AIR PRODUCTS

GCEP Energy Workshop

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Production of Hydrogen

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Air Products

Why Hydrogen?

$H_2 + ½\ O_2 \rightarrow H_2O \quad \Delta H\ -57.8$ kcal/mole

- H_2 is an energy vector, is converted to water which has minimal environmental impact.
- H_2 is a non-polluting fuel for transportation vehicles and power production
- Currently road vehicles emit about the same quantity of CO_2 as power production.
- H_2 can be produced from fossil fuels with CO_2 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
	high temperature
≡m conc as function of temp	freeze equilibrium
Fossil fuel Conversion	Heat, water, oxygen, catalytic
Far Future	Non fossil fuel alternatives based on sunlight, renewables and nuclear
Present	Fossil fuels

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Carbon Containing Fuels

Coal	Lignite → Anthracite
Natural gas	
Refined Hydrocarbons	Ethane → Fuel Oil
Heavy refinery waste	Tar → Petcoke
Biomass	

Reactions

Reforming With Steam - Catalytic **Natural gas and light hydrocarbons**	$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad + \Delta H$ $CO + H_2O \leftrightarrow H_2 + CO_2 \quad - \Delta H$
Partial Oxidation - Non Catalytic **Any hydrocarbon or carbonaceous feedstock**	$C + ½O_2 \rightarrow CO \quad - \Delta H$ $CO + H_2O \leftrightarrow CO_2 + H_2 \quad - \Delta H$
Thermal Decomposition **Only limited application as co-product in carbon black manufacture**	$CH_4 \rightarrow 2H_2 + C \quad +\Delta H$

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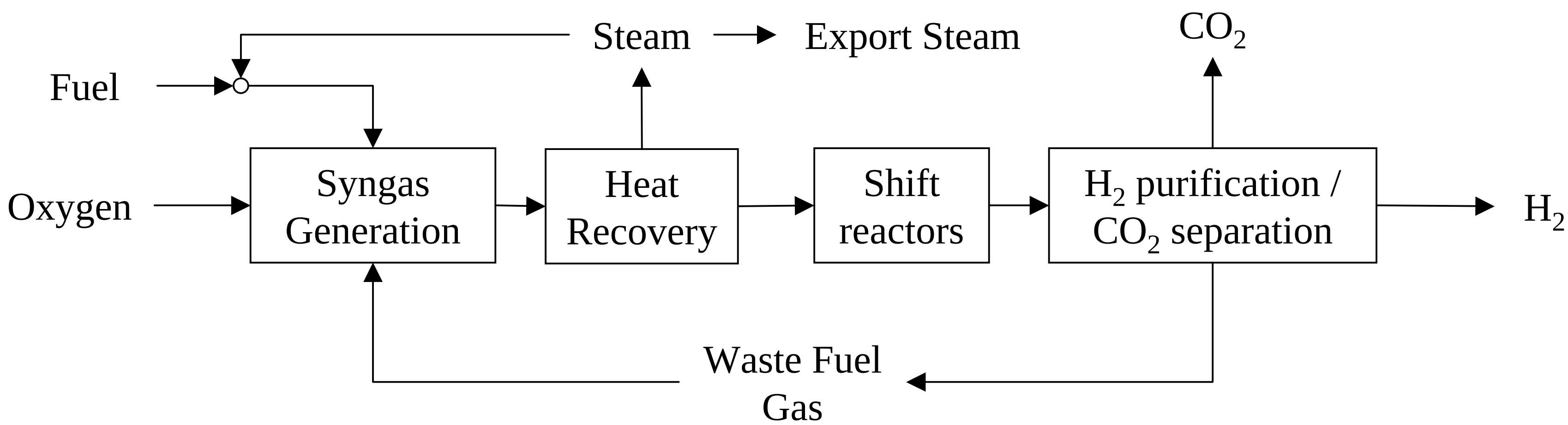
General Arrangement For CO_2-free Hydrogen Production



CO_2 Separation Technologies Capabilities

	Adsorption	Membrane	Absorption	Cryogenic
Feed Pressure	Low to High	Medium to High	Low to High	Medium to High
CO_2 Pressure	Low	Low	Low	Low to Medium
CO_2 Purity	Medium to High	Low to Medium	Medium to High	High
CO_2 Recovery	Medium to High	Low	High	High

H_2 Production Separation Methods

Separation of pure H_2 and pure CO_2 from syngas

<u>Absorption</u>

- **Scrubbing with a solvent**
- **Physical solvents:** **Rectisol – low temperature methanol**
  Selexol – Polyether
  - **Selective for H_2S and CO_2 following COS hydrolysis**
  - **Favour high partial pressure of impurity**
  - **Used primarily when POX coal/tar**

- **Chemical solvents – usually based on amines**
  - **Single component absorption H_2S and CO_2**
  - **High heat requirement**
  - **Suitable for low partial pressure of impurity**

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H_2 Production Separation Methods

Separation of pure H_2 and pure CO_2 from syngas

<u>Adsorption</u>

- **Pressure swing used for most H_2 separations from syngases**
- **Can achieve 90% H_2 recovery from 22 bar SMR gas. Typical 3-10 min cycle time**
- **Low capital cost, high reliability**
- **Can be used for simultaneous pure H_2 and pure CO_2 recovery at high purity**

