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LAMINAR OXY-FUEL DIFFUSION FLAME SUPPORTED BY AN OXYGEN-PERMEABLE-ION-TRANSPORT MEMBRANE

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Key Words: Ion transport membrane reactor; Diffusion flame; Oxygen permeation; Oxy-fuel combustion; Partial oxidation of methane; Syngas production; Fuel dilution; CO$_2$ dilution.

ABSTRACT

A numerical model with detailed gas-phase chemistry and transport was used to predict homogeneous fuel conversion processes and to capture the important features (e.g., the location, temperature, thickness and structure of a flame) of laminar oxy-fuel diffusion flames stabilized on the sweep side of an oxygen permeable ion transport membrane (ITM). We assume that the membrane surface is not catalytic to hydrocarbon or syngas oxidation. It has been demonstrated that an ITM can be used for hydrocarbon conversion with enhanced reaction selectivity such as oxy-fuel combustion for carbon capture technologies and syngas production. Within an ITM unit, the oxidizer flow rate, i.e., the oxygen permeation flux, is not a pre-determined quantity, since it depends on the oxygen partial pressures on the feed and sweep sides and the membrane temperature. Instead, it is influenced by the oxidation reactions that are also dependent on the oxygen permeation rate, the initial conditions of the sweep gas, i.e., the fuel concentration, flow rate and temperature, and the diluent. In oxy-fuel combustion applications, the sweep side is fuel-diluted with CO$_2$, and the entire unit is preheated to achieve a high oxygen permeation flux. This study focuses on the flame structure under these conditions and specifically on the chemical effect of CO$_2$ dilution. Results show that, when the fuel diluent is CO$_2$, a diffusion flame with a lower temperature and a larger thickness is established in the vicinity of the membrane, in comparison with the case in which N$_2$ is used as a diluent. Enhanced OH-driven reactions and suppressed H radical chemistry result in the formation of products with larger CO and H$_2$O and smaller H$_2$ concentrations. Moreover, radical concentrations are reduced due to the high CO$_2$ fraction in the sweep gas. CO$_2$ dilution reduces CH$_3$ formation and slows down the formation of soot precursors, C$_2$H$_2$ and

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C$_2$H$_4$. The flame location impacts the species diffusion and heat transfer from the reaction zone towards the membrane, which affects the oxygen permeation rate and the flame temperature.

1. INTRODUCTION

Ion transport membranes (ITM), composed of mixed ionic and electronic conducting materials, have been proposed for air separation and for fuel conversion in the absence of nitrogen. At elevated temperatures, typically above 700 °C [1], and high oxygen chemical potential gradients across the membrane, oxygen ions selectively permeate from the air side (feed) to the sweep gas side (permeate). Oxygen undergoes gas phase mass transfer and surface exchange on both sides of the membrane, as well as bulk diffusion through the membrane itself (see Fig. 1). In the presence of a fuel on the sweep side, diluted mostly by carbon dioxide, reaction with the permeated oxygen may lead to partial or full oxidation. This, besides enhancing the oxygen flux across the membrane [2-6], makes it possible to perform oxy-fuel combustion for carbon capture applications or partial oxidation, i.e., fuel reforming, using an ITM and without the need for a separate air separation unit, combustion unit or external heat exchanger [7]. The integration of air separation and fuel conversion into a single unit could reduce the size and cost of these promising carbon-capture technologies [8].

It has been demonstrated that an ITM can be used for different applications with enhanced reaction selectivity due to the controlled oxygen permeation across the membrane. When an ITM is employed, oxygen is selectively added to the permeate stream through ion transport (not a convective flow or molecular sieving as in conventional or porous reactors) from the air side to its sweep side, where oxidation reactions occur if a reactive gas such as methane is introduced as part of the sweep gas stream. For overall fuel-rich mixtures, syngas, composed of carbon monoxide and hydrogen, can be produced, rather than carbon dioxide and water. Rhodium-based catalysts added to the membrane surface enhance catalytic partial oxidation and enable higher selectivity (e.g., higher than 98% CH$_4$ conversion and 90% CO selectivity [9]). The residence time in a catalytic membrane reactor is less than 0.1s [10, 11], much faster than conventional syngas production (residence time is 0.5~1.5s), reducing the reactor size and lowering the capital costs of syngas production. In other cases, complete oxidation of the fuel in the absence of nitrogen and using CO$_2$ as a diluent, i.e., oxy-fuel combustion, to form carbon dioxide and water as products is also possible on the sweep side of the ITM [12]. By condensing water, the flue gas stream contains high purity carbon dioxide that could be sequestered. Alternatively, if the membrane is covered with certain catalysts (e.g., Li/MgO [13]), methane oxidation can be routed to form C$_2$ products, such as ethylene or ethane, known as
oxidative coupling. Oxygen ions are reacted directly on the membrane surface with the adsorbed methane [14]. Oxidative coupling using an ITM is a good method to convert methane to higher hydrocarbons or liquid fuels, although the yield with current technologies is too low for commercial applications.

Fuel conversion processes on the sweep side of the ITM have important features that should be investigated for reaction selectivity. The nature of oxygen permeation across the membrane does not enable pre-mixing fuel and oxygen, which results in the establishment of a non-premixed (diffusion) flame in the absence of nitrogen. In a diffusion flame, the state of the reactants is critical for defining the response of the flame to strain rates and controlling the reaction products. On the sweep side of the ITM, the sweep gas stream, i.e., the fuel stream, tends to be preheated and to require diluents such as CO₂ and H₂O along with the fuel in order to control the flow rate and the flame temperature [7, 15]. In addition, the oxygen permeation flux, i.e., the oxidizer stream, is influenced by oxygen consumption and heat released from the oxidation reactions, which affect the oxygen concentration in the immediate vicinity of the membrane and the membrane temperature [16]. Thus, the oxidation reactions and flow conditions near the membrane are highly important for determining the flow rate of the oxidizer, i.e., oxygen permeation rate. The reaction environment on the sweep side of the ITM is different from that in conventional diffusion controlled combustion. Modeling studies are needed to investigate fuel conversion processes and to control reaction selectivity.

Modeling studies on ITM supported fuel conversion so far have been based on reduced chemistry and simplified transport. Jin et al. [17] and Tan et al. [12] showed the dependence of oxygen permeation and fuel conversion rates on the initial gas temperature, air and fuel flow rates and reactor geometry. They assumed a plug flow to model their reactor and used single step chemical reactions for methane oxidation and reforming. The effects of the oxidation reactions on the gas temperature were also neglected. A more detailed model was proposed by Zhang et al. [18] and Smit et al. [7], but species concentrations at equilibrium with reduced chemistry were considered, and the spatial variations of species concentrations and temperature were ignored. Using their membrane reactor model for the partial oxidation of methane, Tan et al. [19] estimated the product selectivity and hydrocarbon conversion with respect to the temperature, fuel flow rate, membrane tube diameter and membrane thickness. They resolved the spatial variation of the species concentrations and temperature and implemented a three-step reaction mechanism accounting for methane combustion, steam and carbon dioxide reforming. However, these modeling studies assumed heterogeneous fuel conversion on the catalyst surface additionally mounted on
the membrane and ignored the homogeneous reactions that play an important role in fuel oxidation at high temperature. We note that an ITM requires high temperature for enabling substantial oxygen permeation to facilitate fuel conversion processes [20]. While a catalyst may contribute to fuel conversion typically at low temperature [21], in this high temperature regime, it has been demonstrated that the chemical reactions in the gas-phase dominate fuel conversion even if the surface catalytic reactions take place [22, 23]. Furthermore, as shown in Fig. 1, spatially resolved solutions in the direction normal to the membrane should be obtained to examine the fundamentals of ITM supported fuel conversion and oxygen permeation. Thus, spatially resolved solutions with detailed gas-phase chemistry and transport are necessary to model fuel conversion processes and to capture important phenomena on the sweep side of the ITM where the oxygen permeation rate and hydrocarbon conversion/product selectivity are strongly coupled through flow conditions and their variations in the vicinity of the membrane [24].

