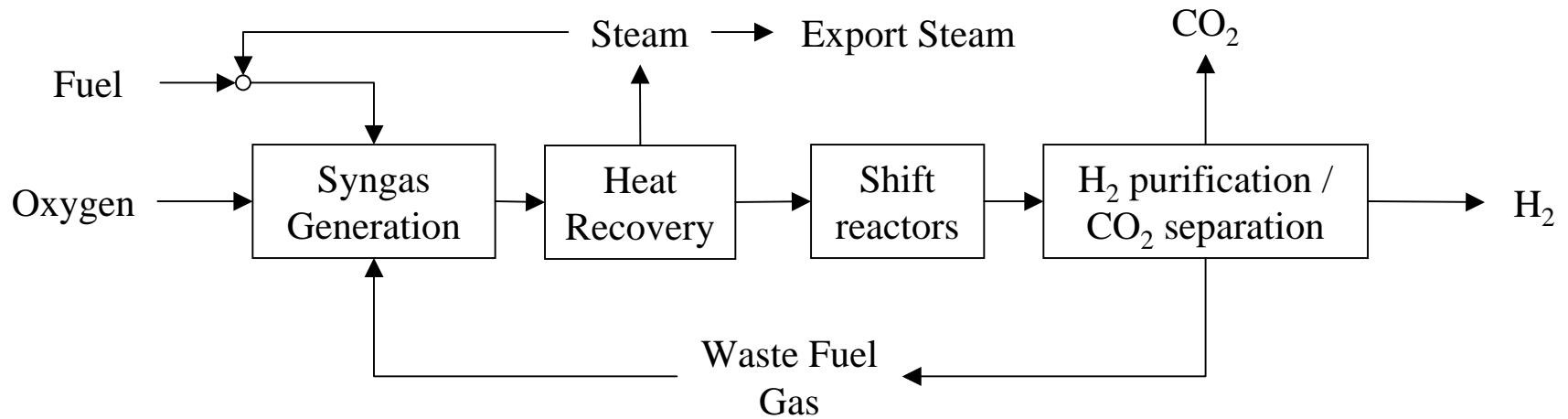
Tar → Petcoke

Biomass

Reactions

<p>Reforming With Steam - Catalytic</p> <p>Natural gas and light hydrocarbons</p>	$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad + \Delta\text{H}$ $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2 \quad - \Delta\text{H}$
<p>Partial Oxidation - Non Catalytic</p> <p>Any hydrocarbon or carbonaceous feedstock</p>	$\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} \quad - \Delta\text{H}$ $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad - \Delta\text{H}$
<p>Thermal Decomposition</p> <p>Only limited application as co-product in carbon black manufacture</p>	$\text{CH}_4 \rightarrow 2\text{H}_2 + \text{C} \quad +\Delta\text{H}$

General Arrangement For CO₂-free Hydrogen Production



CO₂ Separation Technologies

Capabilities

	<u>Adsorption</u>	<u>Membrane</u>	<u>Absorption</u>	<u>Cryogenic</u>
Feed Pressure	Low to High	Medium to High	Low to High	Medium to High
CO₂ Pressure	Low	Low	Low	Low to Medium
CO₂ Purity	Medium to High	Low to Medium	Medium to High	High
CO₂ Recovery	Medium to High	Low	High	High

H₂ Production Separation Methods

Separation of pure H₂ and pure CO₂ from syngas

Absorption

Scrubbing with a solvent

**Physical solvents: Rectisol – low temperature methanol
 Selexol – Polyether**

Selective for H₂S and CO₂ following COS hydrolysis

Favour high partial pressure of impurity

Used primarily when POX coal/tar

Chemical solvents – usually based on amines

Single component absorption H₂S and CO₂

High heat requirement

Suitable for low partial pressure of impurity



H₂ Production Separation Methods

Separation of pure H₂ and pure CO₂ from syngas

Adsorption

- Pressure swing used for most H₂ separations from syngases
- Can achieve 90% H₂ recovery from 22 bar SMR gas. Typical 3-10 min cycle time
- Low capital cost, high reliability
- Can be used for simultaneous pure H₂ and pure CO₂ recovery at high purity



PROJECT 82695
C. 501 E

HEAT TREATING
WELDING POINT

Process Characteristics

Open Systems

- **External heating of a catalytic reactor**
- **Combustion products vented to atmosphere**
- **CO₂-free flue gas requires H₂ fuel for the furnace, or**
- **Oxyfuel furnace operation could be used.**



Current Technology

Steam Methane Reforming (SMR)

● Limitations

- Carbon formation at low steam; carbon ratio
- Higher hydrogen pressure limits CH₄ conversion
- High CH₄ conversion requires high temperature
- Excess steam production
- Cooling by waste heat boiler to limit Boudouard carbon formation
- Low NO_x levels required in stack gas