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PROJECT

Process Characteristics
Open Systems

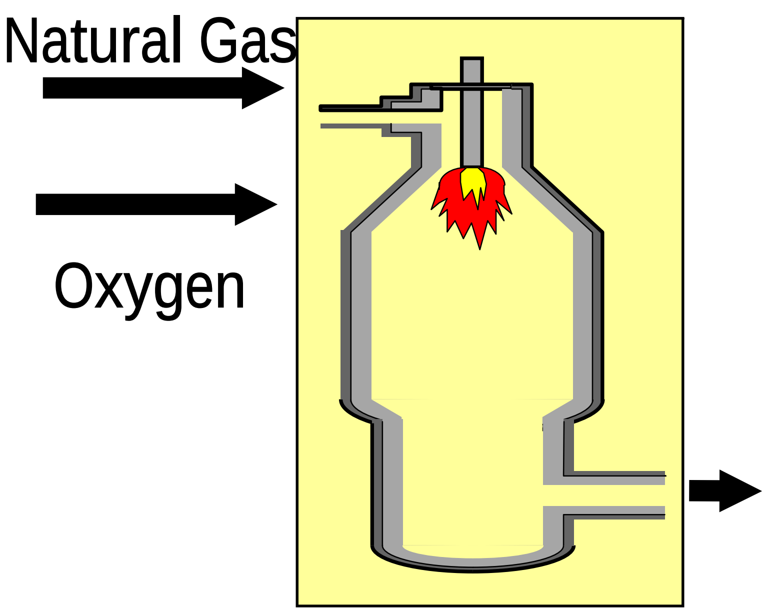
- External heating of a catalytic reactor
- Combustion products vented to atmosphere
- CO_2-free flue gas requires H_2 fuel for the furnace, or
- Oxyfuel furnace operation could be used.

Current Technology
Steam Methane Reforming (SMR)

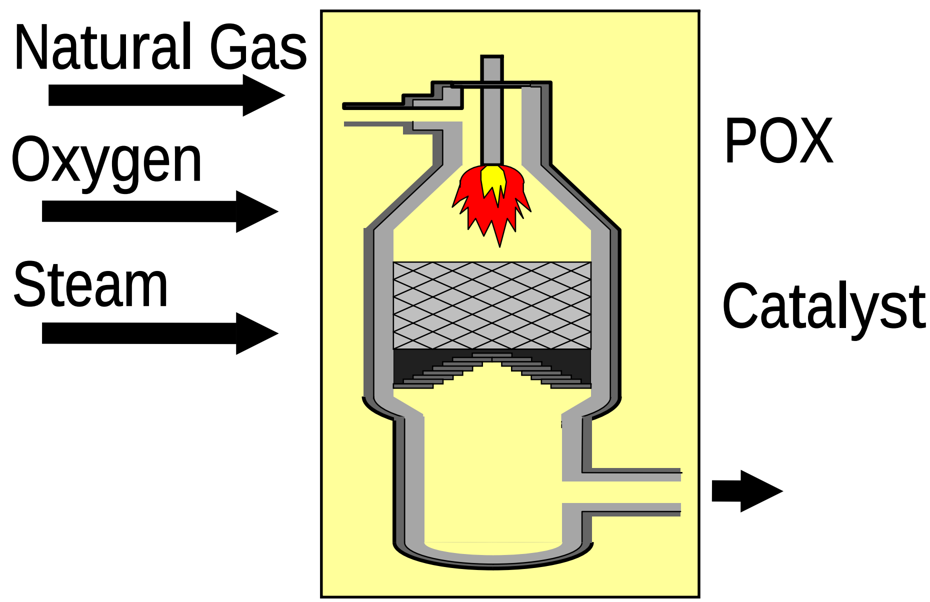
- **Limitations**
  - Carbon formation at low steam; carbon ratio
  - Higher hydrogen pressure limits CH_4 conversion
  - High CH_4 conversion requires high temperature
  - Excess steam production
  - Cooling by waste heat boiler to limit Bouduard carbon formation
  - Low NO_x levels required in stack 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



Partial Oxidation



Autothermal Reformer

Current Technology
Autothermal Reformer (ATR)

- **Limitations**
  - **Must use a clean, light hydrocarbon feed**
  - **Cost of oxygen**
  - **Limitation in H_2 pressure**
  - **Limitation in exit temperature**
  - **Excess steam production**
  - **Needs waste heat boiler to limit Bouduard carbon formation**
- **Challenges**
  - **Reduce steam to carbon ratio**
  - **Increase CH_4 conversion by increasing temp**
  - **Carbon free burner operation**
  - **Increase in vessel size/throughout**