In this paper, fuel conversion and some important features (e.g., the flame location, temperature, thickness and structure) of a non-premixed flame established on the sweep side of an ITM are investigated using a model with detailed gas-phase chemistry and transport. The model is based on the planar, finite gap stagnation flow configuration of an experimental ITM reactor aimed at characterizing the spatially resolved thermodynamic state [25]. An oxygen permeation flux expression developed in our previous study [16] is implemented in the thermochemical-fluid dynamic model to couple the oxygen permeation with a spatially resolved, reactive gas-phase flow field. It is assumed that no additional catalyst is mounted on the membrane, and the membrane surface is not catalytically active for hydrocarbon or syngas conversion so that the impact of the homogeneous phase reactions can be independently considered. Dry CO₂ is assumed as the diluent in the sweep gas stream with CH₄ as a fuel, and results are compared with those in which the fuel is diluted with N₂. We examine the chemical reactions occurring on the sweep side of the ITM and their effects on the reaction products, flame structure and oxygen permeation rate. In addition, important phenomena such as hydrocarbon pyrolysis and the formation of possible soot precursors are discussed. In Section 2, the physical model, numerical approach, oxygen permeation flux expression and detailed gas-phase chemistry and transport employed in this study are described. Section 3 explains the important features of a laminar oxy-fuel diffusion flame supported by the ITM. Fuel conversion processes and phenomena observed in the analysis are discussed in Section 4.
2. PHYSICAL MODEL AND SOLUTION METHODOLOGY

To examine the fuel conversion processes and associated important phenomena (e.g., the relationship between the oxygen permeation rate and the oxidation reactions, hydrocarbon pyrolysis and the formation of possible soot precursors) occurring on the sweep side of the ITM, a stagnation flow configuration has been used. The corresponding experimental reactor, whose geometry is based on a planar, finite-gap stagnation flow shown in Fig. 2, has been developed in our laboratory [25]. The gas flow in the neighborhood of the stagnation line is self-similar, and the dimensionality of the model is reduced to one dimension. Thus, detailed chemistry and transport can be employed with manageable computational resources. Note that flames described by self-similar solutions have been very useful in fundamental studies of fuel conversion processes and flame properties [26, 27]. It should be noted that such solutions are only valid in the region near the axis of symmetry in the reactor, as has been demonstrated for this reactor configuration [28]. The knowledge obtained from these analyses can be applied to other flow fields or multi-dimensional problems [29]. The membrane divides the overall physical domain into an air domain and a sweep gas (fuel plus diluents) domain, each of which is considered numerically. The two computational domains are coupled by implementing flux-matching boundary conditions for the oxygen permeation rate and the heat flux across the membrane.

2.1. Governing Equations and Boundary Conditions

The flow fields in each domain, i.e., the air and sweep gas domains, are determined by the system of governing equations derived from the general three-dimensional equations of reacting flow [30]. As shown in Fig. 2, \( x \) is a transverse coordinate along the membrane direction, and \( y \) is an axis normal to the membrane. It is assumed that variations in the \( z \)-direction, normal to the \( x - y \) plane of the flow, are negligible. The species and thermal diffusion along the \( x \)-direction are neglected with respect to those in the \( y \)-direction. A self-similar solution is obtained, in which all the normalized flow variables are function of the direction normal to the membrane and time. In addition, a low Mach number assumption is employed because gas flow velocities are low, as discussed in Section 3. The stagnation flow formulation has been known to be valid over almost the entire range of Reynolds number with good accuracy [31]. Moreover, using a CH\(_4\)/air flame with the inlet velocity of 5.4 cm/s, which is smaller than the velocity considered in the current study, Kee et al. demonstrated that the reaction zone shows no radial dependence, confirming that the self-similar solution is valid in this low Reynolds number regime [30]. The pressure variations are negligible in comparison with the thermodynamic pressure, and the oxygen partial pressure that determines the oxygen permeation flux [1] depends only on its mole fraction and the
total pressure. Gas-phase radiation and surface reactions are also neglected. The solution variables and the system of governing equations are as follows:

\[ V(t,y) = \rho u \] : Mass flux in the \( y \)-direction; normal to the membrane \([\text{kg/m}^2/\text{s}]\)

\[ U(t,y) = \frac{u}{x} \] : Scaled transverse velocity in the \( x \)-direction; parallel to the membrane \([1/\text{s}]\)

\[ Y_k(t,y) \] : Species mass fraction

\[ T(t,y) \] : Temperature \([\text{K}]\)

\[ \Lambda_x(t) = \frac{1}{x} \frac{dp}{dx} \] : Scaled transverse pressure gradient \([\text{kg/m}^3/\text{s}^2]\)

\[
\frac{\partial \rho}{\partial t} + \frac{\partial V}{\partial y} + \rho U = -\frac{\rho}{T} \frac{\partial T}{\partial t} - \sum_{k=1}^{N} \rho \frac{W_k}{W} \frac{\partial Y_k}{\partial t} + \frac{\partial V}{\partial y} + \rho U = 0
\] : Continuity \hspace{1cm} (Eq. 1)

\[
\rho \frac{\partial U}{\partial t} + V \frac{\partial U}{\partial y} + \rho U^2 + \Lambda_x - \frac{\partial}{\partial y} \left( \mu \frac{\partial U}{\partial y} \right) = 0
\] : \( x \)-momentum \hspace{1cm} (Eq. 2)

\[
\rho \frac{\partial Y_k}{\partial t} + V \frac{\partial Y_k}{\partial y} + \frac{\partial j_k}{\partial y} - \dot{\omega}_k W_k = 0
\] : Species \hspace{1cm} (Eq. 3)

where, \( j_k = -\rho D_{km} \left( \frac{\partial Y_k}{\partial y} + \frac{Y_k}{W} \frac{\partial W}{\partial y} \right) - \frac{D_{T}^T}{T} \frac{\partial T}{\partial y} \)

\[
\rho \frac{\partial T}{\partial t} + V \frac{\partial T}{\partial y} + \frac{1}{c_p} \left[ \sum_{k=1}^{N} \dot{\omega}_k + \sum_{k=1}^{N} j_k c_{p,k} \frac{\partial T}{\partial y} - \frac{\partial}{\partial y} \left( \frac{k}{\partial T}{\partial y} \right) \right] = 0
\] : Energy \hspace{1cm} (Eq. 4)

\[
\frac{\partial \Lambda_x}{\partial y} = 0
\] : Pressure curvatures \hspace{1cm} (Eq. 5)

where \( \rho \) is the density; \( u \) is the normal velocity; \( u \) is the transverse velocity; \( \mu \) is the dynamic viscosity; \( D_{km} \) is the mixture-averaged diffusion coefficient; \( D_{T}^T \) is the thermal diffusion (Soret effect) coefficient; \( W \) is the mixture molecular weight; \( W_k \) is the molecular weight of species \( k \); \( \dot{\omega}_k \) is the molar production rate of species \( k \); \( c_p \) is the mixture specific
heat; \( c_{p,k} \) is the specific heat of species \( k \); \( \hat{h}_k \) is the molar enthalpy of species \( k \); \( \lambda \) is the mixture thermal conductivity; \( N \) is the number of gas-phase species. To model the finite domain configuration where the inlet velocity is imposed as a boundary condition, the pressure curvature equation is added to the system of governing equations. This is in contrast to the semi-infinite stagnation flow configuration conventionally considered in opposed-flow flame studies. Therefore, the pressure gradient is determined as a part of the solution in order to satisfy the remaining boundary conditions [30]. Along with the system of governing equations, the equation of state is used to compute the density as a function of species mass fractions:

\[
\rho = \frac{p \bar{W}}{RT} \quad \text{(Eq.6)}
\]

where \( R \) is the universal gas constant.

Flux-matching conditions are applied to the continuity, species and energy conservation equations at the membrane surface, \( y = 0 \). The convective and diffusive mass fluxes of the gas-phase species at the membrane surface are based on the oxygen permeation. In an ITM unit, only oxygen is separated from the air. It permeates to the sweep side of the membrane. Thus, boundary conditions for the continuity and species conservation equations include the oxygen permeation rate, \( J_{O_2} \), which is negative on the air side (sink term) and positive on the sweep gas side (source term) as follows:

\[
V_{\text{mem}} = \begin{cases} 
-J_{O_2} & \text{(air)} \\
+J_{O_2} & \text{(sweep)} 
\end{cases}
\quad \text{(Eq.7)}
\]

\[
\dot{j}_k + Y_k V_{\text{mem}} = \begin{cases} 
\pm J_{O_2} & (k = O_2) \\
0 & (k \neq O_2) 
\end{cases}
\quad \text{(Eq.8)}
\]

where \( V_{\text{mem}} \) is the mass flux at the membrane surface. In addition, heat released from chemical reactions on the sweep gas side is transferred to the membrane, which transfers heat to the air domain and to the surrounding walls via radiation.
Radiation heat transfer is considered between the membrane and the reactor walls (Inconel 601 [25]). In the ITM unit configuration [25], the membrane sees a large area of the wall, and the shape factor is taken to be unity. Therefore, the energy conservation across the membrane relates the heat fluxes, $Q_{sweep}^-$ and $Q_{air}^-$, to and from the membrane, respectively, and its temperature, as shown below.

$$Q_{sweep}^- - Q_{air}^- - 2\sigma e_{mem} (T_{mem}^4 - T_\infty^4) = 0$$  \hspace{1cm} (Eq. 9)

where,

$$Q_{air}^- = -\lambda VT + \sum_{k=1}^{N} (j_k + Y_k V_{mem}) \hat{h}_k$$

$$Q_{sweep}^- = \lambda VT - \sum_{k=1}^{N} (j_k + Y_k V_{mem}) \hat{h}_k$$

where $\sigma$ is the Stefan-Boltzmann constant, $T_\infty$ is the surrounding wall temperature, and $e_{mem}$ is the emissivity of the membrane. The emissivity of the membrane, $e_{mem} = 0.8$, has been measured in our laboratory [32]. It is assumed that $T_\infty$ is the same as the gas inlet temperature at steady state. On the other hand, the no-slip condition at the solid surface makes the transverse velocity at the membrane surface ($U_{mem}$) set to zero.