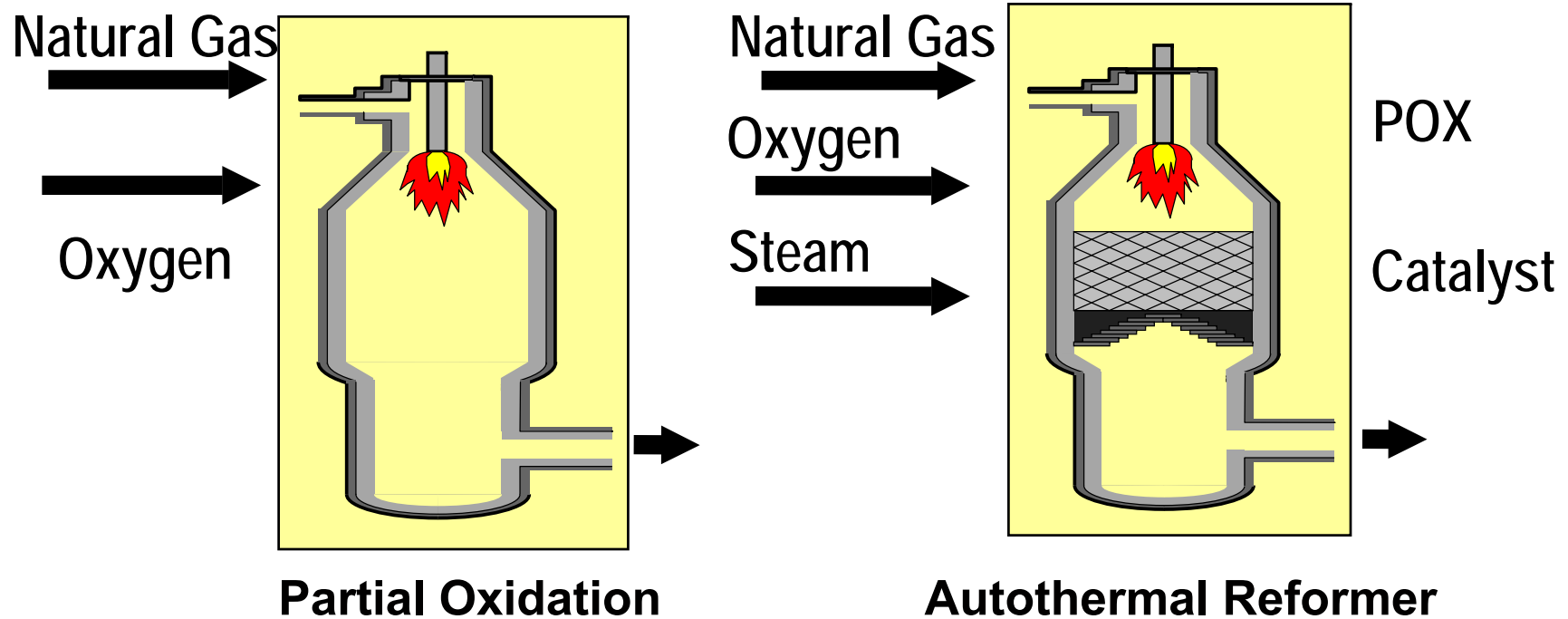
● Challenges

- Reduce steam to carbon ratio
- Low NO_x long flame burners
- Materials limitations in alloys used for tubes
- Reduce excess steam production by air preheat and pre-reforming

Process Characteristics

Closed Systems

- Pressurised reactors with heat supplied by direct oxidation with oxygen
- No venting of combustion products



Current Technology Autothermal Reformer (ATR)

- **Limitations**

- **Must use a clean, light hydrocarbon feed**
- **Cost of oxygen**
- **Limitation in H₂ pressure**
- **Limitation in exit temperature**
- **Excess steam production**
- **Needs waste heat boiler to limit Bouduard carbon formation**

- **Challenges**

- **Reduce steam to carbon ratio**
- **Increase CH₄ conversion by increasing temp**
- **Carbon free burner operation**
- **Increase in vessel size/throughout**

Current Technology

Partial Oxidation (POX)