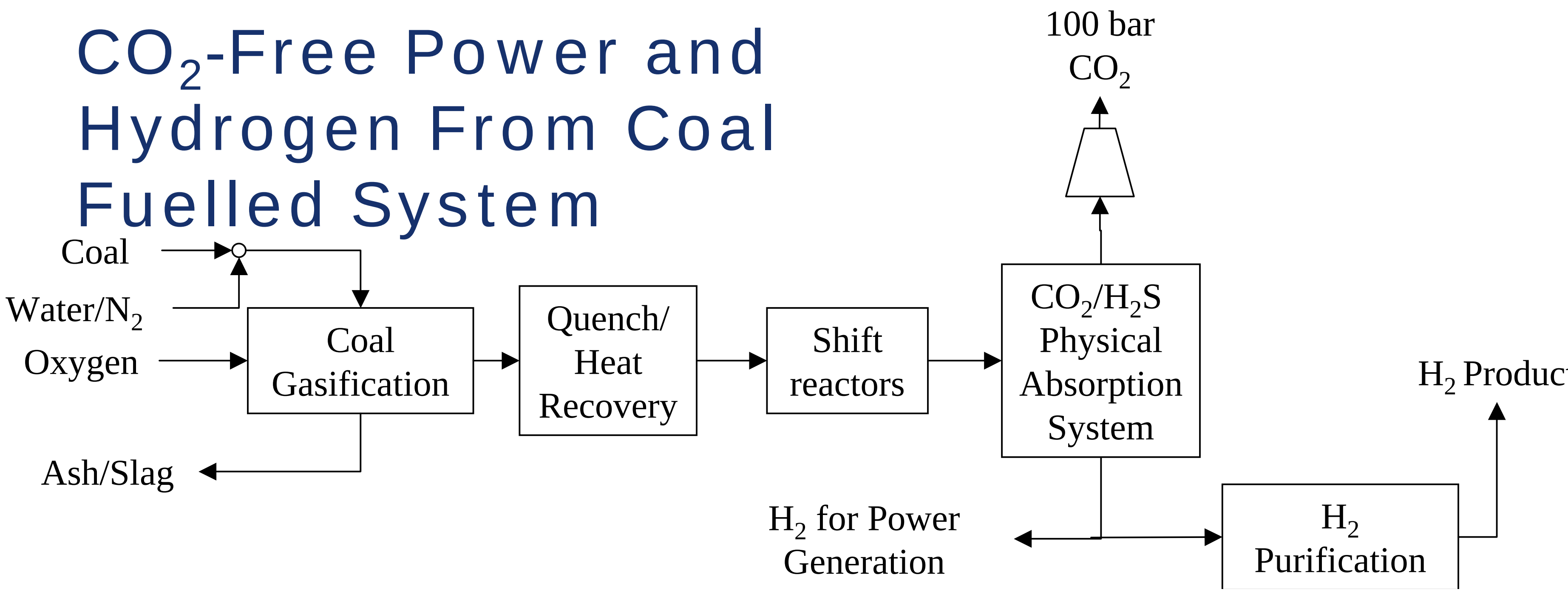
Current Technology
Partial Oxidation (POX)

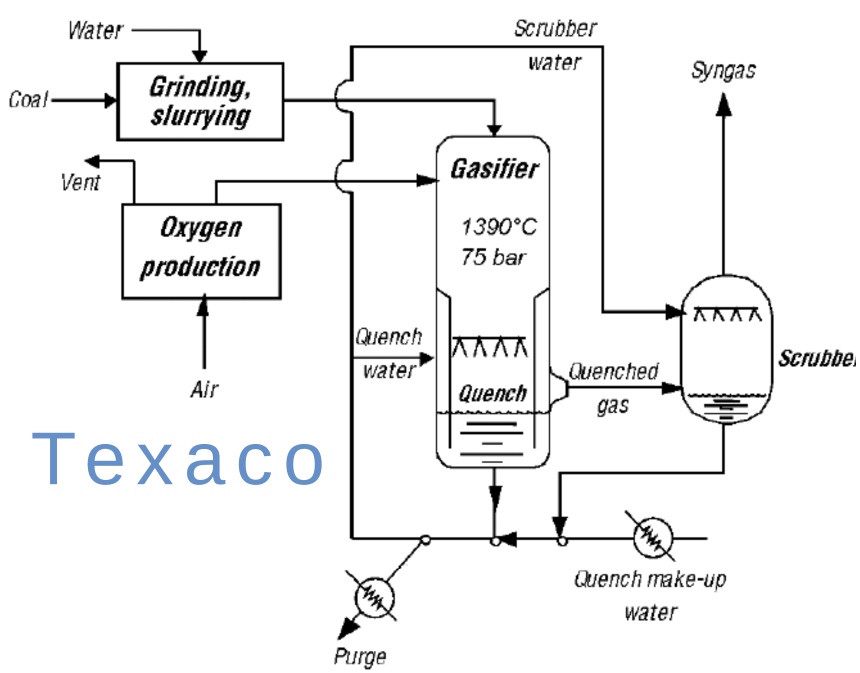
Suitable for any carbonaceous feed – favoured for coal

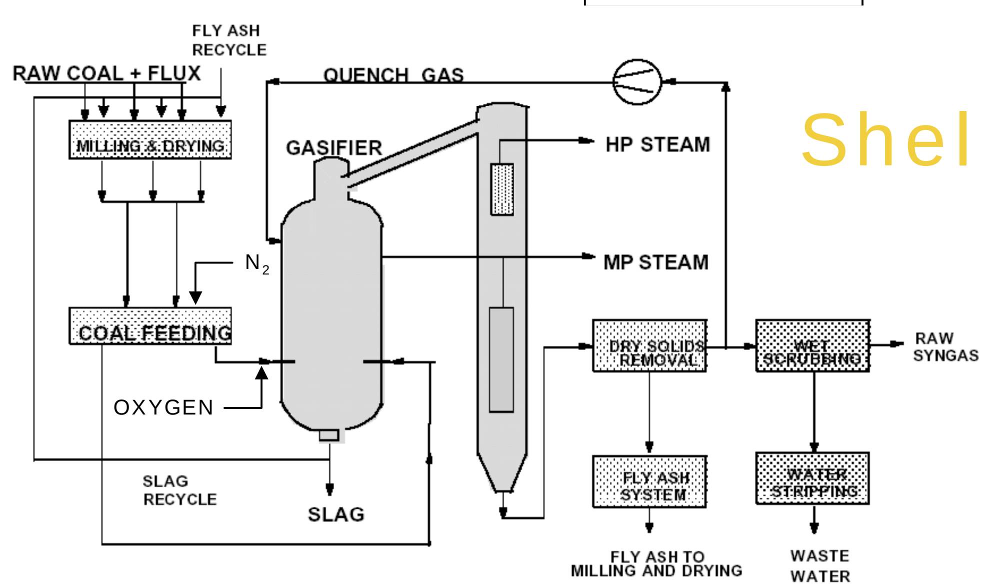
Many configurations…

- **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 H_2 production because of excess H_2O 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 H_2 production**
    - **often configured with a COS hydrolysis reactor upstream of H_2S removal and CO shift reactor downstream of H_2S removal**