$$U_{mem} = 0$$  \hspace{1cm} (Eq. 10)

Input operating conditions are imposed at the inlets, $y = H$. The mass influx, $V_{air}$ and $V_{sweep}$, and the gas inlet temperature, $T_{air}$ and $T_{sweep}$, are known. The mass ratio of oxygen to nitrogen in the air dictates the gas composition, $Y_{k,air}$, at the air inlet, whereas the fuel dilution ratio between methane and the diluent such as carbon dioxide determines the composition of the gas inflow, $Y_{k,sweep}$, in the sweep gas side. The normal flow condition implies a zero transverse velocity, i.e., $u_{in} = U_{in} = 0$. 


\[
V_{in} = \begin{cases} \frac{V_{air}}{V_{sweep}} & (air) \\ \frac{V_{sweep}}{V_{air}} & (sweep) \end{cases} \tag{Eq.11}
\]

\[
Y_{k, in} = \begin{cases} \frac{Y_{k, air}}{Y_{k, sweep}} & (air) \\ \frac{Y_{k, sweep}}{Y_{k, air}} & (sweep) \end{cases} \tag{Eq.12}
\]

\[
T_{in} = \begin{cases} \frac{T_{air}}{T_{sweep}} & (air) \\ \frac{T_{sweep}}{T_{air}} & (sweep) \end{cases} \tag{Eq.13}
\]

\[
U_{in} = 0 \tag{Eq.14}
\]

Note that the mass influx boundary condition is satisfied through the pressure curvature equation. Because the continuity equation is first-order, it needs only one boundary condition at the membrane surface, which is the oxygen permeation rate. However, the finite-gap stagnation flow configuration requires another mass flux boundary condition at the inlets to take into account the given mass influx. The pressure curvature equation does not have an explicit boundary condition and is solved to satisfy the specified mass flux at the inlets.

### 2.2. Oxygen Permeation Flux Expression

The oxygen permeation across the membrane is incorporated into the coupled thermochemical-fluid dynamic model by using the expression developed in [33], and parameterized to consider the local thermodynamic state in [16]. In this expression, the gas phase parameters, i.e., the oxygen partial pressure in the immediate vicinity of the membrane on both air and fuel domains, and the membrane temperature govern the oxygen permeation rate. It is important to note that this is in contrast to conventional oxygen permeation flux expressions that are parameterized in terms of the bulk oxygen partial pressure measured at the air inlet and the sweep gas outlet. The oxygen permeation flux expression considered in this study is given by the following form:

\[
J_{O_2} = \frac{D_{O_2} k_s \left( P_{O_2, air}^{0.5} - P_{O_2, sweep}^{0.5} \right)}{2 L k_f \left( P_{O_2, air} P_{O_2, sweep} \right)^{0.5}} + D_{O_2} \left( P_{O_2, air}^{0.5} + P_{O_2, sweep}^{0.5} \right) \tag{Eq.15}
\]
where $P_{O_2,air,(i)}$ and $P_{O_2,sweep,(i)}$ are the oxygen partial pressures at the membrane surface on the air and the sweep gas domains, respectively; $L$ is the membrane thickness; $D_{VO}$ is the diffusion coefficient of oxygen vacancies; $k_f$ and $k_r$ are the surface exchange reaction rate coefficients. The three parameters, $D_{V0}$, $k_f$ and $k_r$, used in the expression are expressed in an Arrhenius form as shown below.

$$
\Theta_i = A_i \exp \left( \frac{-E_{a,i}}{RT_{mem}} \right)
$$

where, $\Theta_i = D_{V0}, k_f, k_r$

(Eq.16)

The pre-exponential factor, $A_i$, and the activation energy, $E_{a,i}$, for each parameter are summarized in Table 1. The details of derivation for the permeation flux expression and requisite parameters ($D_{V0}$, $k_f$, and $k_r$) are discussed in [16].

### 2.3. Detailed Chemistry and Transport and Numerical Methodology

To examine the fuel conversion processes, detailed chemical kinetic mechanism for methane using GRI-Mech 3.0 [34] is implemented for the homogeneous gas phase chemical reactions. Detailed chemistry is necessary for capturing important phenomena and chemical species appearing in the vicinity of the membrane. To integrate the multi-step chemical reactions and evaluate the thermodynamic and the transport properties shown in the governing equations and reaction kinetics, Cantera [35] is used along with NASA polynomials. Surface reactions are ignored to focus on the gas-phase fuel conversion and their relationship with oxygen permeation. Surface chemistry will be considered in future studies.

A finite difference method is used to discretize the governing equations and boundary conditions. The convective terms are discretized using a first-order upwind differencing to avoid numerical instabilities [30]. The diffusion terms in the momentum equation and the species conservation equations are approximated to second-order accuracy. A first-order fully implicit finite difference is implemented to discretize the continuity equation. The discretized equations are integrated using the Sundials IDA solver [36], which integrates the differential algebraic equations using a variable-order (from 1 to 5) backward differentiation formula. At each time step, this produces a system of nonlinear algebraic equations, which are solved using a preconditioned Newton-Krylov method.
Due to the presence of the membrane, the computational domain is divided into two parts, the air domain and the sweep gas domain. The air and sweep gas domains are coupled to obtain the steady state solution by matching the two flux-matching boundary conditions such as the oxygen permeation rate and the heat flux. Each domain considers the oxygen permeation rate and the heat flux as boundary conditions at the membrane surface during time integration, which are solved for during and intermediate calculation step. After the system of governing equations for each domain is integrated using the inlet boundary conditions and the two flux-matching boundary conditions determined during the previous time step, the oxygen partial pressure profile and the temperature profile in each domain are updated. Note that the oxygen permeation rate and the heat flux depend on the partial pressures of oxygen in the immediate vicinity of the membrane and the temperature profile in both domains, respectively (refer to Eq.9 and Eq.15). Therefore, the new oxygen partial pressures and the new temperature profile must be used to update the oxygen permeation rate and heat flux for the following time step. This simulation procedure is repeated until a steady state solution is acquired.

3. REACTION ENVIRONMENT SUPPORTED BY AN ITM

The presence of a dense ceramic membrane between the air and sweep gas inlets leads to several particular characteristics concerning the fuel conversion processes on the sweep side of an ITM, as compared to the classical opposed-flow diffusion flames. First, oxygen selectively permeates from the air side to the sweep side. In the absence of diluents (other than nitrogen) in the sweep side, this forms a nitrogen-free environment for the chemical reactions. Nitrogen is completely removed prior to combustion, and oxy-fuel combustion takes place without NOx formation. However, the flame temperature in the absence of nitrogen, i.e., oxy-fuel flame, is significantly higher compared to that of CH4/air combustion. Matching the combustion temperature requires the introduction of a substantial amount of an other diluent such as CO2 in the sweep gas stream [37]. In typical oxy-fuel combustion reactors, a fraction of the flue gas stream is recirculated back to the reactor in the form of wet or dry CO2 to control the flame structure and its temperature. In this study, dry CO2 recycle is assumed, and it is mixed with CH4 as a sweep gas stream. Note that CO2 is mixed and fed into the reactor along with CH4, rather than being mixed with oxygen, i.e., the process relies on fuel dilution rather than oxidizer dilution. Since oxygen is introduced into the sweep side of the ITM via permeation, pre-mixing of the recirculated CO2 stream with oxygen is not possible. This will affect fuel pyrolysis, which will be discussed in Section 4.4. In an environment with a mixture diluted by CO2, the thermodynamic and transport properties of gases change greatly from those of a mixture diluted by N2, i.e., air.
CO₂ is a tri-atomic molecule with the higher specific heat capacity and molecular weight than the diatomic N₂ molecule. A higher molecular weight raises the gas density and hence the density-weighted diffusion coefficients, i.e., \( \rho D_k \), of the fuel and oxidizer, i.e., permeated oxygen in the gas-phase. In addition, the chemical effects of CO₂ driven by its reduction reaction with the H radical become important [38, 39]. These effects also become apparent in an ITM reactor as will become evident in Section 4.