Suitable for any carbonaceous feed – favoured for coal

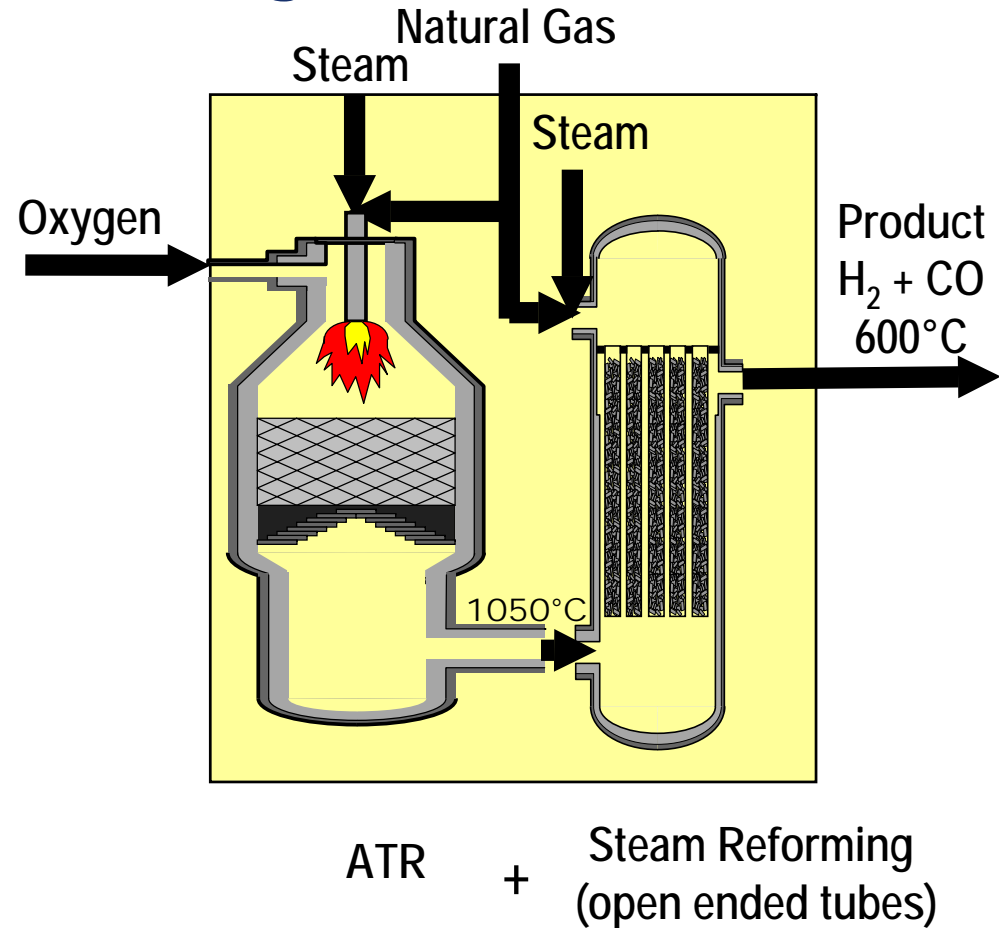
Many configurations...

- **Fixed/moving bed – Lurgi**
- **Fluidised bed – Winkler**
- **Entrained bed (1325°C → 1450°C)**
 - **Texaco**
 - **water slurry coal feed**
 - **high pressure: 70 bar**
 - **usually water quench**
 - **favoured for H₂ production because of excess H₂O present**
 - **combined sour gas CO shift and COS hydrolysis**
 - **Shell**
 - **dry coal feed, nitrogen entrainment**
 - **pressure limitation: 40bar (coal)**
 - **waste heat boiler, higher efficiency**
 - **needs added steam for shift and H₂ production**
 - **often configured with a COS hydrolysis reactor upstream of H₂S removal and CO shift reactor downstream of H₂S removal**

Production of Hydrogen

ATR/GHR Integration

- Possibility of using high temperature $H_2/CO/CO_2$ syngas to heat a Gas Heated Reformer (GHR)
- No excess steam production
- Extra 30% H_2 production
- Bouduard carbon formation in GHR shell side



H₂ Production Emerging Technologies

- **Micro reactor/Multichannel Heat Exchanger**

Either

- **Low temperature POX**

- Air purified
- 45% H₂ – fuel cell feed (PEM)
- Followed by direct air/CO
- Oxidation to reduce CO<10ppm