CO_2-Free Power and Hydrogen From Coal Fuelled System

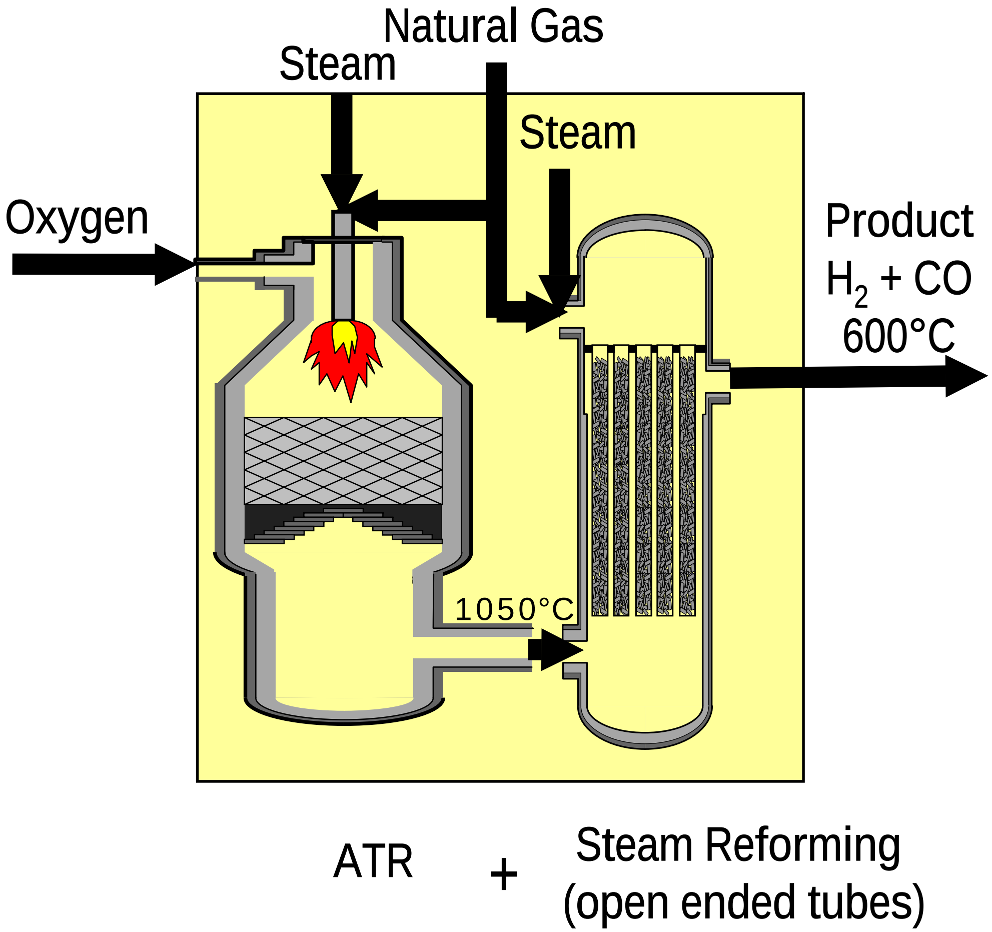






Production of Hydrogen
ATR/GHR Integration

- **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**



H_2 Production
Emerging Technologies

- **Micro reactor/Multichannel Heat Exchanger**

Either

- **Low temperature POX**
  - **Air purified**
  - **45% H_2 – 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**