The oxygen permeation flux across the membrane is relatively low compared to the convective oxidizer feed stream in conventional counter-flow diffusion flames. The stream velocity in typical opposed-flow diffusion flames is on the order of \( 10^{-1} \)–\( 1 \) m/s [26, 40], whereas that in the ITM reactor is limited by low oxygen permeation rates, which is on the order of \( 10^{-4} \)–\( 10^{-3} \) m/s. Accordingly, the fuel stream must be fed to the sweep side at a low flow rate to satisfy the requisite stoichiometry and stabilize the reaction zone between the membrane and the sweep gas inlet. The corresponding Reynolds number for the sweep side, which is defined as below, is on the order of 10 [16].

\[
\text{Re}_{\text{sweep}} = \frac{\rho_{\text{sweep}} \nu_{\text{sweep}} H_{\text{sweep}}}{\mu_{\text{sweep}}} = \frac{V_{\text{sweep}} H_{\text{sweep}}}{\mu_{\text{sweep}}}
\]  
(Eq.17)

where \( H_{\text{sweep}} \) is the sweep gas channel height of the reactor (see Fig. 2). Therefore, the species transport by diffusion is important in this low Reynolds number regime, which further highlights the implications of a CO₂-diluted (rather than N₂-diluted) sweep gas stream. The species diffusion is also critical with respect to the oxygen permeation rate, as will be discussed in Section 4.1. In addition, the air and sweep gas streams are preheated to a high temperature to enhance the oxygen permeation flux and promote the gas-phase kinetics, as the former is predominantly dependent on the membrane temperature and the oxygen partial pressure on the sweep side of the ITM [16].

Lastly, the flow rate of the oxidizer, i.e., the oxygen permeation rate, is not a pre-determined or controlled parameter, but it is a dependent variable. Unlike conventional counter-flow diffusion flames where the oxidizer flow rate can be controlled explicitly, the oxygen permeation rate is not known a priori and depends on the local oxygen partial pressure in the immediate vicinity of the membrane and membrane temperature [1, 16]. These two parameters are strongly influenced by the oxidation reactions and cannot be independently manipulated. Furthermore, the overall reaction rate and
reaction products/selectivity are dependent on the oxygen permeation rate, which is also affected by the chemical reactions [41]. Non-premixed, diffusion-limited reactions occurring on the sweep side are governed by the oxidizer flow rate, i.e., the oxygen permeation rate, as well as the sweep gas initial conditions (e.g., flow rate, initial temperature and fuel concentration). Thus, it is difficult to control the oxygen permeation flux, the mass ratio of oxygen to fuel, i.e., equivalence ratio, and reaction products independently. The operating regime of ITM reactors and associated fuel conversion processes need to be examined using detailed models capable of resolving each of these processes to gain understanding of the complex coupling.

4. FUEL CONVERSION AND FLAME ANALYSIS

To gain insight into the fundamental fuel conversion process, a reference operating condition was defined and the flame, oxygen permeation, chemical kinetic, and thermodynamic characteristics were evaluated. The following results were obtained for a sweep gas fuel concentration of 6% on a molar basis, with the remainder being CO₂, and a sweep gas mass flux of $3.00 \times 10^{-2}$ kg/m²/s, corresponding to $Re_{\text{sweep}} = 15.6$ and sweep gas inlet velocity = $7.56 \times 10^{-2}$ m/s. In addition, it is assumed that the sweep gas stream is preheated to 1300 K in order to obtain a high oxygen permeation rate. These conditions were selected because they are within the realistic operating regime of an ITM unit and allow a sustainable reaction zone to be established. To characterize the impacts of fuel dilution using CO₂ sweep gas stream, the results are compared to those of a N₂-diluted sweep fuel stream in which the Damköhler number (defined as a ratio of the extinction strain rate to the flow strain rate), the fuel concentration on a mass basis in the sweep gas stream and the initial temperature are the same as those of the CO₂-dilution case. Since a diffusion flame structure appears in a complicated coupled manner between thermal input, species transport and chemical kinetics, and is strongly sensitive to the flame regime in Linan's S-curve, the Damköhler number is maintained constant for comparison. Note that, since the temperature on the sweep side of the ITM is sufficiently low, N₂ chemistry does not have significant effects on the flame. The mass flux of air is maintained at $1.00 \times 10^{-1}$ kg/m²/s, corresponding to $Re_{\text{air}} = 100$ and air inlet velocity = $3.70 \times 10^{-1}$ m/s, for both cases. It is assumed that the air is preheated to 1300 K, and the surrounding wall temperature is the same as the gas (i.e., both air and sweep gas) inlet temperature. Results obtained from the CO₂-diluted sweep gas stream are categorized as a base case (CO₂-dilation), while those from the sweep gas stream diluted with N₂ are called a reference case (N₂-dilation).
4.1. Flame Location and Oxygen Permeation

Low oxygen permeation rates result in a stagnation point and a flame front established in the vicinity of the membrane with weak flame stretch. The flame location is defined as the point of maximum heat release. As discussed in Section 3, the oxygen permeation rate from a typical ITM is substantially lower compared to the oxidizer flow rate in conventional opposed-flow diffusion flames. Given the inlet conditions, the oxygen permeation rates obtained from the simulations are $1.13 \times 10^{-3}$ and $1.24 \times 10^{-3}$ kg/m$^2$/s for CO$_2$-dilution and N$_2$-dilution cases, respectively, which are one order of magnitude lower than the sweep gas mass flux. In this case, the stagnation point and the flame front are established in the vicinity of the membrane, as shown in Fig. 3. In addition, low strain rate flames result from the low oxygen permeation flux, as compared to the strain rate of conventional opposed-flow diffusion flames which is on the order of $10^2$–$10^3$ s$^{-1}$ [26, 40]. The strain rate, $K$, is defined as [40],

$$K = -\frac{1}{\rho} \frac{\partial (\rho u)}{\partial y} = -\frac{1}{\rho} \frac{\partial V}{\partial y} \tag{Eq.18}$$

Fig. 3 shows that the strain rates of both CO$_2$-dilution and N$_2$-dilution cases are close to or less than 10 s$^{-1}$. Furthermore, to obtain the same Damköhler number for the CO$_2$-dilution and the N$_2$-diluted fuel stream, the latter needs a higher inlet velocity resulting in a larger strain rate. The differences in the flame location, inlet velocity and strain rate between the two cases are attributed to the chemical effects and transport properties of CO$_2$, which will be discussed in Section 4.2.

The flame location and the high CO$_2$ concentration on the sweep side of the ITM play important roles in determining the oxygen permeation rate and the flame temperature. Table 2 summarizes the results regarding the flame location and several critical parameters in this problem. Since the reaction zone is established close to the membrane, the heat transfer from the flame towards the membrane is substantial, which decreases the flame temperature while increasing the membrane temperature. It can be seen that maximum flame temperature for both CO$_2$-dilution and N$_2$-dilution cases are lower than the corresponding adiabatic flame temperatures, while the membrane is heated and is maintained at a high temperature due to the heat transfer from the reaction zone. If this heat loss is extensive such that the reaction rates are significantly lowered, the flame can be even extinguished [41-43]. Moreover, oxygen consumption and the diffusion of the reaction products towards the membrane surface and the permeated oxygen away from the surface reduce the oxygen
concentration in the immediate vicinity of the ITM and increase the permeation rate. In the CO₂-dilution case, the flame front established closer to the membrane along with the enhancement of the species diffusion because of the larger density-weighted diffusion coefficients in CO₂ with respect to that in N₂ (e.g., \( \rho D_{H_2O} = 1.10 \times 10^{-4} \) and \( 8.94 \times 10^{-5} \) kg/m/s for CO₂-dilution and N₂ dilution cases, respectively) result in a lower oxygen mass fraction at the membrane surface, in comparison with that of the N₂-dilution case. Note that oxygen permeation is enhanced as the oxygen chemical potential gradient across the membrane and the membrane temperature increase (refer to Eq.15 and Eq.16). A lower oxygen concentration induced by a closer flame location increases the oxygen permeation flux. However, the high molecular weight of CO₂ reduces the impact of these effects, as the oxygen permeation rate is a function of oxygen partial pressure, i.e., the O₂ mole fraction (and not mass fraction), as described in Eq.15. Thus, the higher mixture molecular weight in the CO₂-dilution case translates the oxygen mass fraction to a higher oxygen partial pressure in the vicinity of the membrane than when N₂ dilution is used. As a result, the permeation rate in the N₂-dilution case is slightly larger than that of the CO₂-dilution case, despite the CO₂-dilution case having a lower oxygen mass fraction in the vicinity of the membrane.