- **SMR**

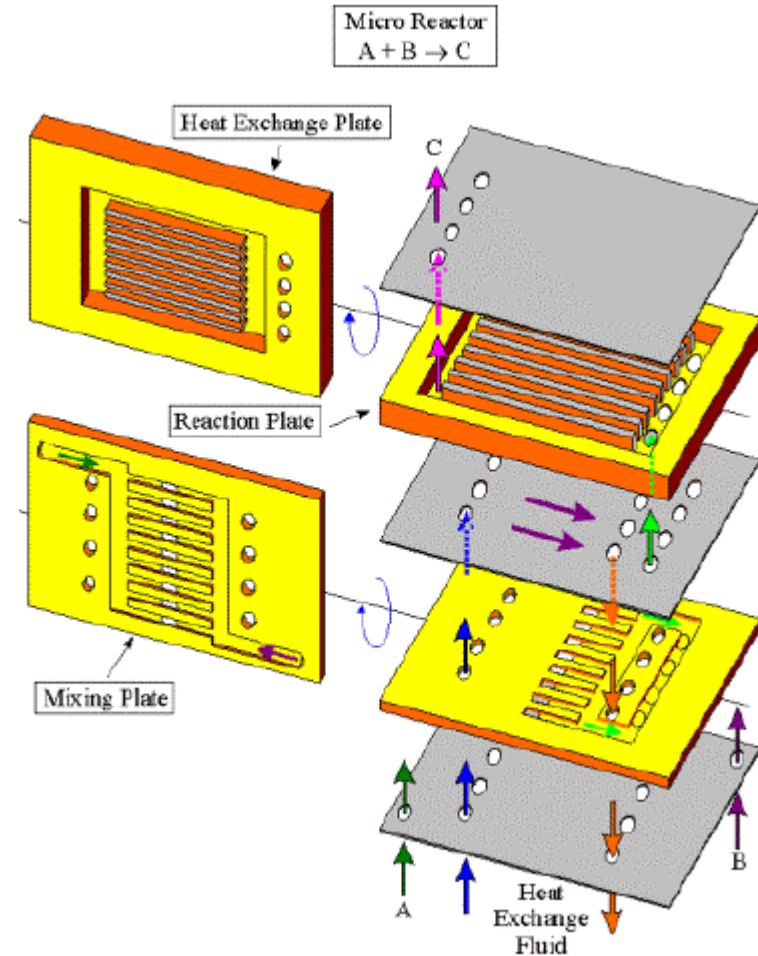
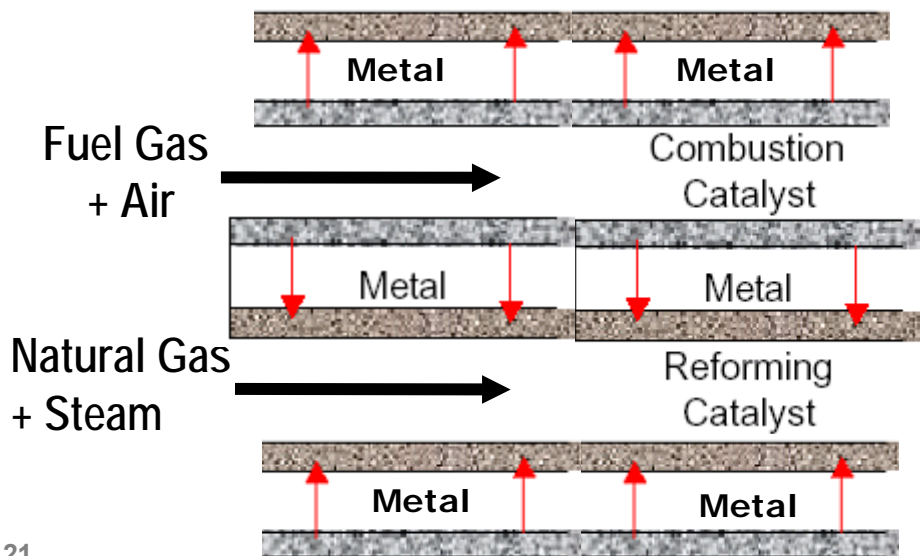
- **Separate air/fuel gas catalytic combustion passages and adjacent SMR passages**

Production of Hydrogen Plate-Fin Reformer

Catalyst can be a surface coating or a porous insert.

Need to match the heat release rate with the steam hydrocarbon reforming rate.

Very compact and potentially low cost system



H₂ Production Emerging Technologies

- **Micro reactor/Multichannel Heat Exchanger**

In General

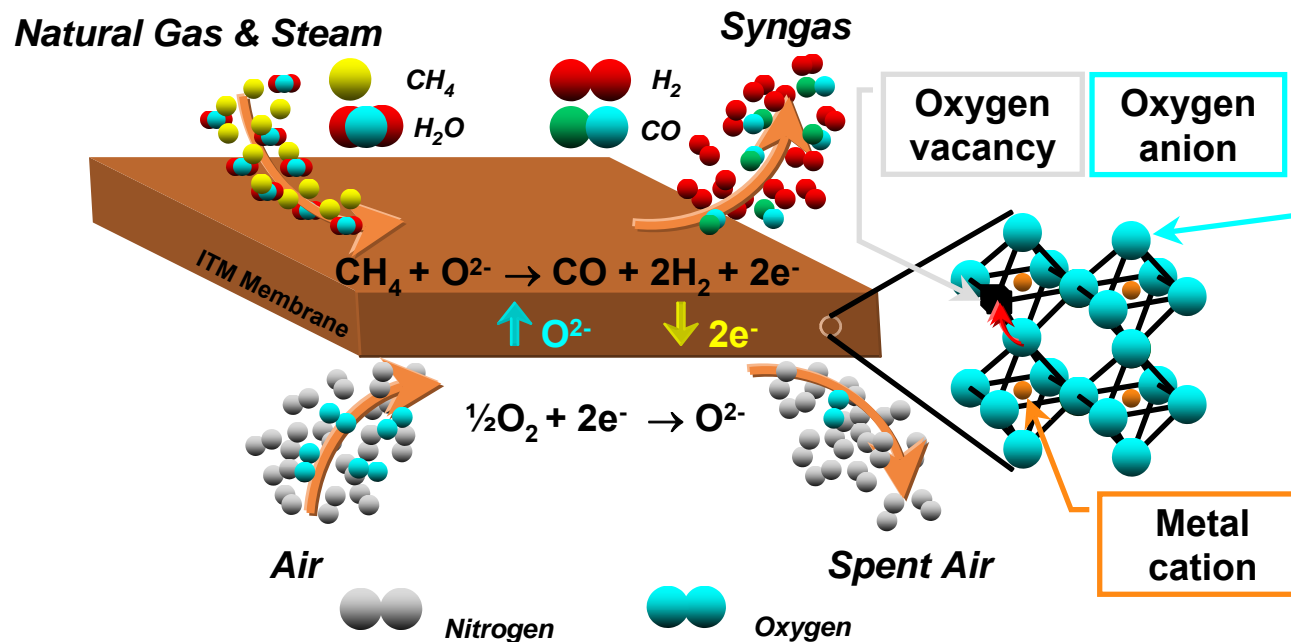
- Catalyst can be deposited on metal surfaces or used in a porous insert
- Removable catalyst elements are possible
- Very high volumetric productivity for SMR reactor
- Whole H₂ plant can be integrated with a plate-fin reformer configuration

