2.29 Course Project

Modeling of Ion Transport Membrane Reactors: A Review and Practice

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Outline

1. Literature review
   - ITM reactor
   - ITM models
   - An Intermediate-fidelity model

2. Modeling practice
   - A monolith reactor with LCF91 membrane
   - FLUENT simulation for permeation channel
ITM Reactor

Ion transport membrane (ITM) technology is a novel approach providing an alternative solution to separate oxygen from air.

Advantages:
1. Potentially achieve 100% CO₂ capture
2. Reducing 70% power consumption compared with conventional O₂ production methods
3. Increase power generation efficiency by 4%

ITM models

Purpose of different levels of ITM models:

1. Material-level analysis  
   \( \text{Transport phenomena} \)
   \[
   \frac{1}{2} O_2 + V_0^* = O_0^* + 2h^*
   \]
   Permeation Equations
   \[
   J_V = 2 \cdot (k_{fO_2} P_{O_2}^{\frac{1}{2}} C'_V - k_{rO_2})
   \]
   \[
   J_V = \frac{D_V C'_V}{L} - D_V \left( \frac{C'_V - C_V}{L} \right)
   \]
   \[
   J_V = k_{fCH_4} (C_{CH_4})^{\frac{1}{3}} C_{O_0}^x
   \]

2. System-level analysis  
   \( \text{Reactor Design and operating conditions} \)

Geometry

- Planar [2]
- Monolith [3]
- Hollow fiber [4]
- etc.
## ITM models

### Purpose of different levels of ITM models:

2. **System-level analysis → Reactor Design and operating conditions**

#### Materials
- $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$
- $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$
- etc.

#### Flow configuration
- Co-current
- Counter-current

#### Reaction
- Non-reactive
- Reactive

### Requirements of a good ITM models:

1) **Capture important physical relationships**
   - Conservation of mass and species
   - Thermodynamics
   - Oxygen permeation phenomena
   - Heat transfer
   - Chemical reactions

2) **Without extreme computational time**
   - Highly-coupled nonlinear system
   - Combustion process could be complicated
An Intermediate-fidelity model [5]

The model simplifies the monolith reactor into a **1-D problem** due to symmetry

- Split the geometry into discrete elements
- Steady-state conservation equations are written for each discrete element

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Conservation equations\cite{Mancini2011}

**Conservation of mass and species:**

\[
\dot{n}_{i+1, O_2} = \dot{n}_{i, O_2} + \varphi A_i J_{i, O_2} + \varphi V_i R''''_{i, O_2}
\]

- \(n\) is the molar flow-rate of \(O_2\) mol/s,
- \(J_{i, O_2}\) is the local oxygen flux [mol/m\(^2\)]
- \(R''''_{i, O_2}\) is the local rate of production of oxygen due to chemical reaction [mol/m\(^3\)]

**First law of thermodynamics:**

\[
\sum_j n_{i+1,j} \hat{h}_j(T_{i+1}) = \sum_j n_{i,j} \hat{h}_j(T_i) - \dot{Q}_i + \dot{H}_{i, O_2, ext}
\]

- \(\dot{Q}_i\) represents the convective heat transfer between streams, where the overall heat transfer coefficient \(U_i\)
- \(\dot{Q}_i = \varphi U_i A_i (T''_i - T'_i)\)
- \(\dot{H}_{i, O_2, ext}\) represents the enthalpy stream transported from the feed to the permeate side

**Second law of thermodynamics:**

\[
\dot{S}_{gen} = \sum_{\text{outlet}} \dot{n}_j \overline{s}_j(T, P_j) - \sum_{\text{inlet}} \dot{n}_j \overline{s}_j(T, P_j)
\]

Transport equations

Heat and mass transfer consideration:

Gnielinski correlation is used for forced convection in turbulent pipe flow.

\[ Nu_{Dh,i} = \frac{f_i/8 \cdot (Re_{Dh,i} - 1000)Pr}{1 + 12.7 \frac{f_i}{8} (Pr^{2/3} - 1)} \]

Due to the small channel sizes of the reactor, the author assumes that the forced convection dominates the heat transfer.

Oxygen permeation mechanisms:

The semi-empirical form:

\[ J_{O_2} = A \exp\left(-\frac{B}{T_M}\right)\left[(P_{O_2}')^n - (P_{O_2}'')^n\right] \]

A stands for pre-exponential factor; B represents the effective activation energy.

Things become complicated when we have reactive ITM:

Methane oxidation kinetics:

1) Fast kinetics assumption (products of chemical reaction is only CO\(_2\) and H\(_2\)O)
2) Thermodynamic equilibrium assumption (CH\(_4\) CO \(_2\) CO H\(_2\) H\(_2\)O O\(_2\))
3) Additional oxidation kinetics scheme

Approach and solver:

Equation-oriented approach is used to solve the system of non-linear equations with JACOBIAN, a general modeling and simulation program.