4.2. Flame Temperature and Thickness

Fuel conversion processes on the sweep side of the ITM show a number of important features regarding the temperature and thickness of the flame. Fig. 4(a) shows the temperature for both CO₂-dilution and N₂-dilution cases, in the direction normal to the membrane. It can be seen that the flame temperature and its gradient in the CO₂-dilution case are lower than those of the N₂-dilution case. This can be attributed to the chemical, thermal and transport effects of CO₂ and the oxygen leakage through the flame. To examine the chemical effects of CO₂, Table 3 shows dominant reactions governing the overall fuel conversion processes and the strength of each reaction, as described by the spatially averaged reaction rate, \( \bar{\eta}_i \) (defined as below), for both CO₂-dilution and N₂-dilution cases.

\[
\bar{\eta}_i = \frac{1}{H_{sweep}} \int_0^{H_{sweep}} \dot{\eta}_i \, dy \quad \text{(Eq.19)}
\]

where \( \dot{\eta}_i \) is the rate of reaction \( i \). Note that \( \bar{\eta}_i \) of R.1 and R.7 are shown for each side, i.e., the oxidizer and fuel sides, of the flame in Table 3, because their directions change from the forward reaction on the fuel side of the flame, i.e.,
\[
\frac{1}{H_{\text{sweep}} - y_{\text{flame}}^\prime} \int_{y_{\text{flame}}^\prime}^{H_{\text{sweep}}} \dot{\theta} \, dy > 0, \text{ to the backward reaction on the oxidizer side of the flame, i.e., } \frac{1}{y_{\text{flame}}} \int_{0}^{y_{\text{flame}}} \dot{\theta} \, dy < 0, \text{ where } y_{\text{flame}}^\prime \text{ is the flame location. Other reactions vary monotonically such that the forward reaction is dominant throughout the sweep gas channel. When high concentration CO}_2 \text{ is introduced with a hydrocarbon fuel into a high temperature environment such as the sweep side of the ITM, the endothermic reaction of CO}_2 \text{ with the H radical, R.1, forming CO is favored [38] while approaching the flame, i.e., on the fuel side of the flame. The radical H is formed through thermolysis of CH}_4 \text{ prior to the flame. Compared to the N}_2\text{-dilution case, the reaction rate of R.1 and consumption of the H radical in the CO}_2\text{-dilution case is faster on the fuel side of the flame because of the high concentration CO}_2, \text{ which leads to a reduction in the flame temperature. On the oxidizer side of the flame, high concentration CO}_2 \text{ acts as a third body in R.5, which is a chain terminating reaction, to promote the H radical consumption and to inhibit the most important chain branching reaction, R.3. The lower flame temperature and consumption of the H radical due to R.1 and R.5 slow down R.3, which is weakly endothermic and depends strongly on temperature. R.3 is the primary reaction for consuming oxygen and producing more radicals hence enhancing the overall reaction rates. As a result, in the CO}_2\text{-dilution case, oxygen is not fully consumed in the reaction zone due to the lack of the H radical and instead leaks through the flame, as shown in Fig. 4(b). The unconverted oxygen further lowers the flame temperature. The leakage of oxygen through the flame results in a lower peak flame temperature, flame instability and possible extinction in conventional diffusion flames under the impact of high strain rates [44, 45]. Moreover, since CO}_2 \text{ has a higher specific heat capacity than N}_2, \text{ the temperature rise due to the exothermic reactions of fuel combustion is lower. Consequently, the flame temperature is reduced in comparison with that of N}_2\text{-dilution. To differentiate the chemical effects of CO}_2 \text{ from its thermal effects on the flame temperature, Fig. 4(a) also shows the temperature in a case in which CO}_2 \text{ was assumed to be chemically inert. Inert-CO}_2 \text{ has the same thermodynamic and transport properties as CO}_2, \text{ but it is chemically inactive and hence does not contribute to the chemical reactions. The flame temperature in the inert-CO}_2 \text{ dilution case is similar to that of the N}_2\text{-dilution case, indicating that the chemical effects of CO}_2 \text{ on a lower flame temperature are more dominant. In addition, the enhanced species diffusion in the CO}_2\text{-dilution case promotes the transport of the reaction products away from the reaction zone, leading to a smaller temperature gradient, in particular, on the fuel side of the flame. This reduces the conductive heat transfer towards the fuel stream, and hence preheating of the reactants.}
The presence of high concentration CO\textsubscript{2} in the sweep gas stream also affects CH\textsubscript{4} oxidation, the flame thickness and location. Fig. 4(b) shows that CH\textsubscript{4} conversion is delayed, and it diffuses closer to the membrane in the CO\textsubscript{2}-dilution case. The suppression of the chain branching reactions, R.3 and R.4, and the enhancement of the chain terminating reaction, R.5, reduce the radical concentrations, as will be discussed in Section 4.4, and lower the overall reaction rates. The initiation of CH\textsubscript{4} kinetics through reaction with the H radical via R.6 is delayed by the consumption of the H radical in R.1 on the fuel side of the flame. These two effects suppress CH\textsubscript{4} oxidation and delay the onset of fuel conversion. Moreover, the flame stretch is smaller in the CO\textsubscript{2}-dilution case than that with N\textsubscript{2} (see Fig. 3). The leakage of oxygen in the CO\textsubscript{2}-dilution case makes the reaction environment unstable and brings it closer to the extinction limit. In this case, to obtain the same Damköhler number as that of the CO\textsubscript{2}-dilution case, the N\textsubscript{2}-diluted fuel stream requires a higher strain rate, which needs a higher inlet velocity. Consequently, given the same Damköhler number, fuel concentration and inlet temperature, the lower reaction rates and smaller flame stretch in the CO\textsubscript{2}-dilution case form a thicker diffusion flame, as evidenced by the smaller slope of the local equivalence ratio in Fig. 4(a) (see comments on the figure). The local equivalence ratio, \( \phi_{\text{local}} \), is defined as,

\[
\phi_{\text{local}} = \frac{(m_{O_2}/m_{CH_4})_{\text{stoich}}}{(m_{O_2}/m_{CH_4})} = \frac{(2W_{O_2}/W_{CH_4})}{(Y_{O_2}/Y_{CH_4})} \quad \text{(Eq. 20)}
\]

A lower slope of the local equivalence ratio represents a wider overlap of fuel and oxidizer, and hence a thicker diffusion flame. In addition, the suppression of CH\textsubscript{4} oxidation shifts the flame towards the membrane. Fig. 4 highlights the chemical effects of CO\textsubscript{2}, showing that they result in a thicker diffusion flame and shifts the flame further towards the membrane, as seen in comparison with the inert-CO\textsubscript{2} dilution case.

### 4.3. Reaction Products Governed by Suppressed H and Enhanced OH Radical Chemistry

The dominant reactions governing the overall reaction rates are different from those of CH\textsubscript{4}/air flames and consequently impact the products on the sweep side of the ITM. Fig. 5 shows the profiles of CO\textsubscript{2}, CO, H\textsubscript{2} and H\textsubscript{2}O concentrations. It can be seen that the CO concentration in the CO\textsubscript{2}-dilution case is larger than that of the N\textsubscript{2}-dilution case throughout the sweep gas channel. The higher CO concentration is attributed to the enhanced CO\textsubscript{2} reduction reactions, R.1 and R.2 in Table 3. Note that a small fraction of CO reaches the membrane surface in the CO\textsubscript{2}-dilution case, as compared to
the \(N_2\)-dilution case in which the CO concentration at the membrane surface is nearly zero. Due to its higher concentration of CO and the relative proximity of the flame location to the membrane, CO oxidation cannot be completed. On the other hand, the \(H_2\) concentration in the \(CO_2\)-dilution case is lower, in comparison with that of the \(N_2\)-dilution case. This can be explained by the suppressed H radical reactions, R.6 to R.8 in Table 3, because of the lower H radical concentration as a result of R.1 on the fuel side of the flame. R.6, R.7 and R.8 are the primary reactions for the production of \(H_2\), which takes place on the fuel side of the flame (see Fig. 6(b)). Because the H radical is consumed by R.1, the forward rates of these three reactions are reduced, hence lowering the \(H_2\) concentration. With respect to \(H_2O\) production, R.9, R.10 and R.11 (see Table 3) are more dominant in the \(CO_2\)-dilution case. The OH radical is produced in the \(CO_2\) reduction reaction, R.1, before reaching the flame, while the H radical is consumed. This promotes the forward reactions of R.9, R.10 and R.11, and a slightly larger \(H_2O\) concentration in \(CO_2\)-dilution. Therefore, suppressed H radical chemistry and enhanced OH-driven reactions change the products on the sweep side of the ITM and lead to higher CO and lower \(H_2\) concentrations.