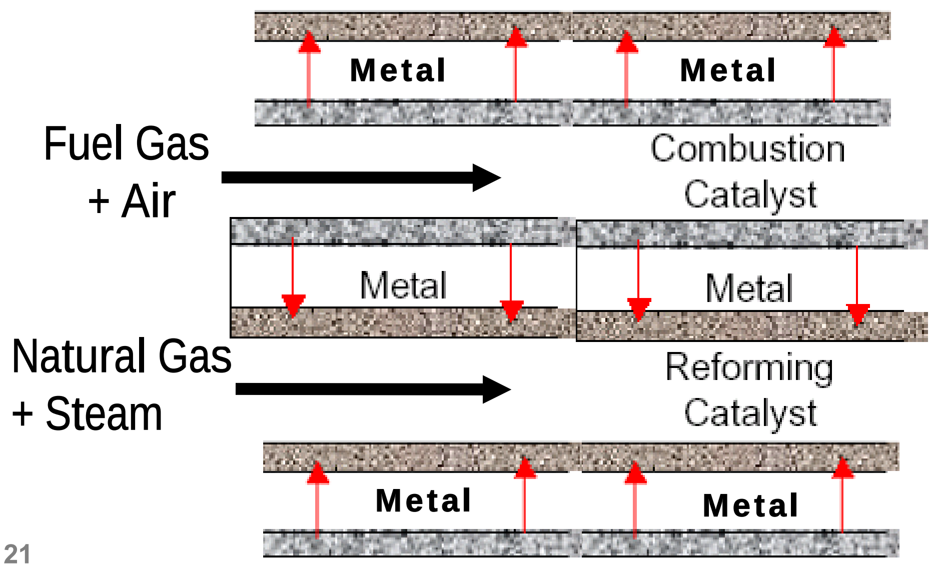
Production of Hydrogen

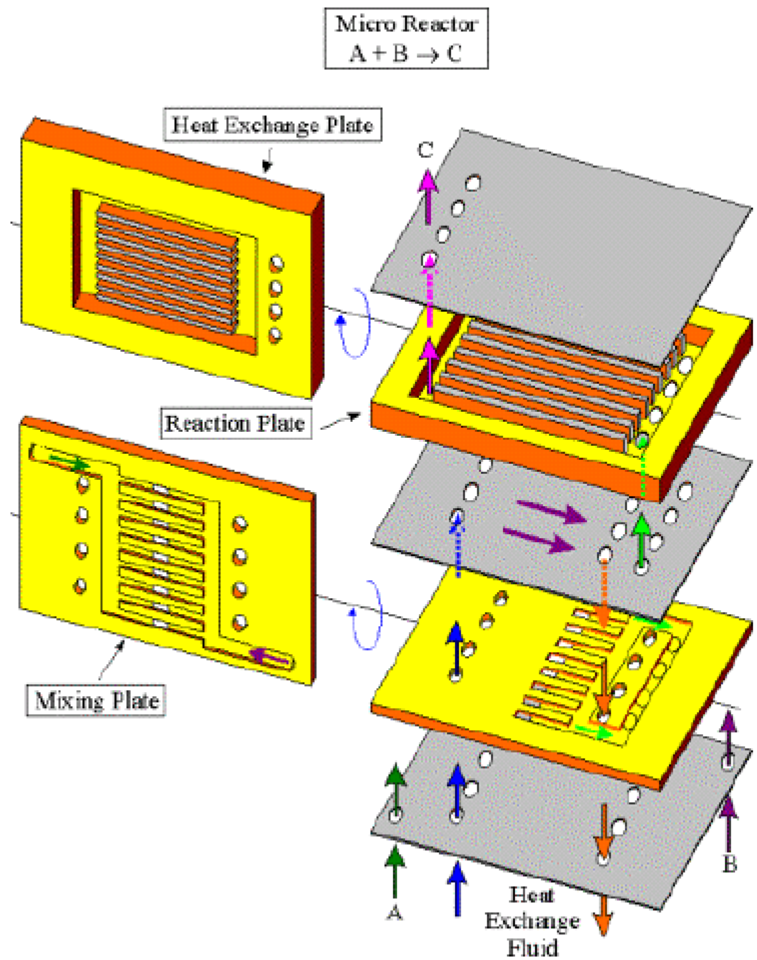
Plate-Fin Reformer

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





H_2 Production Emerging Technologies

- **Micro reactor/Multichannel Heat Exchanger**

In General

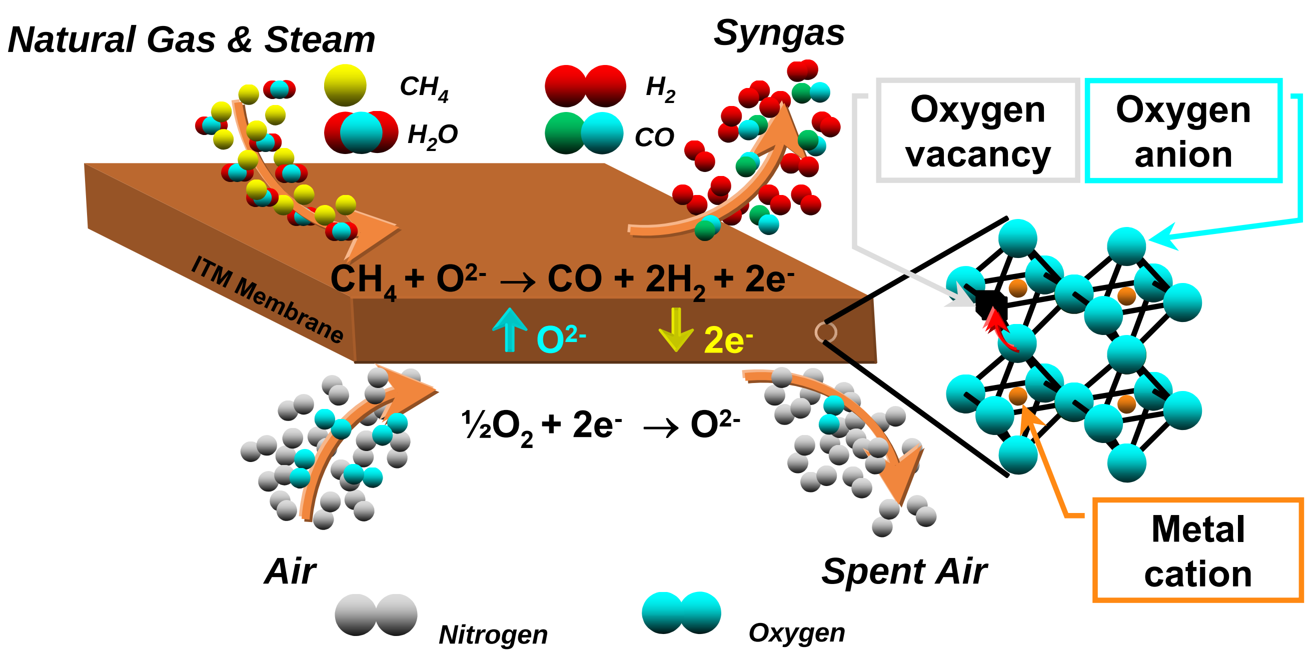
- Catalyst can be deposited on metal surfaces or used in a porous insert
- Removable catalyst elements are possible
- Very high volumetric productivity for SMR reactor
- Whole H_2 plant can be integrated with a plate-fin reformer configuration