Challenges

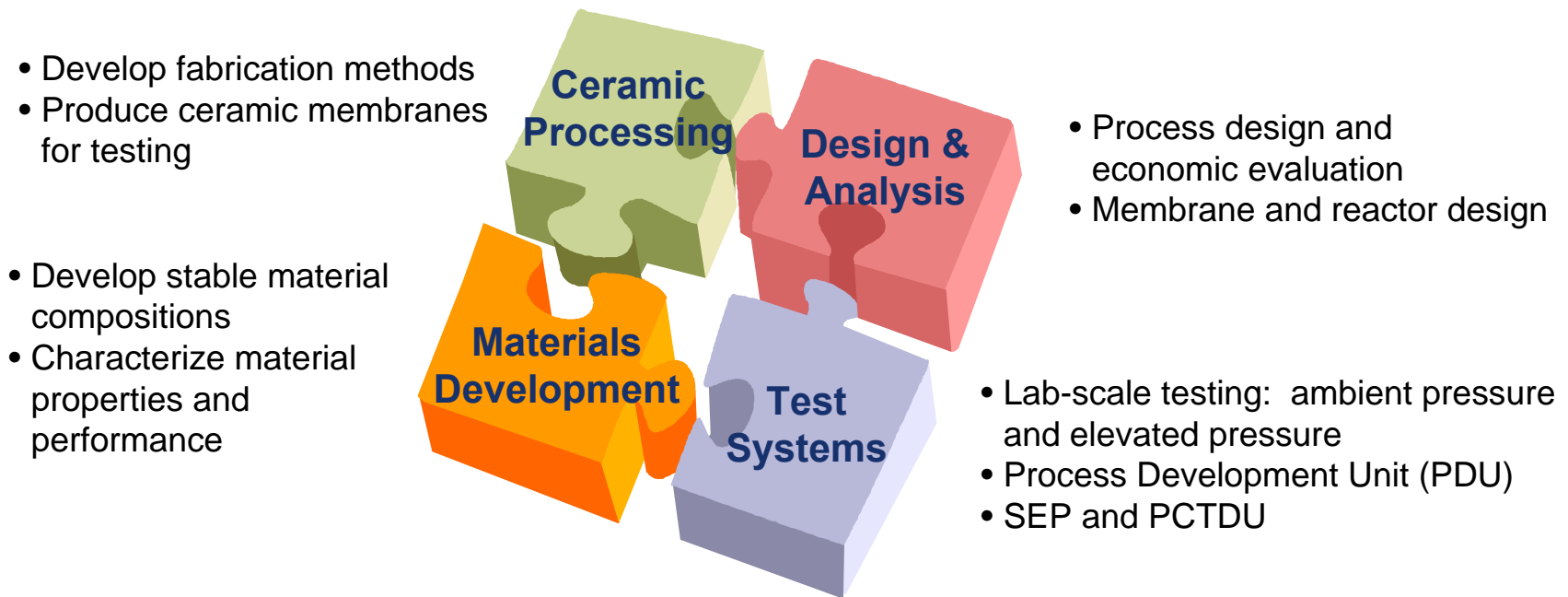
- Novel arrangements to allow catalyst change out
- Capable of either small scale or very large scale use
- Requires balanced performance between SMR/fuel combustion

ITM Hydrogen/Syngas: A Revolutionary Technology Using Ceramic Membranes

- **Ion Transport Membranes (ITM)**
 - Non-porous multi-component ceramic membranes
 - High oxygen flux and high selectivity for oxygen
 - Operate at high temperatures, typically over 700 °C
- **ITM Hydrogen/Syngas combines air separation and methane partial oxidation into a single unit operation, resulting in significant cost savings**