Changing the H and OH radical chemistry impacts the location of \(CO_2\), CO, \(H_2\) and \(H_2O\) production. Fig. 6 shows the molar production rate profiles of the four species along with the gross heat release rate for \(CO_2\)-dilution ((a) and (b)) and \(N_2\)-dilution ((c) and (d)) cases. In the \(CO_2\)-dilution case, CO is produced via R.1 while approaching the primary reaction zone (defined by the major peak in the heat release rate). It can be seen that CO production and \(CO_2\) destruction proceed together, and they are accelerated in comparison with the \(N_2\)-dilution case (compare Fig. 6(a) and (c)). Their production and destruction rates are maximized in the high temperature primary reaction zone driven by both R.1 and R.2. As these two reactions become dominant when the sweep gas approaches the primary reaction zone, the \(H_2O\) production rate increases significantly via R.9 to R.11, whereas \(H_2\) production is suppressed (compare Fig. 6(b) and (d)). On the other hand, in the \(CO_2\)-dilution case, CO oxidation (the backward reaction of R.1) in the secondary reaction zone (defined by the secondary peak in the heat release rate) is substantially enhanced (refer to Fig. 6(a) and Table 3) due to the high CO concentration, which inhibits the \(H_2O\) production and \(H_2\) destruction in this region (see Fig. 6(b)) by competing for the OH radical with the backward reaction of R.7. As a result, suppressed H radical chemistry (R.6 to R.8) and OH-driven reactions (R.9 to R.11) on the fuel side of the flame, and enhanced CO oxidation on the oxidizer side of the flame confine species production to a small region in the high temperature primary reaction zone, relative to the \(N_2\)-dilution case. This effect will be discussed further in Section 4.5.
4.4. Low Radical Concentrations

Suppressed chain branching reactions due to CO₂ decomposition affect the radical concentrations. Fig. 7 shows the profiles of the radicals, H, O, OH and CH₃. In general, the radical concentrations in the CO₂-dilution case are significantly reduced in comparison with those of the N₂-dilution case. The small amount of hydrogen-oxygen radicals, i.e., H, O and OH, are attributed to the suppression of the chain branching reactions, R.3 and R.4, and the enhancement of the chain terminating reaction, R.5 (refer to Table 3 for their reaction rates). The consumption of the H radical by the CO₂ reduction reaction, R.1, on the fuel side of the flame and the chain terminating reaction, R.5, on the oxidizer side of the flame lower the reaction rate of R.3, while the low H₂ concentration in the CO₂-dilution case slows down R.4. In addition, high concentration CO₂ promotes the chain termination via R.5. The suppression of R.3 and R.4 and the enhancement of R.5 lower the radical concentrations and reduce the overall reaction rates in the CO₂-dilution case as compared to the N₂-dilution case. In addition, the concentration of CH₃, which is a precursor for the initiation of CH₄ oxidation, is substantially lowered before reaching the primary reaction zone due to R.6. As discussed in Section 4.2, the reaction rate of R.6 is reduced by competing with R.1 for the H radical. As a consequence, the CH₄ kinetics is delayed, and the CH₄ mass fraction is lowered. Therefore, the higher concentration of CO₂ on the sweep side of the ITM reduces the radical concentrations and slows the overall fuel conversion processes.

Lowering the CH₃ radical concentration also has an impact on the fuel pyrolysis. In a diffusion flame with temperature of approximately 1500 K, such as that established on the sweep side of the ITM, the CH₄ kinetics have additional pathways that lead to the formation of C₂ hydrocarbons [46]. Before reaching the flame, i.e., on the fuel side of the flame, CH₃ molecules are combined to form C₂H₆ and C₂H₅ via R.12 and R.13 (see Table 3). C₂H₆ and C₂H₅ react further via R.14, R.15 and R.16 to form C₂H₂ and C₂H₄, which are known soot precursors [47]. However, high CO₂ concentration in the sweep gas stream lowers CH₃ formation and concentration before reaching the primary reaction zone via R.1 and R.6 by reducing the H radical concentration, as shown in Fig. 7. Accordingly, the reaction rates of R.12 and R.13 are reduced, and the formation of soot precursors, C₂H₂ and C₂H₄, are suppressed, as shown in Fig. 8. Note that, because CO₂ is mixed and fed into a reaction zone with the fuel stream, i.e., fuel dilution, the formation of soot precursors is reduced, as discussed in [48, 49]. In conventional diffusion flames in which oxidizer dilution via N₂ is typically used, such a reduction in the formation of soot precursors does not take place. Thus, the presence of high concentration CO₂ in
the sweep gas (fuel) stream may suppress hydrocarbon pyrolysis and the formation of soot precursors. This conclusion needs further investigations by implementing more comprehensive soot chemistry.

4.5. Reaction Pathway and Flame Structure

A reaction pathway analysis shows that the dominant reactions governing the overall fuel conversion processes and the flame structure on the sweep side of the ITM are also impacted by CO\textsubscript{2} dilution. Fig. 9 shows the reaction rate of the important reactions, which determine the reaction products and govern predominantly the overall fuel conversion, and the gross heat release rate for CO\textsubscript{2}-dilution ((a) and (b)) and N\textsubscript{2}-dilution ((c) and (d)) cases. Fig. 9(a) and (c) show the primary reaction zone where CH\textsubscript{4} conversion forming CO takes place, while the secondary reaction zone in which CO oxidation and H\textsubscript{2}/O\textsubscript{2} reactions occur is shown in Fig. 9(b) and (d). In the CO\textsubscript{2}-dilution case, the major peak in the heat release rate is attributed to R.2, R.9, R.10, R.11 and R.17, while the secondary peak in the heat release rate is contributed by R.1, R.5, R.7, R.18 and R.19, most of which are not prominent in the N\textsubscript{2}-dilution case (see Table 3 for reactions and their relative reaction rates). Note that CO and CO\textsubscript{2} in the secondary reaction zone are important third bodies, \( M \), in R.5 and R.17 promoting their forward reaction rates. We also note that CO oxidation, which is the reverse of R.1, is dominant in the secondary reaction zone and is not completed by the time it reaches the membrane, while the reverse of R.7 is suppressed. As a result, the concentration of CO can be non-zero at the membrane surface, and the H\textsubscript{2}O production is limited to the primary reaction zone. It can be observed that the dominant reactions in the CO\textsubscript{2}-dilution case coincide with the major peak in the heat release rate, as discussed in Section 4.3, in comparison with the N\textsubscript{2}-dilution case where its dominant reactions, R.6, R.8, R.9, R.11 and R.17 (see Table 3 for reaction numbers), are spatially more distributed across the primary reaction zone. Thus, the flame structure in the CO\textsubscript{2}-dilution case is governed by CO\textsubscript{2} reactions and OH-driven chemistry. The results from the reaction pathway analysis are depicted in Fig. 10, showing the importance of the reaction pathways for CO\textsubscript{2} dilution relative to N\textsubscript{2} dilution. This shows the important carbon-containing species and dominant reactions that govern the overall fuel conversion processes in ITM reactors (CO\textsubscript{2}-dilution). The thickness of the arrows represents the ratio of the reaction rates between the CO\textsubscript{2}-dilution case and the reference case (N\textsubscript{2}-dilution), i.e., thick-solid arrows mean that the corresponding reactions are enhanced, whereas thin-dashed arrows show suppressed reactions in CO\textsubscript{2}-dilution in comparison with N\textsubscript{2}-dilution. In the N\textsubscript{2}-dilution case where both H and OH radical reactions are relevant, the dominant reactions follow the characteristics of typical counter-flow diffusion flames as discussed in [50].
5. CONCLUSIONS

A numerical model is used to examine fuel conversion processes and associated important phenomena, which includes the location, temperature, thickness and structure of a flame, the relationship between the oxygen permeation rate and the oxidation reactions, hydrocarbon pyrolysis and the formation of possible soot precursors, occurring on the sweep side of the ITM. The model incorporates detailed gas-phase chemistry and transport enabling us to obtain the spatially resolved profiles of species concentration, temperature and reaction rates. The presence of an ITM that permeates oxygen into the sweep side supports oxy-fuel combustion with high fuel dilution with CO₂. Since the oxygen permeation rate is typically low compared to the convective oxidizer flow in conventional counter-flow diffusion flames, the flow rate and fuel concentration of the sweep gas stream are limited to meet the requisite stoichiometry. In addition, to achieve a sufficient oxygen permeation flux and enhance the chemical kinetics, the sweep gas, i.e., the fuel feed stream, is preheated, leading to a relatively high temperature pre-flame environment. The oxygen permeation rate is not known a priori and is dependent on the local flow conditions, i.e., the species concentration and temperature near the membrane, which are affected by the chemical reactions in the vicinity of the membrane. As a result, under the conditions modeled in this study, the sweep side of the ITM features a preheated laminar oxy-fuel diffusion flame composed of a CO₂-diluted fuel stream and an oxidizer, the flow rate of which is coupled with the fuel conversion characteristics such as reaction zone position, flame temperature and diluent composition.

