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THE COUPLING EFFECT OF GAS-PHASE CHEMISTRY AND SURFACE REACTIONS ON OXYGEN PERMEATION AND FUEL CONVERSION IN ITM REACTORS

Jongsup Hong a, Patrick Kirchen b, Ahmed F. Ghoniem c,*

a High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Korea
b Department of Mechanical Engineering, University of British Columbia, 2054-6250 Applied Science Lane, Vancouver BC, V6T 1Z4, CANADA
c Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

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ABSTRACT

The effect of the coupling between heterogeneous catalytic reactions supported by an ion transport membrane (ITM) and gas-phase chemistry on fuel conversion and oxygen permeation in ITM reactors is examined. In ITM reactors, thermochemical reactions take place in the gas-phase and on the membrane surface, both of which interact with oxygen permeation. However, this coupling between gas-phase and surface chemistry has not been examined in detail. In this study, a parametric analysis using numerical simulations is conducted to investigate this coupling and its impact on fuel conversion and oxygen permeation rates. A thermochemical model that incorporates heterogeneous chemistry on the membrane surface and detailed chemical kinetics in the gas-phase is used. Results show that fuel conversion and oxygen permeation are strongly influenced by the simultaneous action of both chemistries. It is shown that the coupling somewhat suppresses the gas-phase kinetics and reduces fuel conversion, both attributed to extensive thermal energy transfer towards the membrane which conducts it to the air side and radiates to the reactor walls. The reaction pathway and products, in the form of syngas and C₂ hydrocarbons, are also affected. In addition, the operating regimes of ITM reactors in which heterogeneous- or/and homogeneous-phase reactions predominantly contribute to fuel conversion and oxygen permeation are elucidated.

* Corresponding author. Tel.: +1 617 253 2295; Fax: +1 617 253 5981
Email address: ghoniem@mit.edu (Ahmed F. Ghoniem)
1. Introduction

Ion transport membrane (ITM) reactors have been proposed as promising hydrocarbon conversion technologies with enhanced product selectivity. In conventional catalytic reactors, product selectivity is of great concern because successive, uncontrolled gas-phase reactions with residual oxygen and nitrogen can result in undesired products or thermal states. To overcome these barriers, dense perovskite membranes or mixed ionic-electronic conducting membranes have been proposed for hydrocarbon conversion reactors. They have been shown to have both oxygen perm-selectivity [1] and catalytic activity for hydrocarbon conversion [2]. In contrast to conventional catalytic reactors where a fuel and air are premixed before reaching the catalyst surface, in ITM reactors, the fuel and air are introduced in separate streams on different sides of the dense membrane. Oxygen selectively permeates via solid state diffusion and subsequently reacts on the catalytic surface or/and in the gas-phase with the fuel. These membranes have been shown to act as hydrocarbon catalysts [3-7]. Their catalytic activity, coupled with oxygen permeation in a controlled manner, enables their use as catalytic membrane reactors with higher product selectivity [2]. Multiple applications have been extensively investigated using typically methane as a feedstock such as; oxidative coupling [7-10]; partial oxidation [5, 6, 11]; and oxy-fuel combustion [12-16]. In spite of these promising applications, the operating regimes, in which fuel conversion and oxygen permeation are predominantly attributed to catalytic or/and gas-phase reactions, have not been examined.

Since the oxygen permeation rate is not known a priori and rather depends on the local thermodynamic state, i.e., oxygen chemical potential on both sides of the membrane and its temperature, hydrocarbon conversion reactions on the sweep side may alter the extent of oxygen permeation significantly, and vice versa. Whereas conventional catalytic reactors operate typically at a low temperature of 300~700 °C, ITM reactors require a high temperature of 800~1000 °C to promote oxygen permeation sufficient for fuel conversion processes [2]. In this high temperature regime, homogeneous-phase as well as catalytic surface reactions may play important roles in determining the extent of fuel conversion and the product selectivity [17]. The coupling between homogeneous and heterogeneous fuel conversion and oxygen permeation can be substantial [9]. Therefore, to investigate ITM reactor operating regimes and control fuel conversion and oxygen permeation, a detailed numerical modeling that accounts for the coupling of oxygen permeation and both homogeneous and heterogeneous chemistry is proposed.
Considering a simple reactor model such as a continuously stirred tank reactor (CSTR) and assuming two limiting oxidation kinetics, extremely fast reaction and no conversion, Akin and Lin [18] examined the sensitivity of the oxygen permeation rate to the extent of chemical reactions, the reactive sweep gas flow rate and the oxygen partial pressure on the air side. Rui et al. [19] built on the same CSTR model and investigated the influence of the finite-rate chemical kinetics on oxygen permeation rate. Although the results from these two studies have elucidated that fuel oxidation reactions and their chemical kinetic rates have substantial influences on oxygen permeation, their models considered a simple well-stirred reactor which does not resolve the state near the surface. Ben-Mansour et al. [13], Habib et al. [14] and Nemitallah et al. [15, 16] modeled two dimensional reactors and considered the local thermodynamic state to evaluate the permeation rate, but assumed one- or two-step global reactions without examining the coupling of homogeneous and heterogeneous chemistry to minimize computational costs. Wang and Lin [20] and Tan et al. [12] assumed the kinetic parameters of perovskite membranes, but they ignored homogeneous-phase reactions that may take place at the temperature considered in their study. Zhang et al. [21] accounted for gas-phase reactions for methane, carbon monoxide and hydrogen, but they assumed one-step global reactions at equilibrium. Modeling studies have been also performed on ITM reactors for syngas production [22-25], but these models used single-step global reactions ignoring the coupling. The key features of the previous modeling studies are summarized in Table 1.

