2.29 Course Project

Modeling of Ion Transport Membrane Reactors: A Review and Practice

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05.16.2018

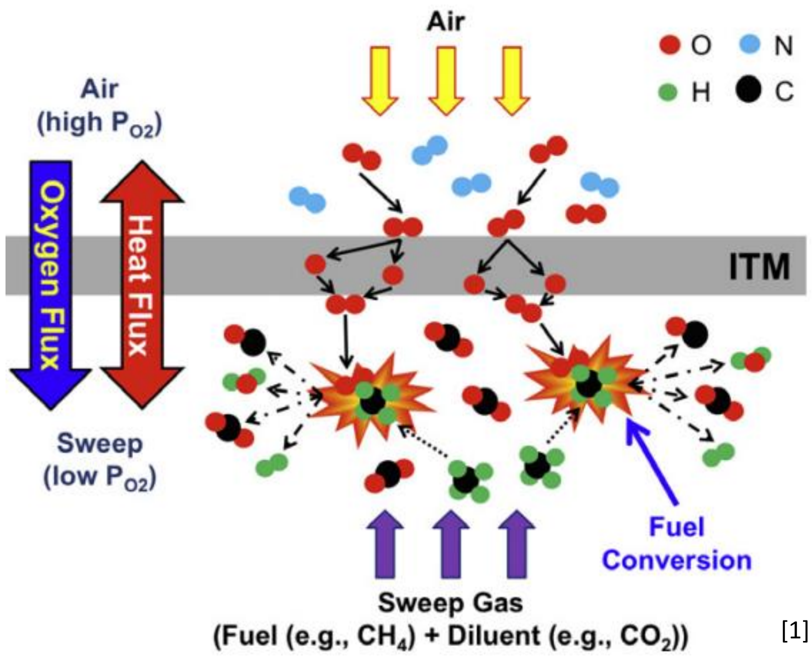
Outline

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.



[1]

Feed side (high P_{O2})

Mixed-ionic electronic conducting (MIEC) ceramic membrane

Sweep side (low P_{O2})

Advantages:

1. Potentially achieve **100% CO_2 capture**
2. Reducing **70% power consumption** compared with conventional O_2 production methods
3. Increase power generation efficiency by **4%**

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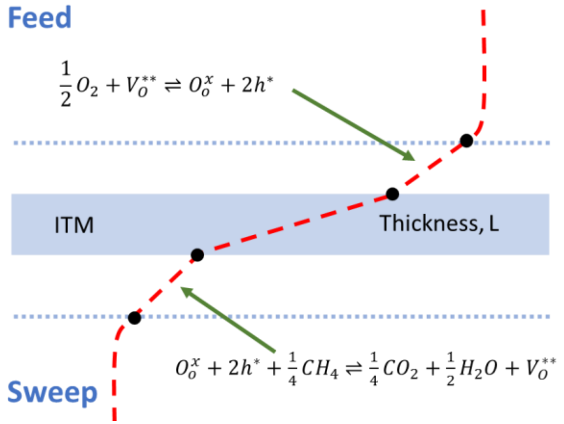
[1] J. Hong, P. Kirchen, A.F. Ghoniem, Laminar oxy-fuel diffusion flame supported by an oxygen-permeable-ion-transport membrane, Combust. Flame 160 (2013) 704–717.

ITM models

Purpose of different levels of ITM models:

1. Material-level analysis → **Transport phenomena**



Steps

(1) Mass Diffusion

(2) Surface Exchange

(3) Bulk Diffusion

(4) Surface Exchange

(5) Mass Diffusion

Permeation Equations

$$J_V = 2 \cdot (k_{f_{O_2}} P'^{\frac{1}{2}}_{O_2} C'_V - k_{r_{O_2}})$$

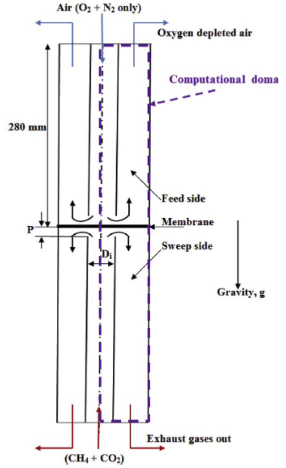
$$J_V = -D_V \frac{c_V}{dy} = D_V \frac{(C''_V - C'_V)}{L}$$