Fuel conversion processes on the sweep side of the ITM show the interesting features of a laminar oxy-fuel diffusion flame. The chemical effects of a high CO₂ concentration in the sweep gas stream result in a lower flame temperature and the suppression of the CH₄ kinetics, relative to the case with the N₂-diluted sweep gas. The endothermic reduction reaction of CO₂ and the chain terminating reaction promoted by CO₂ compete with the chain branching reaction for the H radical and leads to a reduction in the flame temperature, low radical concentrations and oxygen leakage through the flame. The leakage of unconverted oxygen through the flame further lowers the flame temperature. Moreover, the initiation of CH₄ oxidation is delayed due to the reduction of the H radical chemistry, and hence a thicker flame is established near the membrane surface. The location of the flame determines the flame temperature and the oxygen permeation rate via species diffusion and heat transfer from the flame towards the membrane. CO₂ decomposition consumes the H radical while producing the OH radical. As a result, H radical chemistry is suppressed, whereas OH-driven
reactions are enhanced. This produces more CO and H$_2$O and less H$_2$. Fuel dilution with CO$_2$ also reduces CH$_3$ formation, which slows down fuel pyrolysis and may reduce soot formation. In addition, CO$_2$ and OH driven reactions govern the flame structure to confine species production to a small region in the high temperature primary reaction zone. The flame location close to the membrane implies that surface reactions may play important roles in fuel conversion processes. This along with gas radiation effects will be investigated in a subsequent study.

6. ACKNOWLEDGEMENTS

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7. NOMENCLATURE

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<tr>
<td>$U$</td>
<td>Scaled transverse velocity</td>
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<tr>
<td>$Y_k$</td>
<td>Mass fraction of gas-phase species $k$</td>
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<td>Temperature</td>
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$W_k$  Molecular weight of species $k$

$\dot{\omega}_k$  Molar production rate of species $k$

$c_p$  Mixture specific heat

$c_{p,k}$  Specific heat of species $k$

$\dot{h}_k$  Molar enthalpy of species $k$

$\lambda$  Mixture thermal conductivity

$N$  Number of gas-phase species

$R$  Universal gas constant

$J_{O_2}$  Oxygen permeation rate

$\sigma$  Stefan-Boltzmann constant

$\varepsilon$  Emissivity

$P_{O_2}$  Oxygen partial pressure

$L$  Membrane thickness

$D_{VO}$  Diffusion coefficient of oxygen vacancy

$k_i$  Surface exchange rate coefficient of reaction $i$

$A$  Pre-exponential factor

$E_a$  Activation energy

$H$  Reactor channel height

$K$  Strain rate

$\Delta H_{STP}$  Heat of reaction at standard temperature and pressure

$\bar{\eta}_i$  Spatially averaged reaction rate of reaction $i$

$\dot{\eta}_i$  Rate of reaction $i$

$y_{flame}$  Flame location

$\phi_{local}$  Local equivalence ratio
subscripts

air  Air (feed) side of membrane

sweep  Sweep gas (permeate) side of membrane

in  Inlet

mem  Membrane

stoich  Stoichiometry

(s)  Membrane surface

∞  Surrounding wall

8. REFERENCES


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List of Figures

Figure 1 Ion transport membrane (ITM) for air separation and fuel conversion in the absence of nitrogen. Oxygen selectively permeates from the air side to the sweep side of an ITM. On the sweep side, fuel conversion takes place in a nitrogen-free environment, as the fuel approaches the membrane while the permeated oxygen transports in the opposite direction.

Figure 2 ITM unit configuration based on a planar, finite-gap stagnation flow considered in this investigation (air channel height $H_{\text{air}} = 50.8\, \text{mm}$; sweep gas channel height $H_{\text{sweep}} = 25.4\, \text{mm}$). ITM divides the overall physical domain into an air domain and a sweep gas domain, each of which is considered numerically. $y_{\text{air}} = 0$ and $y_{\text{sweep}} = 0$ are located on the membrane surfaces of the air and sweep side, respectively.

Figure 3 Normal velocity and strain rate along with the flame location (where, solid lines represent CO$_2$-dilution, and dotted lines stand for N$_2$-dilution). $y_{\text{sweep}} = 0$ is located on the membrane surface of the sweep side.

Figure 4 The variations of (a) temperature and the local equivalence ratio and (b) CH$_4$ and O$_2$ concentrations, along with the flame location (where, solid lines represent CO$_2$-dilution, dash lines are for CO$_2$ (inert, eliminating the chemical effects of CO$_2$)-dilution, and dotted lines stand for N$_2$-dilution). A lower slope of the local equivalence ratio represents a wider overlap of CH$_4$ and O$_2$, and hence a thicker flame. $y_{\text{sweep}} = 0$ is located on the membrane surface of the sweep side.

Figure 5 The concentrations of the reaction products (a) CO$_2$ and CO and (b) H$_2$ and H$_2$O, throughout the sweep gas channel, along with the flame location (where, solid lines represent CO$_2$-dilution, and dotted lines stand for N$_2$-dilution). $y_{\text{sweep}} = 0$ is located on the membrane surface of the sweep side.

Figure 6 The molar production rates of the reaction products, CO$_2$, CO, H$_2$ and H$_2$O, along with the gross heat release rate and the flame location for CO$_2$-dilution ((a) and (b)) and N$_2$-dilution ((c) and (d)). $y_{\text{sweep}} = 0$ is located on the membrane surface of the sweep side.

Figure 7 The concentrations of the important radicals (a) H and O and (b) OH and CH$_3$, along with the flame location (where, solid lines represent CO$_2$-dilution, and dotted lines stand for N$_2$-dilution). $y_{\text{sweep}} = 0$ is located on the membrane surface of the sweep side.

Figure 8 Soot precursors, C$_2$H$_2$ and C$_2$H$_4$, concentrations, along with the flame location (where, solid lines represent CO$_2$-dilution, and dotted lines stand for N$_2$-dilution). $y_{\text{sweep}} = 0$ is located on the membrane surface of the sweep side.

Figure 9 Gross heat release rate, the flame location and the reaction rate of dominant reactions for the primary reaction zone where CH$_4$ is converted to CO ((a) and (c)) and the secondary reaction zone in which CO oxidation and H$_2$/O$_2$ reactions take place ((b) and (d)). The minus sign in front of a reaction number means by its reverse direction. (a) and (b) belong to CO$_2$-dilution, while (c) and (d) are for N$_2$-dilution. $y_{\text{sweep}} = 0$ is located on the membrane surface of the sweep side.

Figure 10 Reaction pathway analysis showing the important carbon-containing species and dominant reactions in ITM supported fuel conversion processes (CO$_2$-dilution). The thickness of arrows represents the ratio of the reaction rates between the CO$_2$-dilution case and the reference case (N$_2$-dilution), which is summarized in Table 3 (i.e., thick solid arrows = enhanced reactions in CO$_2$-dilution, thin solid arrows = moderate reactions in CO$_2$-dilution, thin dashed arrows = suppressed reactions in CO$_2$-dilution).
Figure 1 Ion transport membrane (ITM) for air separation and fuel conversion in the absence of nitrogen. Oxygen selectively permeates from the air side to the sweep side of an ITM. On the sweep side, fuel conversion takes place in a nitrogen-free environment, as the fuel approaches the membrane while the permeated oxygen transports in the opposite direction.
Figure 2 ITM unit configuration based on a planar, finite-gap stagnation flow considered in this investigation (air channel height $H_{\text{air}} = 50.8 \, \text{mm}$, sweep gas channel height $H_{\text{sweep}} = 25.4 \, \text{mm}$). ITM divides the overall physical domain into an air domain and a sweep gas domain, each of which is considered numerically. $y_{\text{air}} = 0$ and $y_{\text{sweep}} = 0$ are located on the membrane surfaces of the air and sweep side, respectively.
Figure 3 Normal velocity and strain rate along with the flame location (where, solid lines represent CO₂-dilution, and dotted lines stand for N₂-dilution). $y_{sweep} = 0$ is located on the membrane surface of the sweep side.
Figure 4 The variations of (a) temperature and the local equivalence ratio and (b) CH$_4$ and O$_2$ concentrations, along with the flame location (where, solid lines represent CO$_2$-dilution, dash lines are for CO$_2$ (inert, eliminating the chemical effects of CO$_2$)-dilution, and dotted lines stand for N$_2$-dilution). A lower slope of the local equivalence ratio represents a wider overlap of CH$_4$ and O$_2$, and hence a thicker flame. \( y_{\text{mem,exp}} = 0 \) is located on the membrane surface of the sweep side.
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Figure 7 The concentrations of the important radicals (a) H and O and (b) OH and CH$_3$, along with the flame location (where, solid lines represent CO$_2$-dilution, and dotted lines stand for N$_2$-dilution). $y_{sw\text{ gap}} = 0$ is located on the membrane surface of the sweep side.
Figure 8 Soot precursors, C$_2$H$_2$ and C$_2$H$_4$, concentrations, along with the flame location (where, solid lines represent CO$_2$-dilution, and dotted lines stand for N$_2$-dilution). $y_{sweep} = 0$ is located on the membrane surface of the sweep side.
Figure 9 Gross heat release rate, the flame location and the reaction rate of dominant reactions for the primary reaction zone where \( \text{CH}_4 \) is converted to CO ((a) and (c)) and the secondary reaction zone in which CO oxidation and \( \text{H}_2/\text{O}_2 \) reactions take place ((b) and (d)). The minus sign in front of a reaction number means by its reverse direction. (a) and (b) belongs to CO\(_2\)-dilution, while (c) and (d) are for N\(_2\)-dilution. \( y_{\text{ave} / \text{exp}} = 0 \) is located on the membrane surface of the sweep side.
Figure 10 Reaction pathway analysis showing the important carbon-containing species and dominant reactions in ITM supported fuel conversion processes (CO\textsubscript{2}-dilution). The thickness of arrows represents the ratio of the reaction rates between the CO\textsubscript{2}-dilution case and the reference case (N\textsubscript{2}-dilution), which is summarized in Table 3 (i.e., thick solid arrows = enhanced reactions in CO\textsubscript{2}-dilution, thin solid arrows = moderate reactions in CO\textsubscript{2}-dilution, thin dashed arrows = suppressed reactions in CO\textsubscript{2}-dilution).
List of Tables

Table 1 Pre-exponential factors and activation energies of $D_{\rho_{0}}$, $k_f$ and $k_r$ used in the oxygen permeation flux expression considered in this study (obtained from [16]).