In our previous studies, a homogeneous-phase reaction zone established on the sweep side and its interaction with oxygen permeation were examined, and the heterogeneous chemistry for perovskite membranes was developed. We formulated a spatially resolved physical model, which incorporates detailed gas-phase chemical kinetics and transport to parameterize an oxygen permeation rate expression in terms of the local thermodynamic state in the immediate vicinity of the membrane [26]. The numerical model was then used to characterize a diffusion-controlled reaction zone on the sweep side [27], as well as its interaction with the oxygen permeation rate through the local thermodynamic state [17]. Key features of the reaction zone stabilized on the sweep side including its location, temperature, thickness and structure were elucidated. The feedback interactions between fuel conversion and oxygen permeation through the reaction zone location relative to the membrane, gas-phase chemical kinetics and flow field have been examined, highlighting that the local thermodynamic state near the membrane and homogeneous chemical kinetics should be accounted for in high temperature ITM reactors in order to accurately characterize the oxygen permeation. Furthermore, to characterize the catalytic activity of perovskite membranes, the kinetic parameters for catalytic oxidation reactions on the ITM surface were estimated [28].
To develop a heterogeneous kinetic mechanism for \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d} \) membranes, which accounts for oxygen surface exchange and catalytic fuel conversion, we built on the spatially resolved physical model to take into account the concentrations of surface and bulk-phase (solid state) species. The kinetic parameters for oxygen surface exchange processes and catalytic reactions for methane, carbon monoxide and hydrogen were estimated using the model and the oxygen permeation rates measured experimentally. It was shown that both catalytic and gas-phase reactions play important roles.

In this study, the effect of catalytic surface reactions supported by an ITM and their coupling with homogeneous-phase chemistry on fuel conversion and oxygen permeation is investigated using numerical simulations. Our physical model incorporates both homogeneous and heterogeneous chemistry, conductive and radiative heat transfer and flow near the surface, and is able to examine their coupling and interaction with oxygen permeation by resolving the local gas-phase, surface and bulk-phase thermodynamic state. By considering sweep gas conditions at which both gas-phase and surface reactions contribute to the overall fuel conversion, their coupling through the local thermodynamic state and chemical kinetics is analyzed. Then, a parametric study of key independent variables, which include the fuel concentration in the sweep gas and its inlet temperature, is conducted to examine ITM reactor operating regimes.

In Section 2, the numerical model employed in this study is described. Section 3 includes the discussion regarding the coupling between homogeneous-phase and catalytic oxidation reactions and its effect on the fuel conversion and oxygen permeation rate. In Section 4, ITM reactor operating regimes are examined to show the dependence of oxygen permeation and fuel conversion on sweep side conditions.

2. **Numerical approach**

ITM reactor operating regimes and the effect of homogenous-phase and surface catalytic reactions on the oxygen permeation rate and fuel conversion are examined using numerical simulations. Fig. 1 illustrates the key physical and chemical processes occurring in the vicinity of the ITM. As oxygen molecules approach the membrane surface on the air side, they experience oxygen surface exchange and successive bulk diffusion inside the membrane lattice. When the oxygen reaches the other side (sweep side) of the membrane, it goes through not only oxygen surface exchange processes to be
released to the gas-phase, but also catalytic fuel oxidation and homogeneous-phase chemical reactions. Both mass, i.e., oxygen permeation, and heat transfer take place across the membrane, which links the air and sweep gas sides. To investigate these coupled physical and chemical processes, i.e., oxygen permeation and fuel conversion, detailed chemistry and transport in both homogeneous- and heterogeneous-phase should be considered [18, 19] in terms of the local thermodynamic state near the membrane. To minimize computational costs, while still considering all relevant processes, a self-similar stagnation-flow configuration was selected.