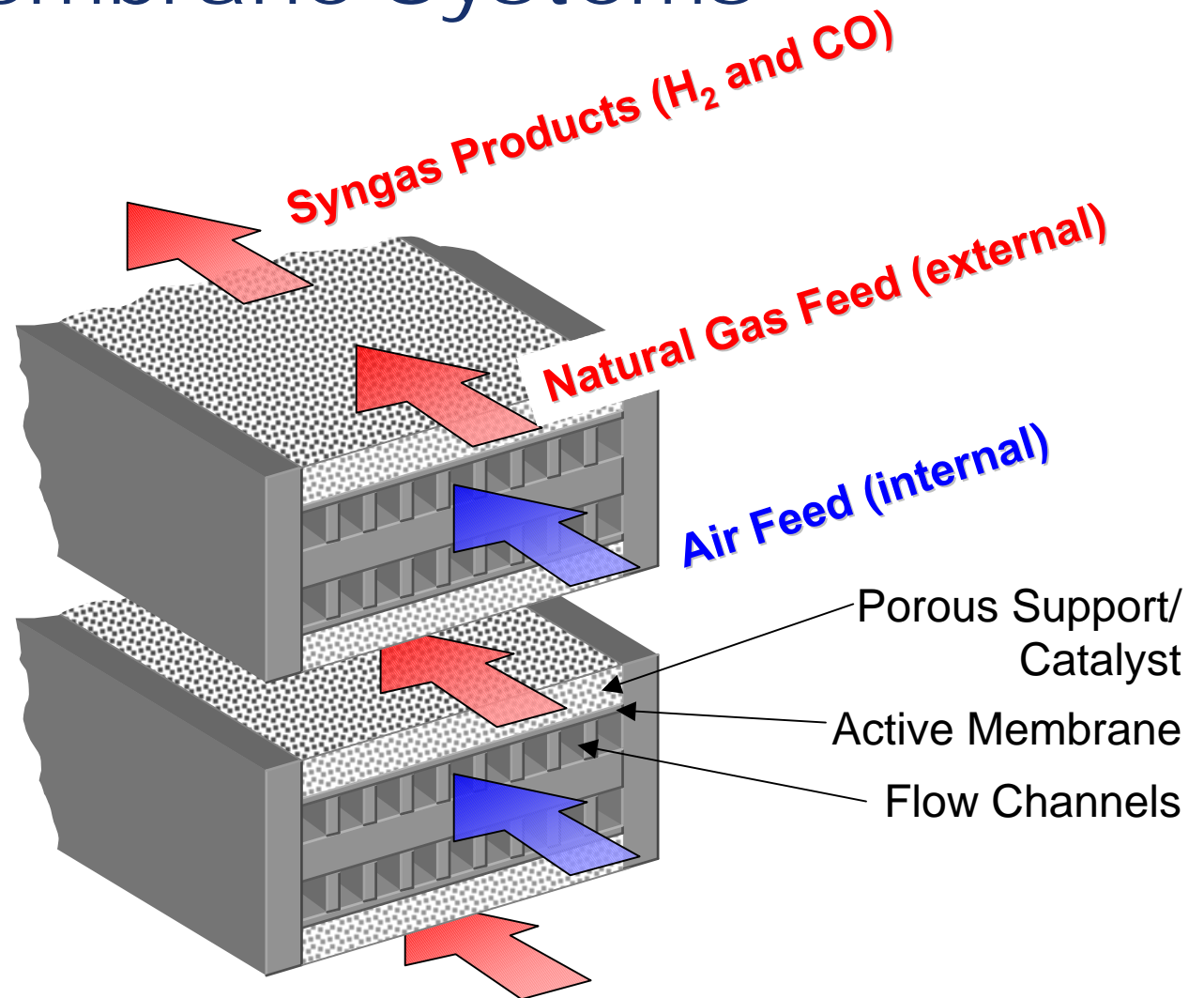


Integrated Development Program Addresses Key Technical Challenges with Broad Development Team



Advantages of Planar Membrane Systems

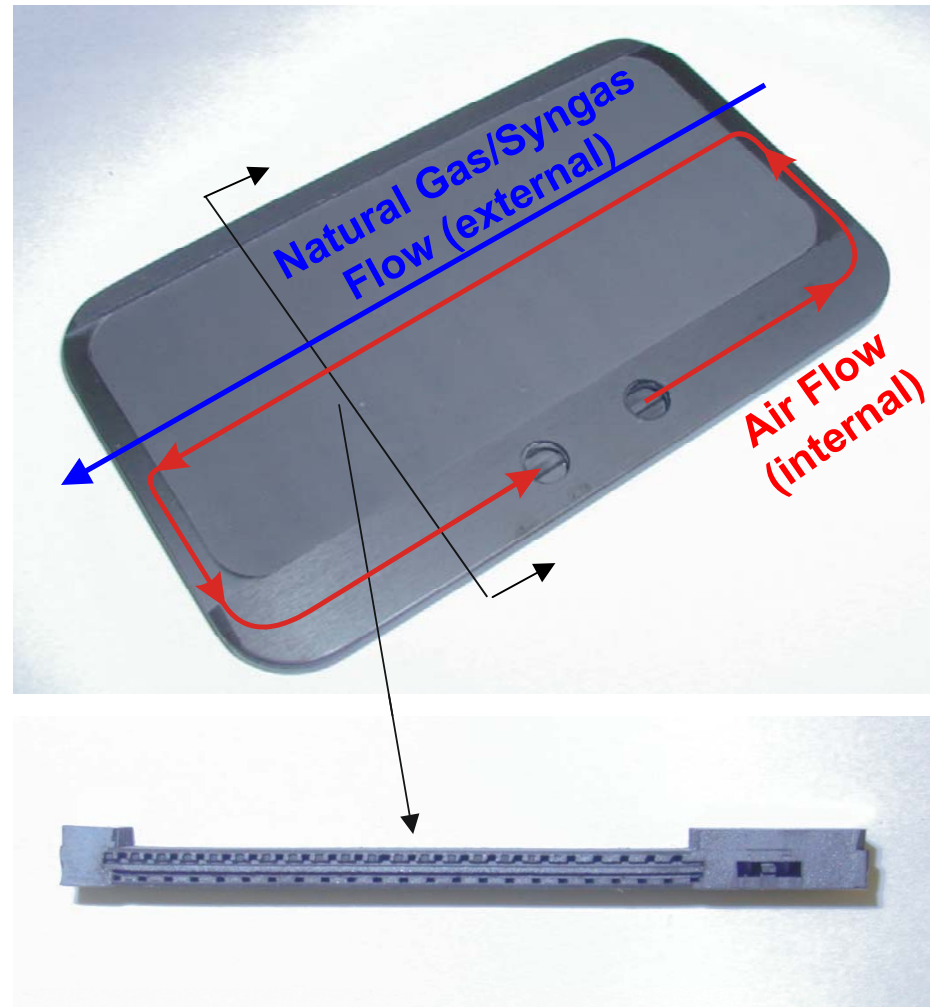
- Compactness
- Good mass and heat transfer
- Amenable to standard ceramic processing methods