$$J_V = k_{f_{CH_4}} (C_{CH_4})^{\frac{1}{4}} C_{O_O^x}$$

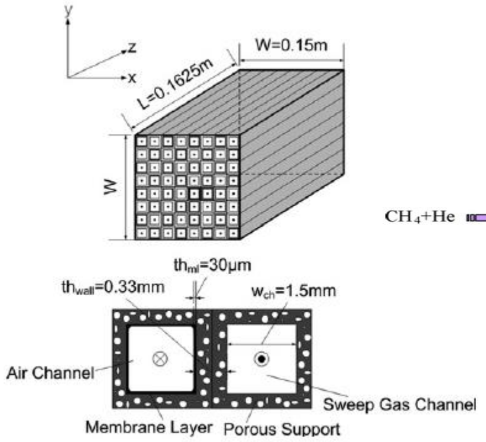
2. System-level analysis → **Reactor Design and operating conditions**

Geometry

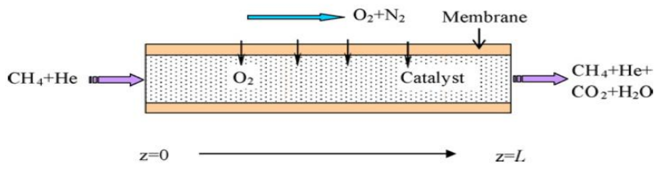
- Planar [2]
- Monolith [3]
- Hollow fiber [4]
- etc.



Planar [2]



Monolith [3]



Hollow fiber [4]

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[2] Nemitallah MA, Habib MA, Mezghani K. Experimental and numerical study of oxygen separation and oxy-combustion characteristics inside a button-cell LNO-ITM reactor. Energy 2015;84:600–11.
[3] Colombo K. E., Kharton, V. V., and Bolland, O., 2010, "Simulation of an Oxygen Membrane-Based Gas Turbine Power Plant: Dynamic Regimes With Operational and Material Constraints," Energy Fuels, 24, pp. 590–608
[4] X. Tan, K. Li, A. Thursfield, I.S. Metcalfe, Oxyfuel combustion using a catalytic ceramic membrane reactor, Catalysis Today 131 (1–4) (2008) 292–304.

ITM models

Purpose of different levels of ITM models:

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

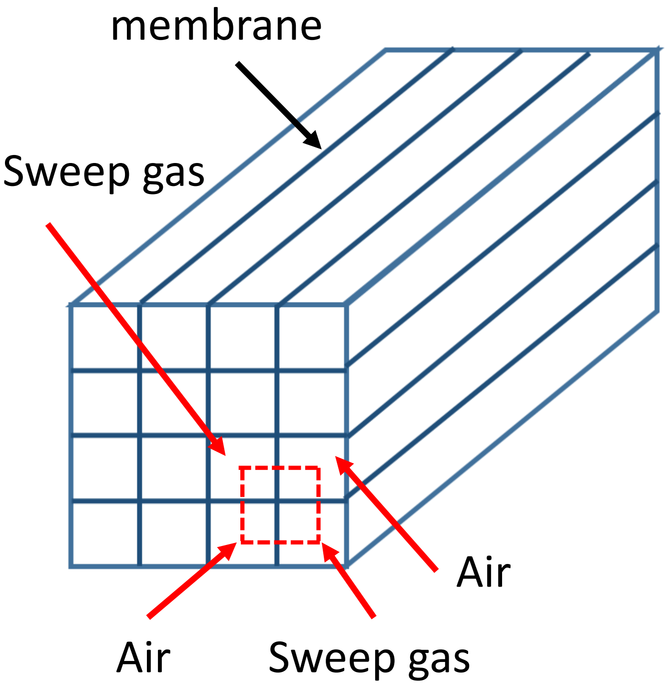
- **Materials**
  - $La_{0.9}Ca_{0.1}FeO_{3-\delta}$
  - $Ba_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$
  - etc.
- **Flow configuration**
  - Co-current
  - Counter-current
- **Reaction**
  - Non-reactive
  - Reactive