Table 2 The effects of the flame location on the flame temperature and the oxygen permeation rate.

Table 3 Important reactions considered in this investigation (obtained from the reaction pathway analysis), which determine the reaction products and govern predominantly the overall fuel conversion processes, and their enthalpy of reaction at standard temperature and pressure, $\Delta H_{STP}$. The spatially averaged reaction rate, $\bar{n}_i$, represents the strength of each reaction for both CO$_2$-dilution and N$_2$-dilution cases. The CH$_2$ exists in two electric states, singlet and triplet, and (S) in R.2 and R.10 represents its singlet state.
Table 1 Pre-exponential factors and activation energies of $D_{\text{VO}}$, $k_f$ and $k_r$ used in the oxygen permeation flux expression considered in this study (obtained from [16]).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pre-exponential factor, $A$</th>
<th>Activation energy, $E_a$ [J/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unit</td>
<td>Value</td>
</tr>
<tr>
<td>$D_{\text{VO}}$</td>
<td>[cm$^2$/s]</td>
<td>$(1.01\pm0.05) \times 10^2$</td>
</tr>
<tr>
<td>$k_f$</td>
<td>[cm/atm$^{0.5}$/s]</td>
<td>$(9.21\pm0.44) \times 10^8$</td>
</tr>
<tr>
<td>$k_r$</td>
<td>[mol/cm$^2$/s]</td>
<td>$(1.75\pm0.087) \times 10^{11}$</td>
</tr>
</tbody>
</table>
Table 2 The effects of the flame location on the flame temperature and the oxygen permeation rate.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Base case (CO₂ diluted sweep gas)</th>
<th>Reference case (N₂ diluted sweep gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame location (from the membrane)</td>
<td>[mm]</td>
<td>3.82</td>
<td>4.28</td>
</tr>
<tr>
<td>Stagnation point (from the membrane)</td>
<td>[mm]</td>
<td>2.10</td>
<td>1.80</td>
</tr>
<tr>
<td>Heat transfer towards the membrane</td>
<td>[W/m²]</td>
<td>7436</td>
<td>7496</td>
</tr>
<tr>
<td>Adiabatic flame temperature</td>
<td>[K]</td>
<td>1980</td>
<td>2056</td>
</tr>
<tr>
<td>Maximum flame temperature</td>
<td>[K]</td>
<td>1537</td>
<td>1589</td>
</tr>
<tr>
<td>Membrane temperature</td>
<td>[K]</td>
<td>1311</td>
<td>1311</td>
</tr>
<tr>
<td>Oxygen mass fraction at the membrane surface</td>
<td>[\text{--}]</td>
<td>$5.01 \times 10^{-2}$</td>
<td>$6.41 \times 10^{-2}$</td>
</tr>
<tr>
<td>Oxygen partial pressure at the membrane surface</td>
<td>[atm]</td>
<td>$6.37 \times 10^{-2}$</td>
<td>$5.65 \times 10^{-2}$</td>
</tr>
<tr>
<td>Oxygen permeation rate</td>
<td>[\mu mol/cm²/s]</td>
<td>3.53</td>
<td>3.87</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction</th>
<th>( \Delta H_{\text{STP}} ) [kJ/mol]</th>
<th>( \overline{\eta}_\text{r} ) [mol/m(^3)/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO(_2)-dilution</td>
<td>N(_2)-dilution</td>
</tr>
<tr>
<td>(R.1)</td>
<td>( H + CO_2 \leftrightarrow OH + CO )</td>
<td>104.3</td>
<td>0 : ( y_{\text{flame}} : -5.76 )</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>( y_{\text{flame}} : H_{\text{sweep}} : 2.31 \times 10^{-1} )</td>
</tr>
<tr>
<td>(R.2)</td>
<td>( CH_2(s) + CO_2 \leftrightarrow CH_2O + CO )</td>
<td>-255.5</td>
<td>2.26 \times 10^{-1}</td>
</tr>
<tr>
<td>(R.3)</td>
<td>( H + O_2 \leftrightarrow O + OH )</td>
<td>70.5</td>
<td>1.02</td>
</tr>
<tr>
<td>(R.4)</td>
<td>( O + H_2 \leftrightarrow H + OH )</td>
<td>8.2</td>
<td>5.39 \times 10^{-2}</td>
</tr>
<tr>
<td>(R.5)</td>
<td>( H + O_2 + M \leftrightarrow HO_2 + M )</td>
<td>-205.5</td>
<td>2.85 \times 10^{-1}</td>
</tr>
<tr>
<td>(R.6)</td>
<td>( H + CH_4 \leftrightarrow CH_3 + H_2 )</td>
<td>3.5</td>
<td>1.02 \times 10^{-1}</td>
</tr>
<tr>
<td>(R.7)</td>
<td>( H + H_2O \leftrightarrow OH + H_2 )</td>
<td>63.2</td>
<td>0 : ( y_{\text{flame}} : -1.62 )</td>
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<tr>
<td></td>
<td></td>
<td>( y_{\text{flame}} : H_{\text{sweep}} : 1.36 \times 10^{-2} )</td>
<td>( y_{\text{flame}} : H_{\text{sweep}} : 1.71 \times 10^{-1} )</td>
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<tr>
<td>(R.8)</td>
<td>( H + CH_2O \leftrightarrow HCO + H_2 )</td>
<td>-67.4</td>
<td>7.57 \times 10^{-2}</td>
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<tr>
<td>(R.9)</td>
<td>( OH + CH_4 \leftrightarrow CH_3 + H_2O )</td>
<td>-59.7</td>
<td>5.58 \times 10^{-1}</td>
</tr>
<tr>
<td>(R.10)</td>
<td>( OH + CH_3 \leftrightarrow CH_3(s) + H_2O )</td>
<td>1.8</td>
<td>2.67 \times 10^{-1}</td>
</tr>
<tr>
<td>(R.11)</td>
<td>( OH + CH_2O \leftrightarrow HCO + H_2O )</td>
<td>-130.6</td>
<td>3.12 \times 10^{-1}</td>
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<tr>
<td>(R.12)</td>
<td>( 2CH_3 + M \leftrightarrow C_2H_6 + M )</td>
<td>-377.7</td>
<td>5.87 \times 10^{-2}</td>
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<tr>
<td>(R.13)</td>
<td>( 2CH_3 \leftrightarrow H + C_2H_5 )</td>
<td>-175.1</td>
<td>1.85 \times 10^{-2}</td>
</tr>
<tr>
<td>(R.14)</td>
<td>( C_2H_6 + OH \leftrightarrow C_2H_5 + H_2O )</td>
<td>-78.7</td>
<td>3.90 \times 10^{-2}</td>
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<tr>
<td>(R.15)</td>
<td>( C_2H_5 + M \leftrightarrow H + C_2H_4 + M )</td>
<td>151.8</td>
<td>7.36 \times 10^{-2}</td>
</tr>
<tr>
<td>(R.16)</td>
<td>( C_2H_4 + M \leftrightarrow H_2 + C_2H_2 + M )</td>
<td>175.7</td>
<td>4.05 \times 10^{-3}</td>
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<tr>
<td>(R.17)</td>
<td>$HCO + M \leftrightarrow H + CO + M$</td>
<td>65.5</td>
<td>$2.74 \times 10^{-1}$</td>
</tr>
<tr>
<td>(R.18)</td>
<td>$OH + HO_2 \leftrightarrow O_2 + H_2O$</td>
<td>−293.7</td>
<td>$4.02 \times 10^{-1}$</td>
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<tr>
<td>(R.19)</td>
<td>$H + O_2 + H_2O \leftrightarrow HO_2 + H_2O$</td>
<td>−205.5</td>
<td>$1.83 \times 10^{-1}$</td>
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<tr>
<td>(R.20)</td>
<td>$CH_3 + O_2 \leftrightarrow OH + CH_2O$</td>
<td>−216.1</td>
<td>$1.63 \times 10^{-2}$</td>
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