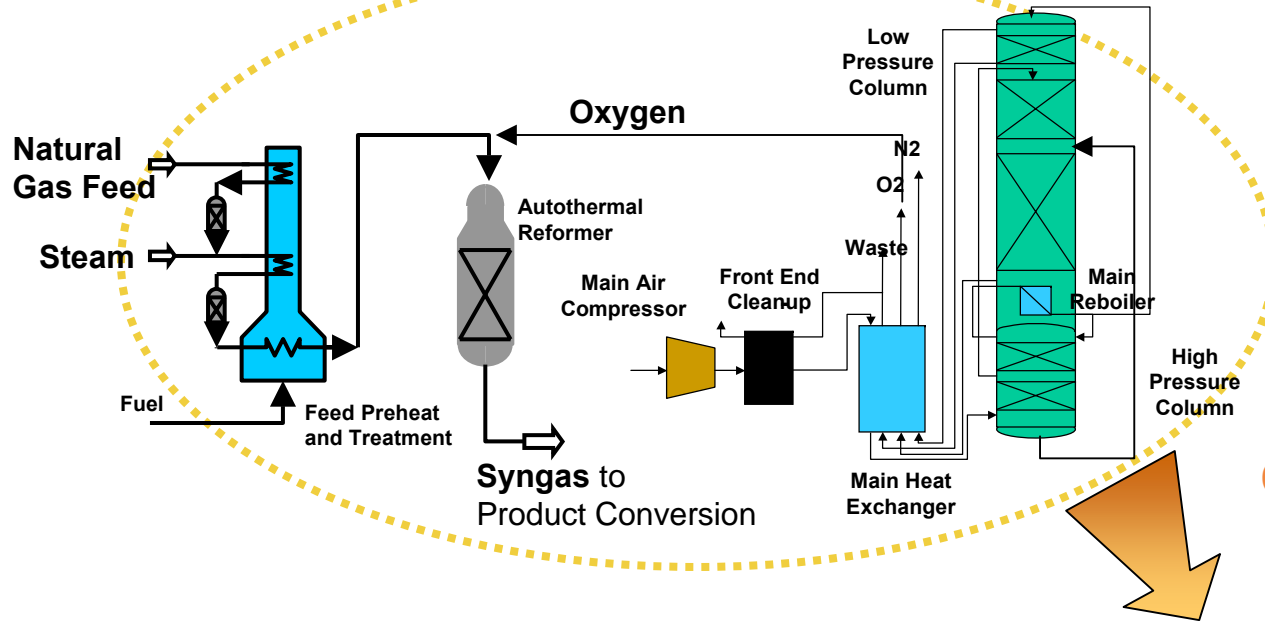
Ceramic Wafer Stack

PDU Ceramic Membranes Contain Essential Features of Full-Size Commercial Membranes

- ITM Hydrogen/Syngas ceramic membranes have internal features for manifolding and air flow, while supporting > 400 psi pressure differential
- Membrane fabrication processes are robust and scaleable



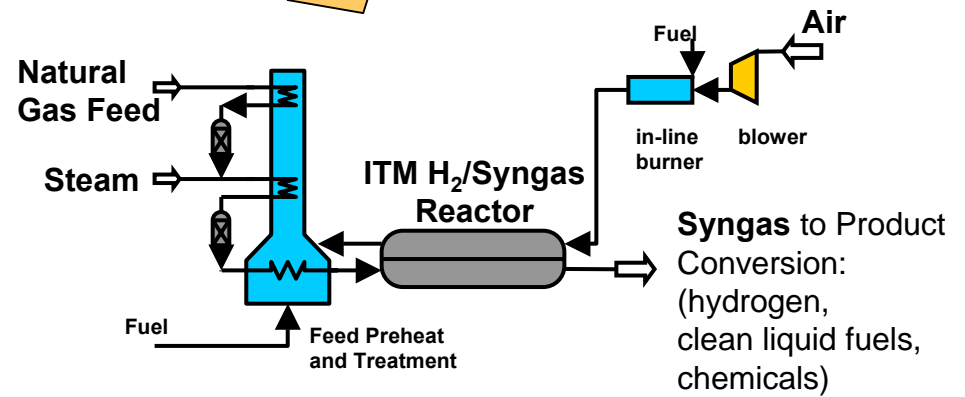
ITM Hydrogen/Syngas: Combines Oxygen Production and Syngas Production Into a Single Reactor to Achieve Over 30% Capital Cost Savings