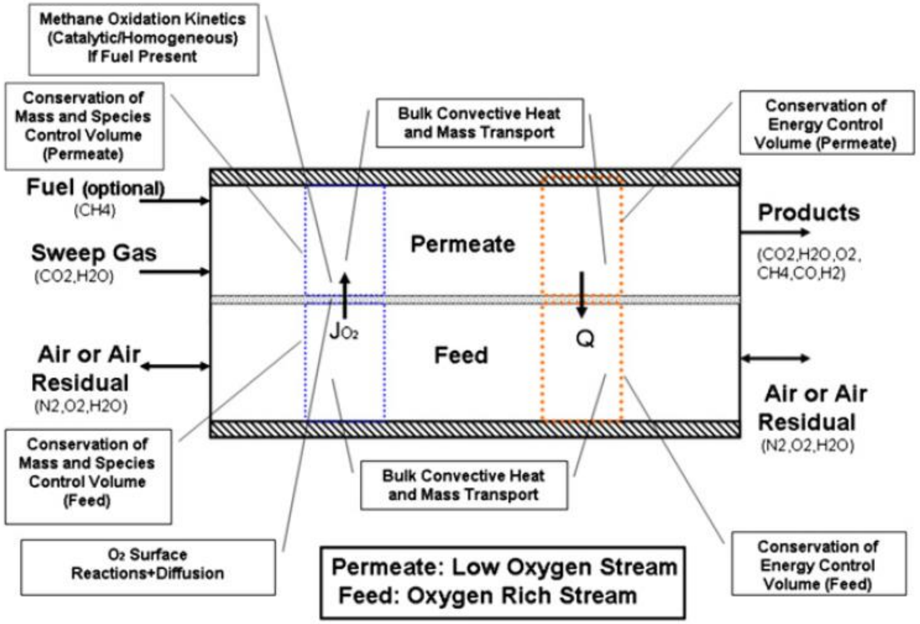
Requirements of a good ITM models:

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

[5] Mancini ND, Mitsos A. Ion transport membrane reactors for oxy-combustion - Part I: intermediate-fidelity modeling. Energy 2011;36:4701-20.

Conservation equations [5]

Conservation of mass and species:

$$\dot{n}_{i+1,O_2} = \dot{n}_{i,O_2} + \emptyset A_i J_{i,O_2} + \emptyset V_i R'''_{i,O_2}$$

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:

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

Q_i represents the convective heat transfer between streams, where the overall heat transfer coefficient U_i

$$\dot{Q}_i = \emptyset \overline{U}_i A_i (T_i^{"} - T_i')$$

$\dot{H}_{i,O_2,ext}$ represents the enthalpy stream transported from the feed to the permeate side

Second law of thermodynamics:

$$\dot{S}_{gen} = \sum_{outlet} \dot{n}_j \bar{s}_j (T, P_j) - \sum_{inlet} \dot{n}_j \bar{s}_j (T, P_j)$$

[5] Mancini ND, Mitsos A. Ion transport membrane reactors for oxy-combustion - Part I: intermediate-fidelity modeling. Energy 2011;36:4701-20.

Transport equations

Heat and mass transfer consideration:

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

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

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

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_2O)
2) Thermodynamic equilibrium assumption (CH_4 CO_2 CO H_2 H_2O O_2)
3) Additional oxidation kinetics scheme

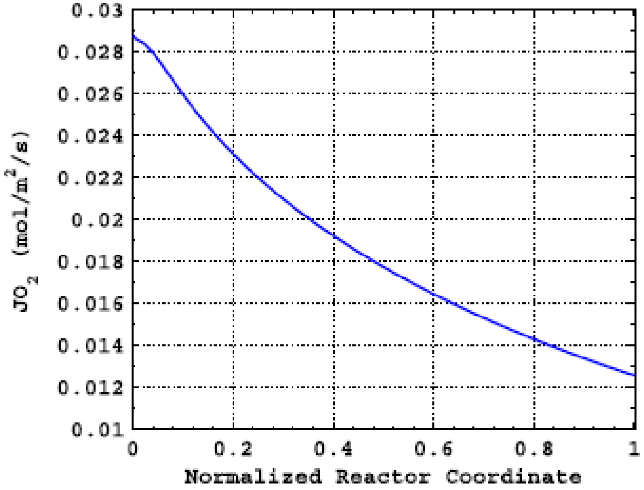
Approach and solver:

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

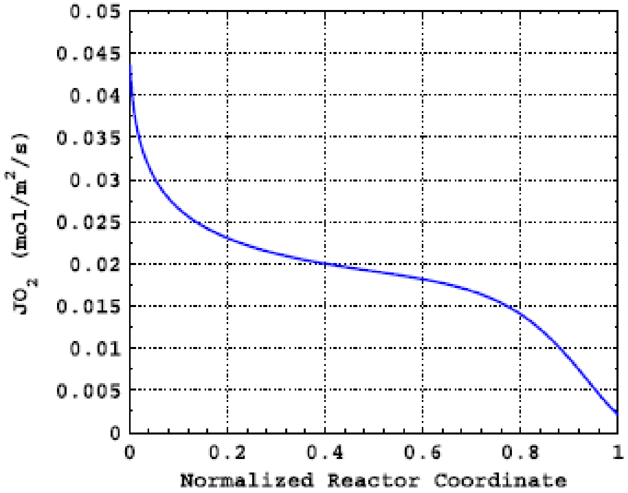
[5] Mancini ND, Mitsos A. Ion transport membrane reactors for oxy-combustion - Part I: intermediate-fidelity modeling. Energy 2011;36:4701-20.

Sample results [5]

Separation-only Mode

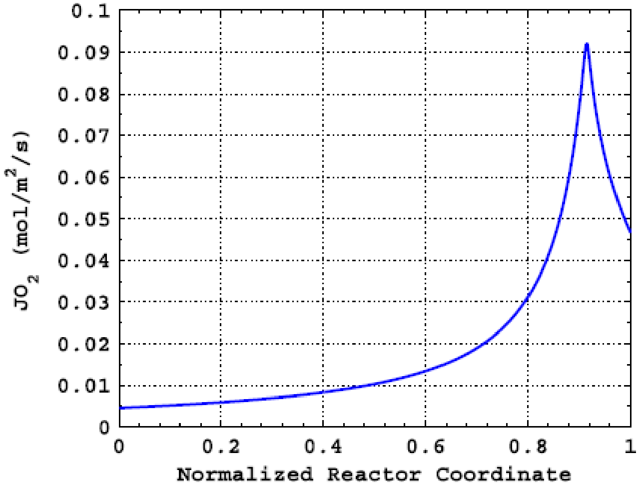


Co-current configuration



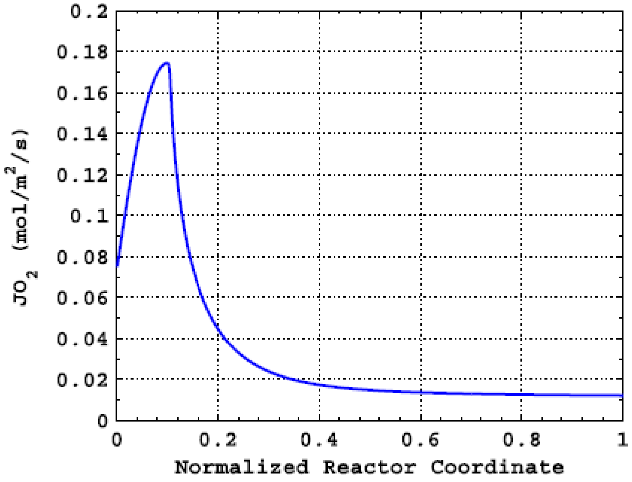
Counter-current configuration

Reactive Mode



Flux

Co-current configuration



Oxygen Flux

Counter-current configuration

[5] Mancini ND, Mitsos A. Ion transport membrane reactors for oxy-combustion - Part I: intermediate-fidelity modeling. Energy 2011;36:4701-20.