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**



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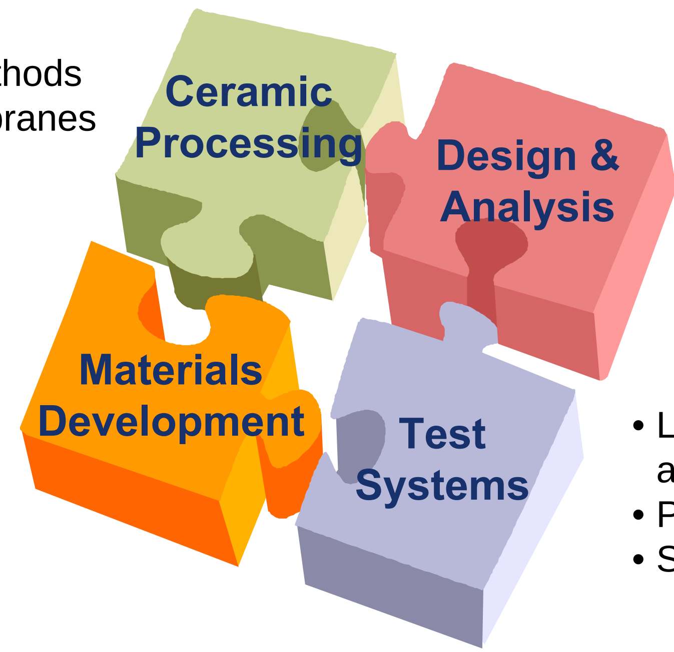
Integrated Development Program Addresses Key Technical Challenges with Broad Development Team

- Develop fabrication methods
- Produce ceramic membranes for testing

- Develop stable material compositions
- Characterize material properties and performance

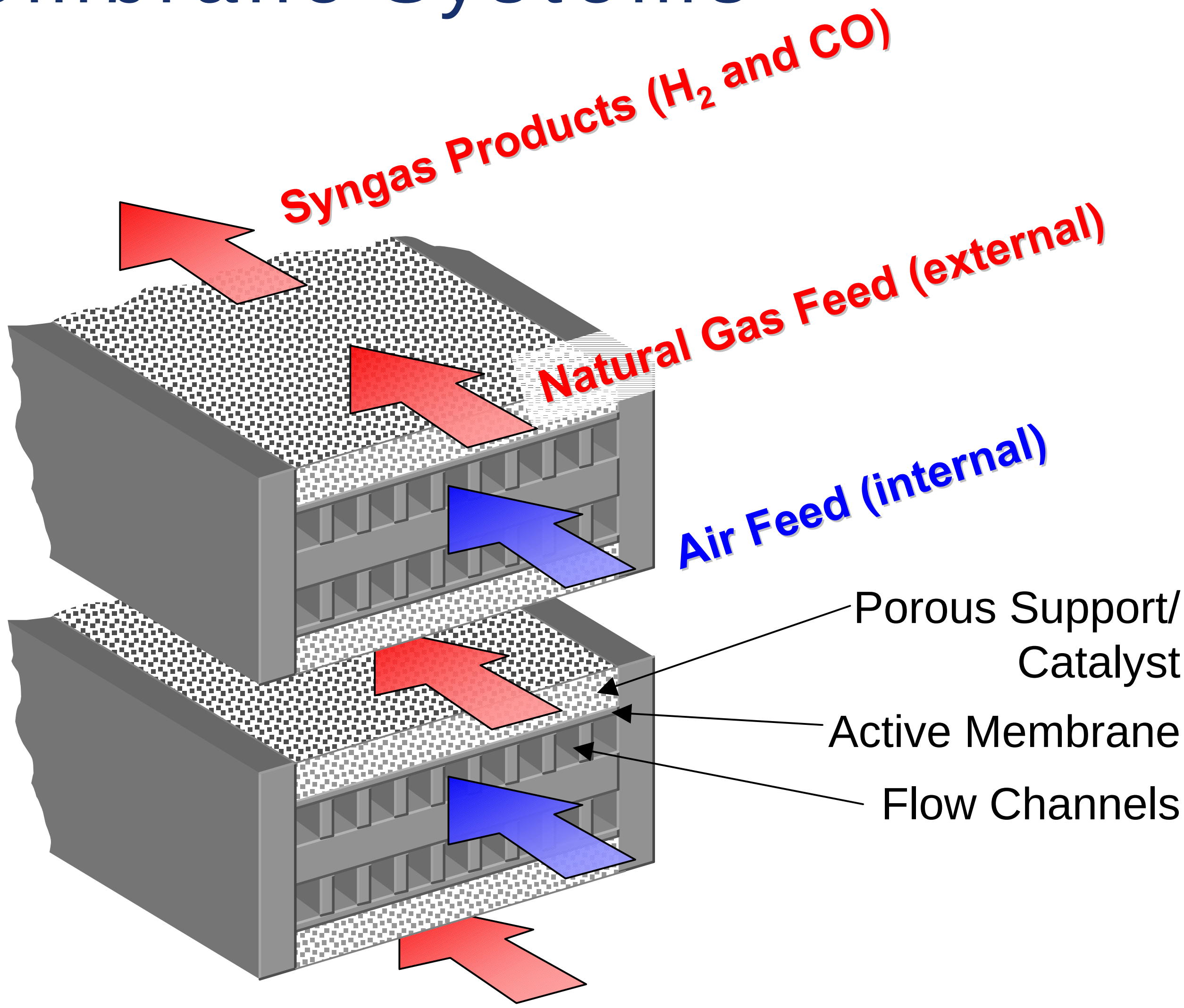


- Process design and economic evaluation
- Membrane and reactor design

- Lab-scale testing: ambient pressure and elevated pressure
- Process Development Unit (PDU)
- SEP and PCTDU