Conventional Process (ATR and Air Sep Unit) with Separate Oxygen and Syngas Production

Over 30% Capital Cost Savings

ITM Hydrogen/Syngas Reactor Combines Oxygen Separation and Syngas Production



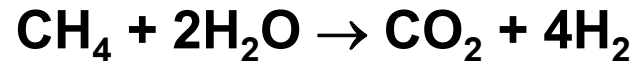
Production of Hydrogen

Simultaneous Separation/Reaction

- Enhanced conversion of feedstock to hydrogen by removing one of the product continuously

- H₂ removal from steam reformer using a palladium diffusion surface

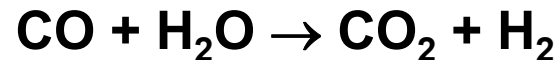
- low pressure H₂, high pressure CO₂



- Adsorption of CO₂ at high temperature in a shift converter/adsorber

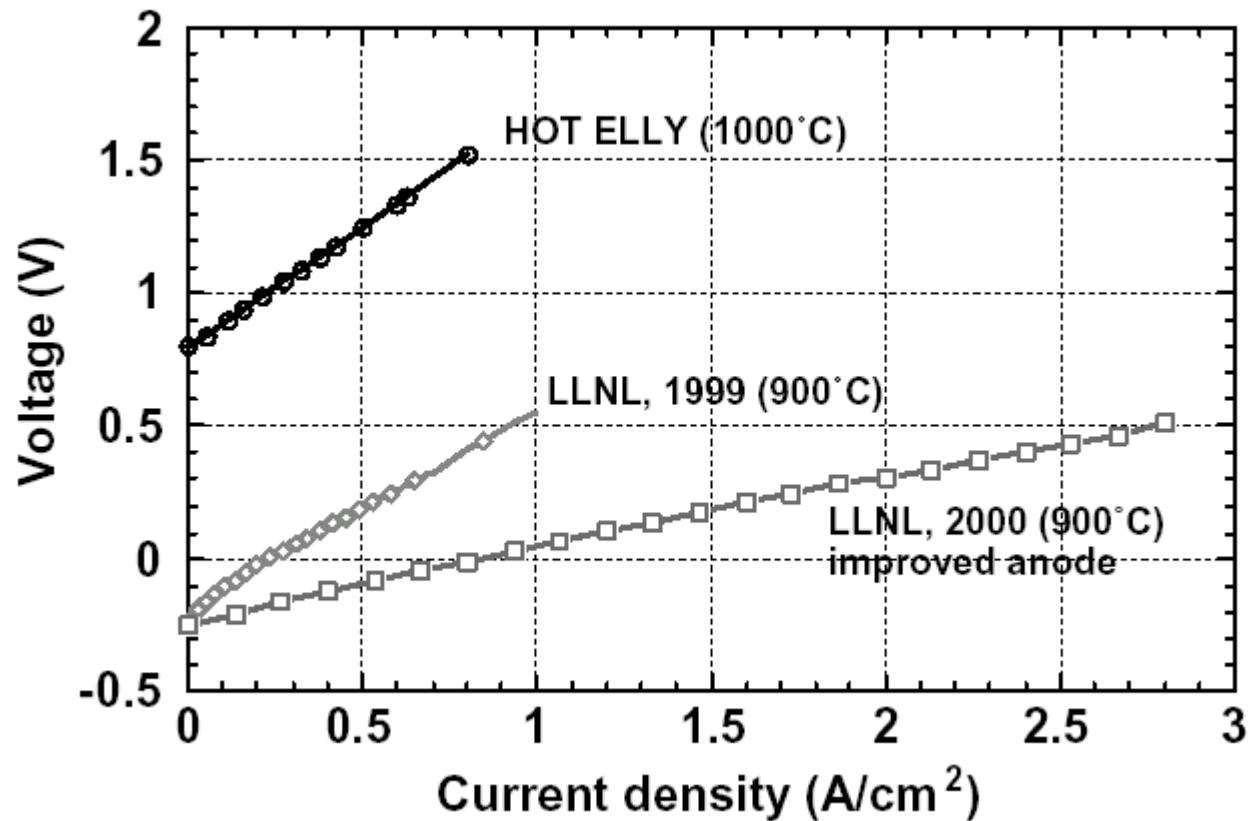
- Typical high temperature adsorbents are substituted hydrotalcites or lithium silicate for CO₂

- high pressure H₂, low pressure CO₂



- In both cases, hot H₂ is produced (400 - 600°C)

Production of Hydrogen Steam Electrolysers



Thank you

tell me more

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