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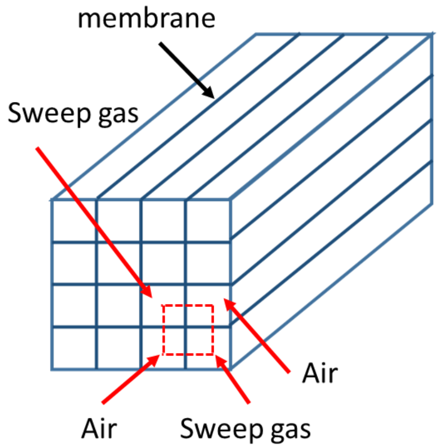
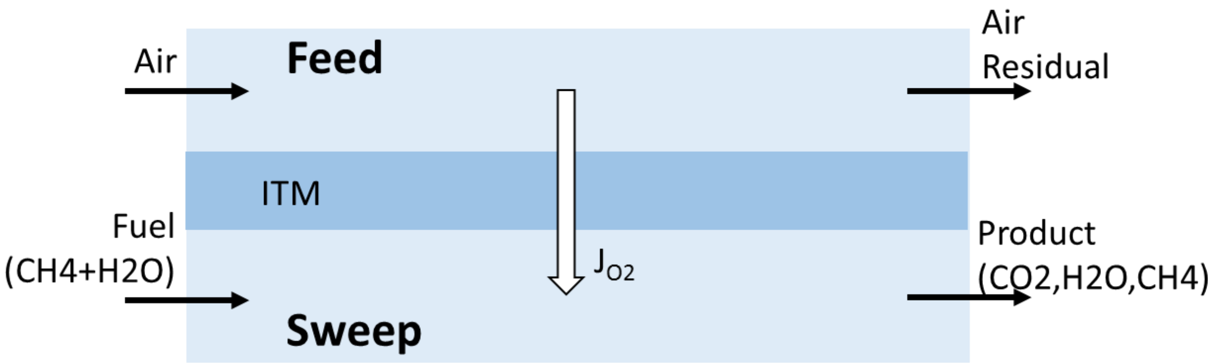
A co-current monolith reactor





Simplifications made:

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

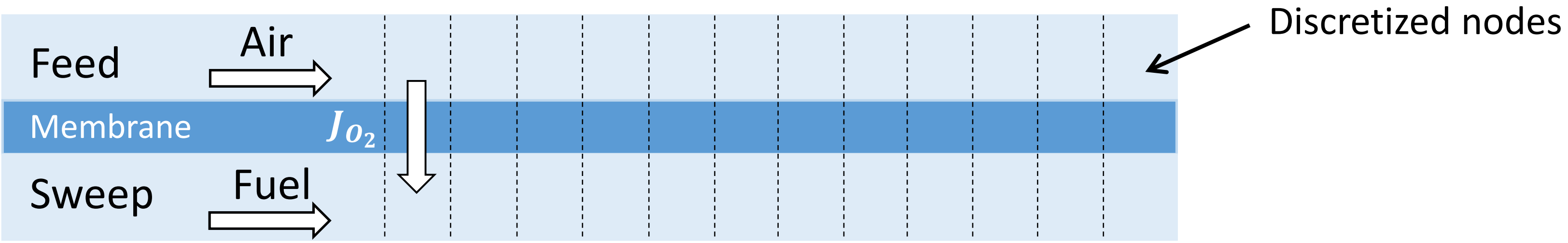
MathWorks®

Cantera
Chemical Kinetics • Thermodynamics • Transport Processes

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

Air

Membrane

J_{O_2}

Sweep

Fuel

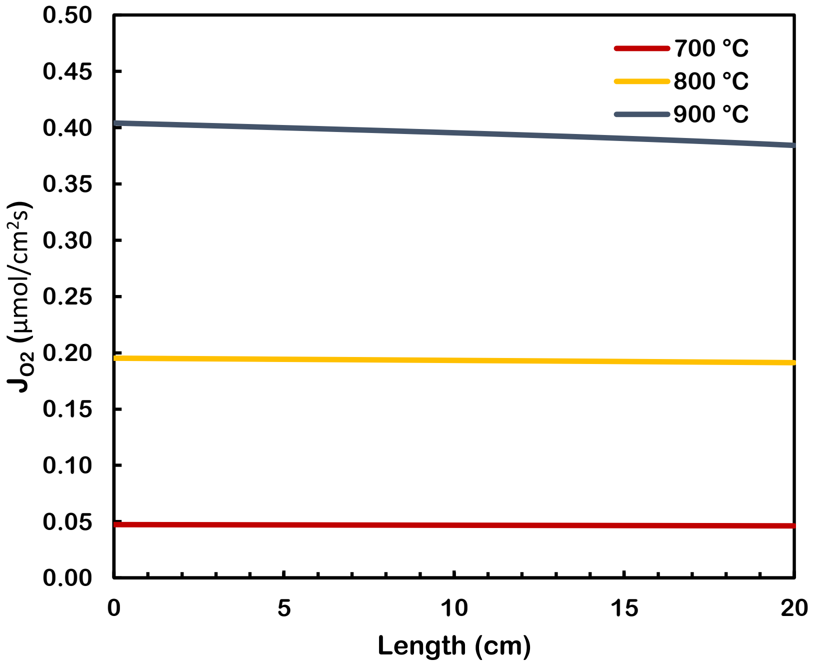
Discretized nodes

$$J_{O_2} = \frac{1}{2} \cdot \frac{C_o - \dfrac{k_{r_{O_2}}}{k_{f_{O_2}} {P'_{O_2}}^{\frac{1}{2}}}}{\dfrac{1}{2k_{f_{O_2}} {P'_{O_2}}^{\frac{1}{2}}} + \dfrac{L}{D_V} + \dfrac{1}{k_{f_{CH_4}} (C_{CH_4})^{\frac{1}{4}}}}$$

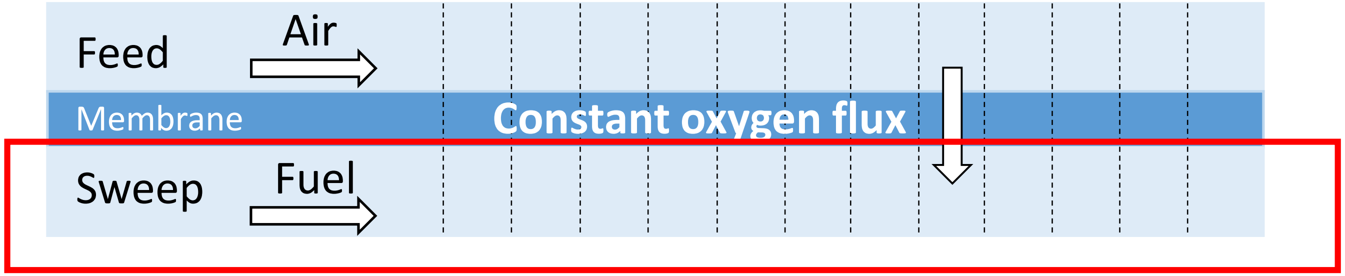
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$\dot{n}_{i+1,O_2} = \dot{n}_{i,O_2} + ØA_i J_{i,O_2} + ØV_i R'''_{i,O_2}$$

Parameter	Value
Channel Height [cm]	1.5
Channel Length [mm]	200
Membrane material	$La_{0.9}Ca_{0.1}FeO_{3\text{-}\delta}$
Membrane Thickness [mm]	1
Sweep side methane concentration	100%
Operation Temperature [°C]	700-9000