Advantages of Planar Membrane Systems

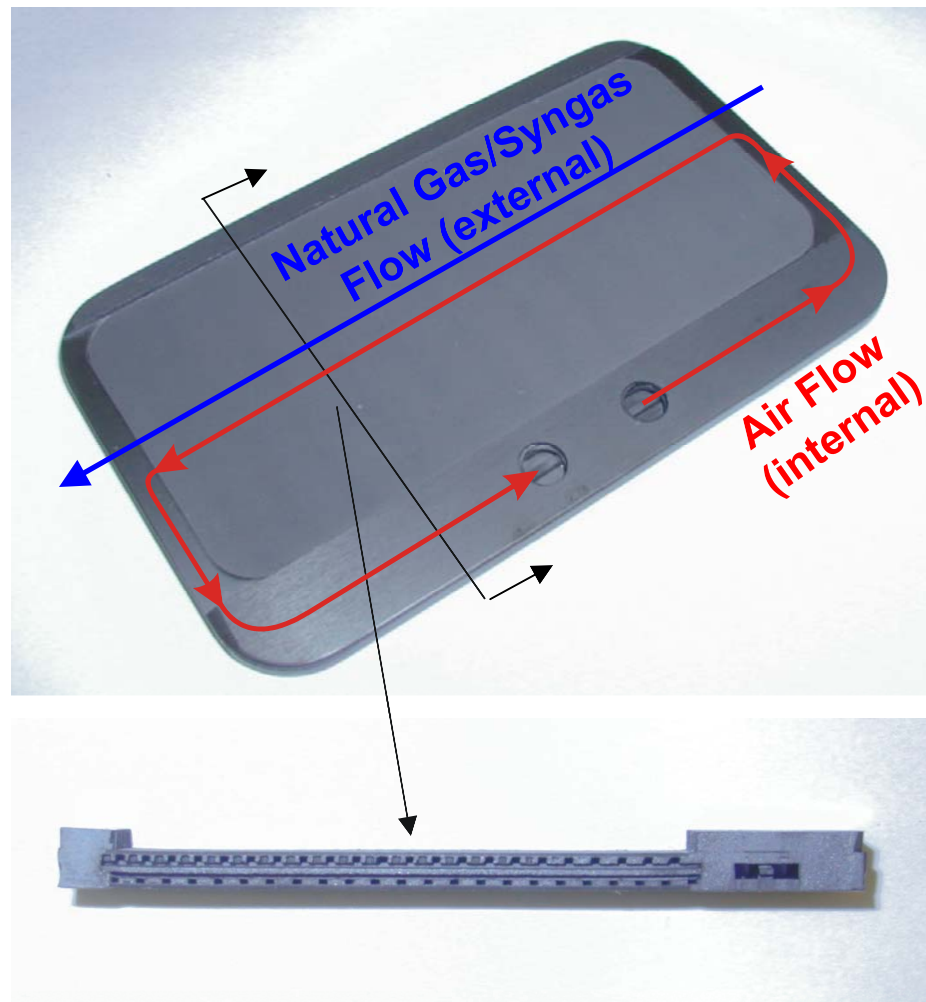
- **Compactness**
- **Good mass and heat transfer**
- **Amenable to standard ceramic processing methods**



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**



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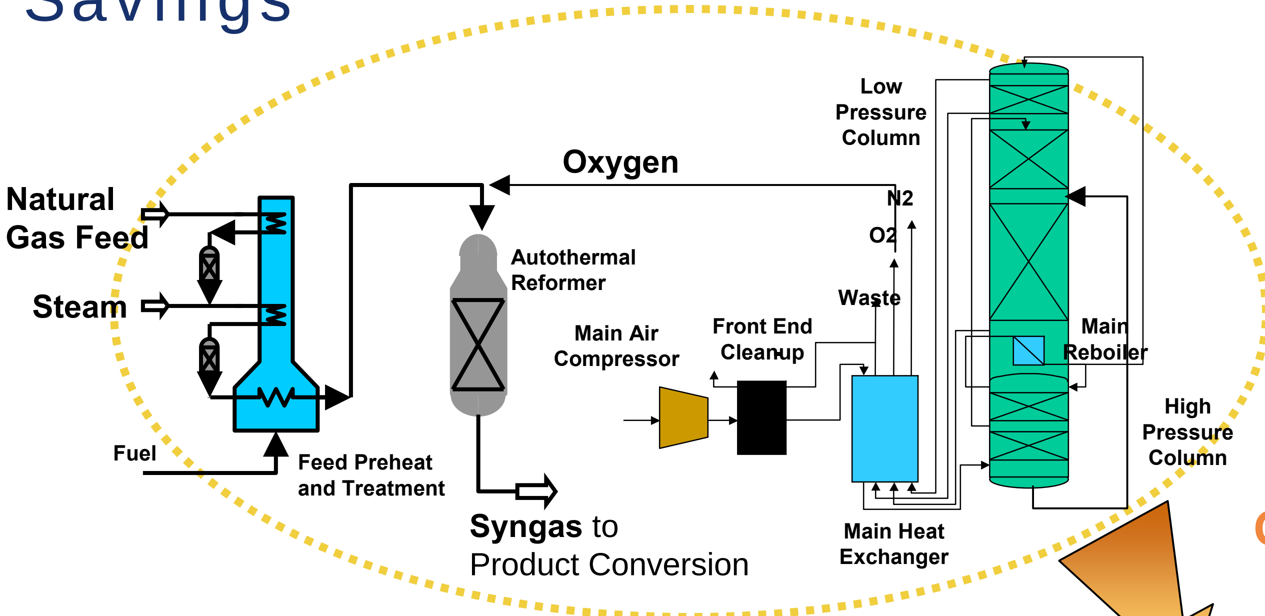
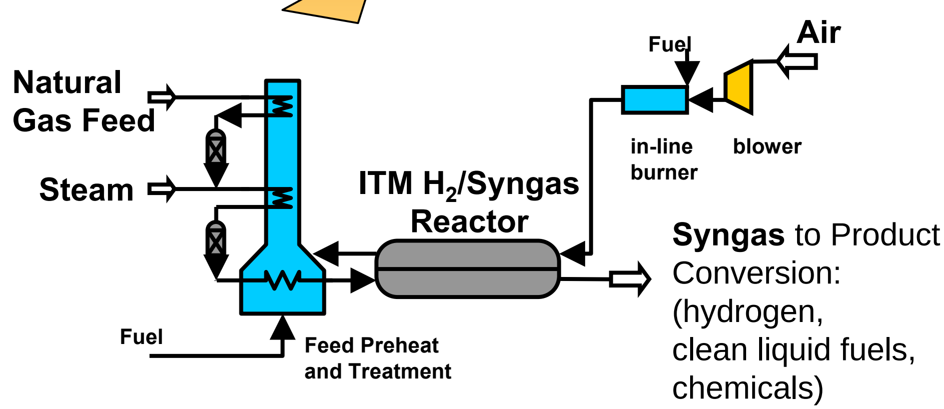
ITM Hydrogen/Syngas: Combines Oxygen Production and Syngas Production Into a Single Reactor to Achieve Over 30% Capital Cost Savings



