Performance and Economics of a Planar WGS Membrane Reactor for Coal Gasification Applications

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Gasification and Syngas Technologies

To improve the understanding of coal performance in gasification technologies, supporting:

- Use of Australian coals in new technologies
- Implementation of advanced coal technologies in Australia
- Development of high efficiency IGCC-CCS systems

- High pressure, high temperature coal conversion measurements
  - Effects of reaction conditions and coal type
  - Development of coal test procedures
- Fundamental investigations of coal gasification reactions
  - Reaction mechanisms and kinetics, model development.
- Slag formation and flow for entrained-flow gasification
- Syngas cleaning & processing
- Gas separation (H₂/CO₂)
- Technology performance models
Viability of Membrane Reactor Concept

- Catalytic Membrane Reactor (CMR)
- Metal membranes for hydrogen separation
- Performance of lab-scale prototype CMR
- Conceptual full-scale module
- Relative capital costs with ‘benchmark’ membrane materials
- Prospects for new membrane materials
Technology development: Syngas Processing & H₂ Separation

Key cost and efficiency drivers:
- Increase temperature of gas cleaning and processing
- Development and application of membrane separation systems
- Integrate gas processing and separation stages with membrane reactors
Conceptual 300 tpd H$_2$-from-coal plant costs

- Total plant cost ~$330-350M
- Shift and separation only ~$55M
  - Plant costs scaled using 0.6 exponent, and dated using Chemical Engineering Plant Cost Indices

Catalytic Membrane Reactor Concept

- In-situ H₂ removal through membrane promotes forward reaction:
  \[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2 \]

- Also applicable for reforming reactions:
  \[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \quad \text{T} \leq 550 \degree \text{C} \]

- CMR configuration provides opportunity for H₂ production to be integrated with concentrated solar-thermal energy systems (‘SolarGas’
Improved shift reaction catalysts

• New ceria-based catalysts demonstrate much greater activity and stability than commercial reference catalysts up to 600°C
• Catalysts used in membrane reactor development

![Catalyst Image]

![Graph Image]
Metal Alloy Membranes

- Infinite selectivity (i.e. 100% pure H₂)
- Operating temperatures compatible with WGS reactions
- CO₂ remains on high pressure side
- Amorphous and crystalline membranes being considered
- Pd considered benchmark

3 steps:
- Dissociation
- Diffusion
- Re-association
20 cm² Membrane Reactor Test Module

- Prototype planar membrane reactor
- Commercial HTWGS catalyst (0.50-0.85 mm)
- Free-standing Pd or Pd-Ag membrane foils
- Porous ceramic support
- Cu gaskets
Reference Case Performance Measurements

- Mk I: 6mm deep catalyst bed, 50 μm Pd membrane ($5,500 m^{-2}$)
- Mk II: 4 mm deep bed, 50 μm Pd membrane
- Mk III: 2 mm deep bed, 50 μm Pd membrane
- Mk IV: 2 mm deep bed, 40 μm Pd$_{75}$Ag$_{25}$ membrane ($4,400 m^{-2}$)

- Syngas composition: 66% H$_2$O, 22% CO, 11% H$_2$ (H$_2$O:C = 3)
- Feed pressure: 20 bar(a)
- Product pressure: ~ 1.0 or ~ 0.0 bar(a)
- Temperature: 400°C
Effect of in-situ H₂ extraction on CO conversion

- CMR significantly improves conversion
- Reduced delivery pressure enhances H₂ flux
- Flow rate effects indicate scope for major performance improvement
- Pure H₂ product
- CO₂ contained at high pressure
CMR performance for reference conditions: CO conversion

- Decreasing catalyst bed depth decreases conversion
- Improves gas-membrane contact which increases yield/conversion
- System performance most sensitive to membrane flux
  - Pd-Ag membrane higher flux than Pd
CMR performance for reference conditions: H₂ yield

- 85% yield was established by Chiesa et al. (2007) as the point at which the efficiency of a CMR is equivalent to that of a conventional plant
- Obtaining higher yields will require a significant increase in plant size

The conceptual full-scale module

- 2 sided planar module (2000 mm x 100 mm)
- Mounted in parallel in cylindrical containment vessel with 80% packing density
**Economics: calculation of capital costs**