CFD analysis for sweep side channel



Feed

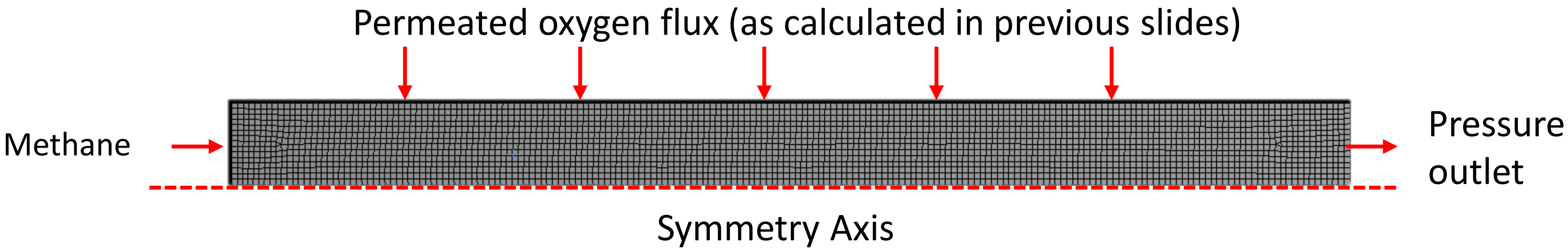
Air

Membrane

Constant oxygen flux

Sweep

Fuel



Permeated oxygen flux (as calculated in previous slides)