Sample results [5]

Separation-only Mode

Reactive Mode

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A co-current monolith reactor

Simplifications made:
1. Assume temperature constant in the channel
2. Pressure drop neglected
3. Fast kinetics assumptions

Equations satisfied:
1. Conservation of mass and species
2. First and second laws of thermodynamics
3. Resistance-network oxygen permeation mechanism
Base case simulation parameters

Feed to Air
Membrane
Sweep to Fuel

Discretized nodes

\[
J_{O_2} = \frac{1}{2} \cdot \frac{c_o - \frac{k_{T_{O_2}}}{k_{f_{O_2}} P_{O_2}^{\frac{1}{2}}}}{2k_{f_{O_2}} P_{O_2}^{\frac{1}{2}}} + \frac{L}{D_v} + \frac{1}{k_{f_{CH_4}} (C_{CH_4})^{\frac{1}{2}}}
\]

\[
CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O
\]

\[
\dot{n}_{i+1,O_2} = \dot{n}_{i,O_2} + \phi A_i J_{i,O_2} + \phi V_i R_{i,O_2}^{\prime\prime\prime}
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel Height [cm]</td>
<td>1.5</td>
</tr>
<tr>
<td>Channel Length [mm]</td>
<td>200</td>
</tr>
<tr>
<td>Membrane material</td>
<td>La_{0.9}Ca_{0.1}FeO_{3-δ}</td>
</tr>
<tr>
<td>Membrane Thickness [mm]</td>
<td>1</td>
</tr>
<tr>
<td>Sweep side methane concentration</td>
<td>100%</td>
</tr>
<tr>
<td>Operation Temperature [°C]</td>
<td>700-9000</td>
</tr>
</tbody>
</table>

Graph showing J_{O_2} (μmol/cm²s) vs. Length (cm) for 700, 800, and 900 °C.
CFD analysis for sweep side channel

Permeated oxygen flux (as calculated in previous slides)

Methane - air

Inlet
Preheated gas
Outlet
Pressure outlet

<table>
<thead>
<tr>
<th>Simplification</th>
<th>2D channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solver</td>
<td>ANASYS Fluent</td>
</tr>
<tr>
<td>Species reaction model</td>
<td>Non-premixed combustion</td>
</tr>
<tr>
<td>Gas Mixture</td>
<td>Methane-air</td>
</tr>
<tr>
<td>Inlet</td>
<td>Preheated gas</td>
</tr>
<tr>
<td>Outlet</td>
<td>Pressure outlet</td>
</tr>
</tbody>
</table>
Simulation Results

Base case: 900°C preheated channel and gases

Temperature comparison
Conclusion and Discussion

**Review:**

- ITM technology is a novel approach to separate oxygen from air, which could provide solutions to CCS.
- ITM reactor modeling varies depending on the geometry, materials, flow configuration and whether the model enables reactions.
- ITM reactor is a highly-coupled nonlinear system and an intermediate-fidelity model is introduced.

**Modeling practice:**

- A monolith reactor was developed enables the oxygen permeation phenomena and fast kinetics reaction
- The simulation shows that the oxygen permeation rate does not decrease much along the reactor
- The 2D sweep channel was simulated for the oxy-combustion process
- The simulated temperature shows the effect of the combustion may not be neglected
Further Improvement

• **Monolith reactor:**
  1. Enables the temperature variable by adding energy equation
  2. Optimize the reactor size

• **CFD modeling**
  1. Try different solvers and kinetics databases
  2. Revise the definition of boundary conditions

Thanks!
Backup Slides
Resistance-network mechanism

Feed

\[ \frac{1}{2} O_2 + V_0^{**} \rightleftharpoons O_0^x + 2h^* \]

ITM

Thickness, L

Sweep

\[ O_0^x + 2h^* + \frac{1}{4} CH_4 \rightleftharpoons \frac{1}{4} CO_2 + \frac{1}{2} H_2 O + V_0^{**} \]

\[ J_{O_2} = \frac{1}{2} J_V \]

\[ J_V = 2 \cdot (k_{fO_2} P_{O_2}^{\frac{1}{2}} C_V^{'} - k_{rO_2}) \]

\[ J_V = -D_V \frac{c_V}{d y} = D_V \frac{(c_V^{''} - c_V^{'})}{L} \]

\[ J_V = k_{fCH_4} (C_{CH_4})^{\frac{1}{4}} C_{O_0^x} \]

\[ C_0 = C_{O_0^x} + C_V \]

\[ C_0 = \frac{k_{rO_2}}{1} \]

\[ J_V = \frac{1}{2k_{fO_2} P_{O_2}^{\frac{1}{2}}} + \frac{L}{D_V} + \frac{1}{k_{fCH_4} (C_{CH_4})^{\frac{1}{4}}} \]