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**
- **H_2 removal from steam reformer using a palladum diffusion surface**
  - **low pressure H_2, high pressure CO_2**

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

- **Adsorbtion of CO_2 at high temperature in a shift converter/adsorber**
  - **Typical high temperature adsorbents are substituted hydrotalcites or lithium silicate for CO_2**
  - **high pressure H_2, low pressure CO_2**

$$CO + H_2O \rightarrow CO_2 + H_2$$

- **In both cases, hot H_2 is produced (400 - 600°C)**

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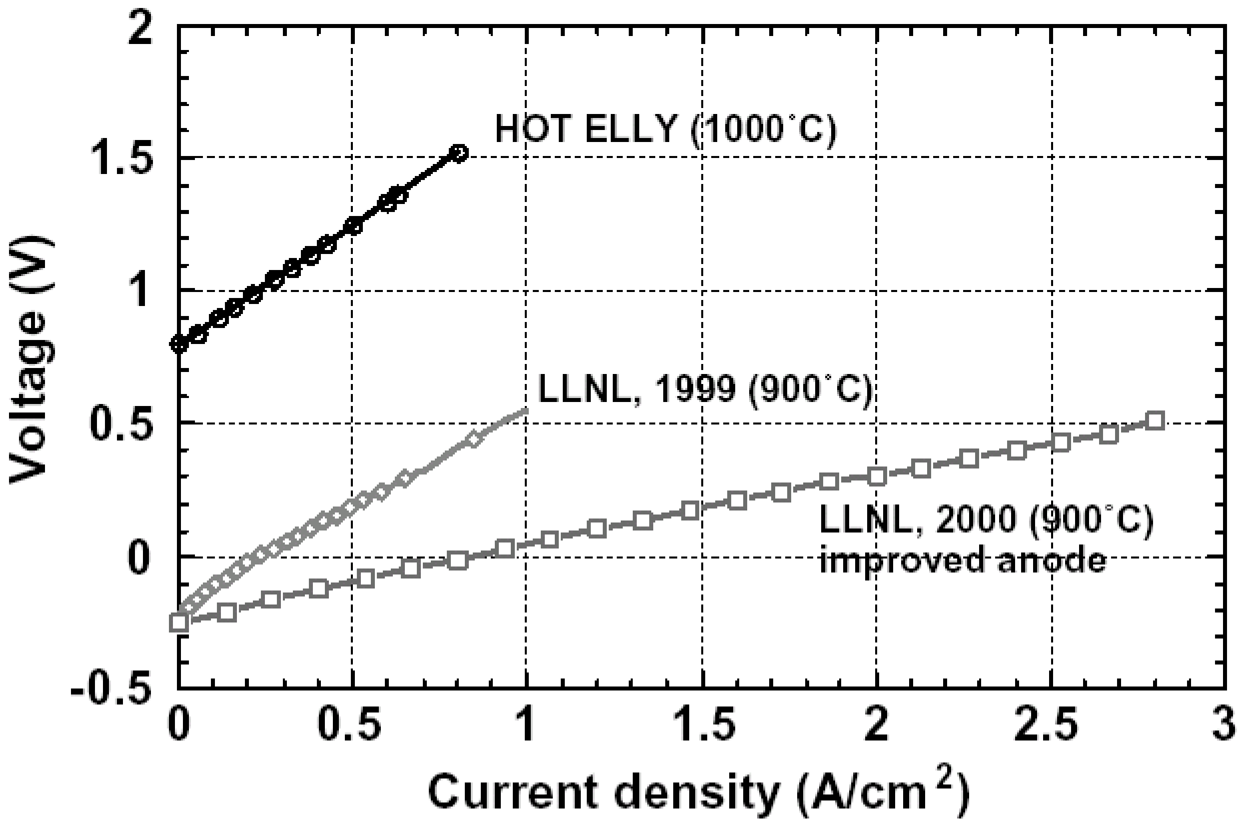
Production of Hydrogen
Steam Electrolysers



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