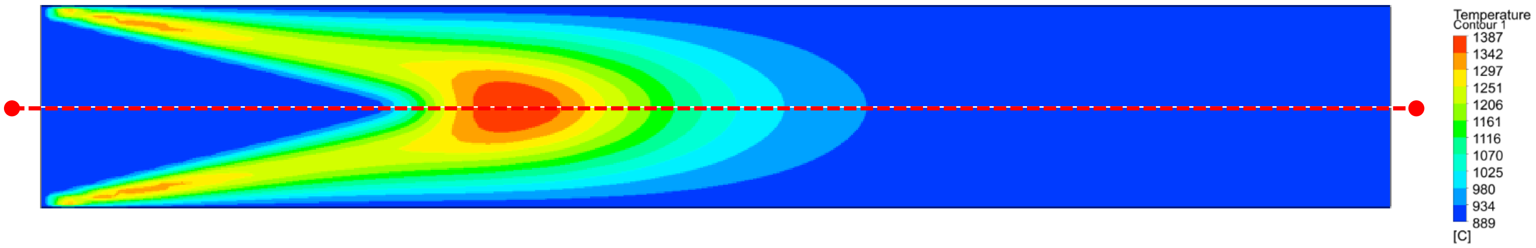
Methane

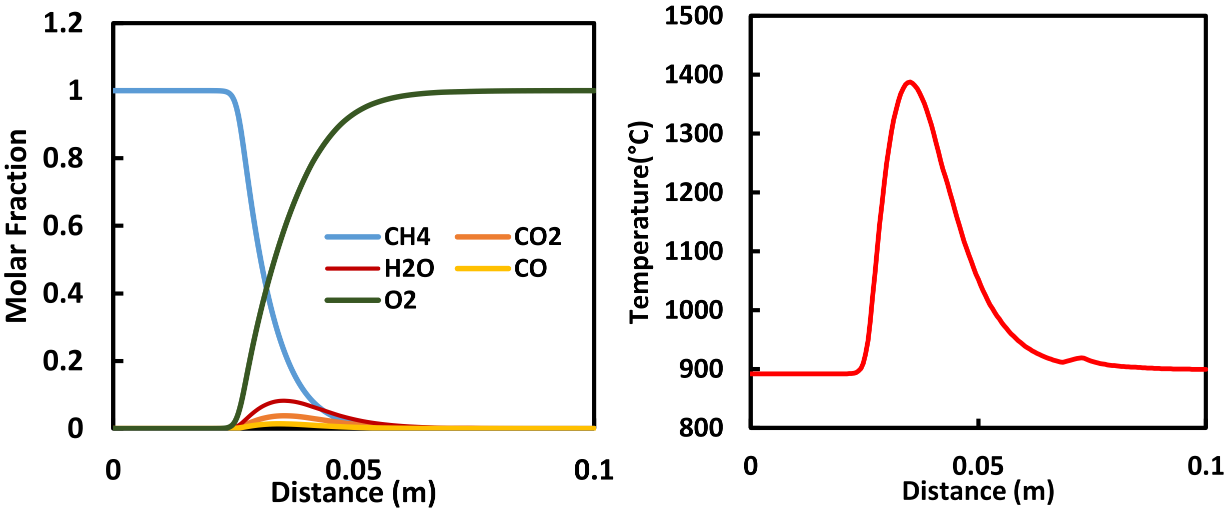
Pressure outlet

Symmetry Axis

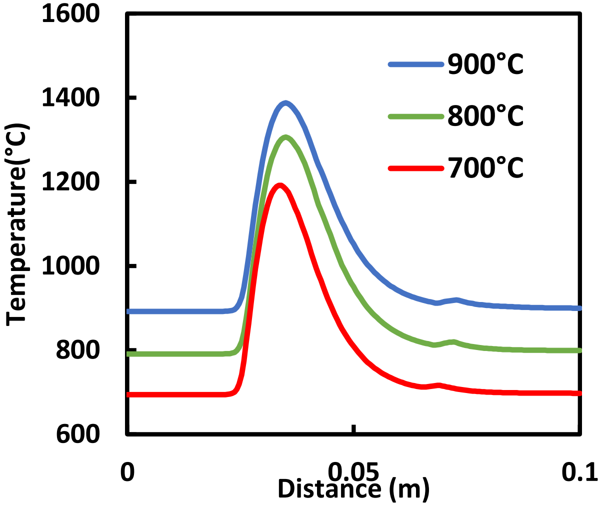
Simplification	2D channel
Solver	ANASYS Fluent
Species reaction model	Non-premixed combustion
Gas Mixture	Methane-air
Inlet	Preheated gas
Outlet	Pressure outlet

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

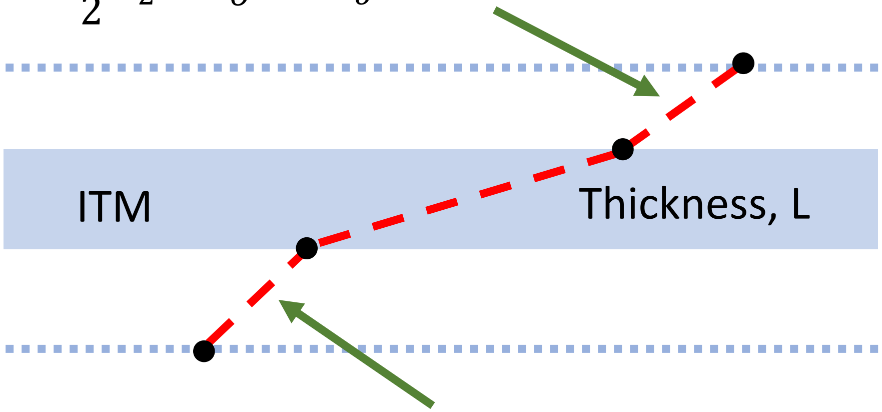
- **Monolith reactor:**
  1. Enables the temperature variable by adding energy equation
  2. Optimize the reactor size

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

Thanks!

Backup Slides

Resistance-network mechanism



Feed

$\frac{1}{2} O_2 + V_O^{**} \rightleftharpoons O_o^x + 2h^*$

ITM

Thickness, L

$O_o^x + 2h^* + \frac{1}{4} CH_4 \rightleftharpoons \frac{1}{4} CO_2 + \frac{1}{2} H_2O + V_O^{**}$

Sweep

$$J_{O_2} = \frac{1}{2} J_V$$

$$J_V = 2 \cdot \left(k_{f_{O_2}} {P'_{O_2}}^{\frac{1}{2}} C'_V - k_{r_{O_2}}\right)$$

$$J_V = -D_V \frac{C_V}{dy} = D_V \frac{(C''_V - C'_V)}{L}$$

$$J_V = k_{f_{CH_4}} (C_{CH_4})^{\frac{1}{4}} C_{O_o^x}$$

$$\mathrm{C_o} = \mathrm{C}_{\mathrm{o}_o^x} + C_V$$

$$J_V = \frac{\mathrm{C_o} - \dfrac{k_{r_{O_2}}}{k_{f_{O_2}} {P'_{O_2}}^{\frac{1}{2}}}}{\dfrac{1}{2k_{f_{O_2}} {P'_{O_2}}^{\frac{1}{2}}} + \dfrac{L}{D_V} + \dfrac{1}{k_{f_{CH_4}} (C_{CH_4})^{\frac{1}{4}}}}$$