<table>
<thead>
<tr>
<th>Components</th>
<th>Description</th>
<th>Unit</th>
<th>Cost</th>
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</thead>
<tbody>
<tr>
<td>Catalyst Retainer</td>
<td>Number per module</td>
<td>$/module</td>
<td>50</td>
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<tr>
<td>Catalyst</td>
<td>HT WGS, 0.50-0.85 mm</td>
<td>$/kg</td>
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<tr>
<td>Hardware</td>
<td>Gaskets, tubing, bolts</td>
<td>$/module</td>
<td>35</td>
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<tr>
<td>Containment vessel</td>
<td>Inconel</td>
<td>$ each</td>
<td>50,000</td>
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<tr>
<td>Vacuum extraction</td>
<td></td>
<td>$/tonne/day</td>
<td>1,000</td>
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<tr>
<td>Module base</td>
<td>Inconel</td>
<td>$/piece</td>
<td>210</td>
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<tr>
<td>Membrane</td>
<td>Pd, 50 microns, 1900mm x 100mm</td>
<td>$/module</td>
<td>2090</td>
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<tr>
<td></td>
<td>Pd-Ag, 40 microns, 1900mm x 100mm</td>
<td>$/module</td>
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</table>

- Membrane costs dominate
## Economics: calculation of capital costs

<table>
<thead>
<tr>
<th></th>
<th>Mk I</th>
<th>Mk II</th>
<th>Mk III</th>
<th>Mk IV</th>
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<tbody>
<tr>
<td><strong>Extraction pressure (bar)</strong></td>
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<tr>
<td><strong>Cost Summary</strong></td>
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<tr>
<td><strong>Module cost ($)</strong></td>
<td>2830</td>
<td>2670</td>
<td>2600</td>
<td>2140</td>
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<tr>
<td><strong>Module Flow Rates</strong></td>
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<tr>
<td><strong>Module flow</strong></td>
<td>1.28</td>
<td>2.30</td>
<td>1.54</td>
<td>2.46</td>
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<tr>
<td>kg H₂/module/day</td>
<td></td>
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<tr>
<td><strong>Reactor Capacity</strong></td>
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<tr>
<td><strong>Modules per reactor</strong></td>
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<td>1824</td>
<td>2479</td>
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<td><strong>Flow per reactor</strong></td>
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<td>2677</td>
<td>2814</td>
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<tr>
<td>kg H₂/day</td>
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<td>4150</td>
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<td><strong>Reactors per 300 tpd plant</strong></td>
<td>201</td>
<td>112</td>
<td>107</td>
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<td>72</td>
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<tr>
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<td>54</td>
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<tr>
<td><strong>Costs</strong></td>
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<tr>
<td><strong>Total cost per reactor ($M)</strong></td>
<td>3.346</td>
<td>4.920</td>
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<td><strong>vacuum H₂ extraction ($M per plant)</strong></td>
<td>0</td>
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<td><strong>Total plant cost ($M)</strong></td>
<td>673</td>
<td>392</td>
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<td>352</td>
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<td><strong>Membrane cost (%)</strong></td>
<td>80</td>
<td>77</td>
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<td>80</td>
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<td></td>
<td>88</td>
<td>82</td>
<td>85</td>
<td>73</td>
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Membrane costs appear prohibitive…

- The best case scenario (Case IV) is $182 million, of which the membranes account for 73%

- Halving thickness to 20μm Pd-Ag membranes would approximately double flux and halve cost ($75 million).
  - Serious durability issues

- Further reductions in thickness for this reactor configuration are impractical
  - would need to shift from free-standing foils to plated/sputtered foils on porous substrates (high cost)
  - Pd appears impractical

- Must increase flux to reduce membrane cost
- Better materials essential
- Operation costs not included here…
  - but the absence of moving parts and continuous throughput expected to decrease operational costs
Membrane reactor performance targets

• 2015 DOE targets
  • Flux: 1.13 mol m\(^{-2}\) s\(^{-1}\) with 7 bar dP(H\(_2\))
  • Cost: $1,000 m\(^{-2}\)
  • Very thin Pd-alloys or high-permeability V-based alloys

• Plant cost incorporating 2015 DOE membrane would be $44 million for Pd

• Non-Pd alloy membranes
  • Amorphous and crystalline membranes developed
  • eg Crystalline ternary V-based alloys
  • High flux
  • Permeability 8 times better than Pd
  • Will meet DOE flux target when 65\(\mu\)m thick
  • Stable operation at 400 - 450°C (compatible with WGS)
  • Relatively low cost – factor of 5 cheaper than Pd at DoE target performance
Conclusions

• Membrane reactors offer:
  • High conversion performance
  • Simplified plant configuration
  • Pure hydrogen product
  • High pressure CO₂ stream

• Membranes that meet the 2015 DOE cost and flux targets could compete with conventional technology using catalytic membrane reactors
  • Pd alloy membranes need to be <<20μm thick to achieve this
  • Unlikely to meet durability and fabrication requirements

• Non-Pd alloy membranes offer high flux, low cost alternatives

• Range of V based alloys have been developed which demonstrate:
  • Improved flux (8x Pd)
  • Reduced cost (~5x less than Pd alloys)
  • Practical membrane thickness (US DoE targets met at 65μm)

• These meet DoE performance targets and could be economic
  • The 2015 DOE durability target is 5 years
  • Durability testing and performance with ‘real’ syngas ongoing
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Thank you