The spatially resolved physical model has been developed to examine the coupling of oxygen permeation and homogeneous and heterogeneous chemical reactions. In our previous study [26], we developed the homogeneous-phase physical model that considers a planar, finite-gap stagnation-flow configuration, on which the experimental apparatus in our laboratory is also based [29, 30]. Considering the similarity behavior of the flow, the dimensionality of the model is reduced to one dimension. In the neighborhood of the stagnation line, a self-similar solution in the direction normal to the membrane can describe the flow variables, i.e., density, velocity, temperature and species concentration. The model resolves spatially the gas-phase flow, transport and chemical reactions, all of which are coupled with the oxygen permeation flux and heat flux across the membrane. To model the gas-phase chemical reactions, a detailed chemical kinetic mechanism (GRI-Mech 3.0 [31]) is employed, while Cantera [32] along with NASA polynomials is used to integrate the multi-step chemical reactions and evaluate thermodynamic and transport properties. Then, we built on this physical model to develop heterogeneous chemistry for perovskite membranes [28]. The governing equations for surface and bulk-phase (solid state) species are added to the spatially resolved physical model, and the flux-matching boundary conditions at the membrane surface are used to couple the surface reactions with the bulk diffusion through the membrane and the gas-phase local thermodynamic state in the immediate neighborhood of the membrane. Heterogeneous oxygen surface exchange, R. 1 and R. 2, and catalytic oxidation reactions for methane, carbon monoxide and hydrogen, R. 3 to R. 5, were accounted for:

\[
\begin{align*}
O_2 + 2(s) &\rightarrow 2O^- (s) + 2h^+ & (R. 1) \\
O^- (s) + V_0 &\rightarrow O_2^+ (s) + h^- & (R. 2) \\
2CH_4 + 2h^- + O_2^+ &\rightarrow 2CH_3 + H_2O + V_0 & (R. 3) \\
CO + 2h^- + O_2^+ &\rightarrow CO_2 + V_0 & (R. 4) \\
H_2 + 2h^- + O_2^+ &\rightarrow H_2O + V_0 & (R. 5)
\end{align*}
\]
where, \( (s) \) is the vacant surface site on the membrane surface; \( O^- (s) \) is the adsorbed singly-charged surface oxygen anion; \( V_o^- \) is the oxygen vacancy; \( O_o^\Delta \) is the lattice (bulk) oxygen ion; \( h^+ \) is the electron hole. It should be noted that the electronic conductivity of typical perovskite membranes is sufficiently high that, at steady state, the concentration of electron holes is assumed constant throughout the membrane and its effect on heterogeneous chemistry is neglected. The governing equations and boundary conditions at the air and sweep gas inlets and the membrane surface considered in this study are summarized in Table 2. The further details of the spatially resolved physical model were discussed in our previous studies [26, 28]. The model has been validated against experimental results [30], and further comparison will be performed although only a few results from ITM reactor experiments are available in literature.

In this study, the numerical model that incorporates both homogeneous and heterogeneous chemistry is used to examine the role of both homogeneous-phase and surface catalytic oxidation reactions in determining the fuel conversion and oxygen permeation rate and elucidate ITM reactor operating regimes. Methane being diluted by carbon dioxide is used as a sweep gas, which features dry reforming of methane and carbon dioxide recirculation in carbon capture applications. A membrane thickness of 100 μm for which both surface exchange and bulk diffusion are relevant [33] is assumed throughout the study. Sweep side conditions characterized based on the fuel concentration in the sweep gas and its inlet temperature are considered key operating conditions, while the sweep gas flow rate of \( 4.39 \times 10^{-4} \text{ m}^3/	ext{s} \) (sweep gas velocity at the inlet = \( 7.56 \times 10^{-2} \text{ m/s} \)) is maintained constant. Air side conditions, which include the air inlet flow rate of \( 1.97 \times 10^{-3} \text{ m}^3/	ext{s} \) (air velocity at the inlet = \( 3.70 \times 10^{-1} \text{ m/s} \)), are maintained constant, while its inlet temperature varies with that of the sweep gas to the same extent. These flow conditions result in sufficient residence time for thermochemical reactions to be stabilized on the sweep side of the ITM [17].

3. Coupling of gas-phase chemistry and surface reactions

A previous parametric study with respect to key operating conditions has shown the sweep side conditions at which homogeneous chemistry plays an important role on the sweep side of the membrane [17]. It has been shown that, when the gas-phase reaction zone approaches the membrane for systems with a high fuel (methane) concentration in the sweep gas or high flow rate, reactants such as methane, carbon monoxide and hydrogen can reach the membrane surface,
which promotes catalytic fuel conversion. Under these conditions, both homogeneous and heterogeneous chemistry may have an important effect on fuel conversion and oxygen permeation, and hence their coupling should be examined. This was done using a sweep gas with conditions summarized in Table 3, under which a gas-phase reaction zone is established in the vicinity of the membrane. Results are compared to the case when only gas-phase reactions are accounted for. It is found that the oxygen permeation rate is slightly raised to 4.62 μmol/cm²/s by catalytic oxidation reactions, i.e., R. 3 to R. 5 (along with homogeneous-phase reactions), in comparison with 4.51 μmol/cm²/s attributed to only gas-phase reactions. On the other hand, the CH₄ conversion is lowered from 22.8%, when only gas-phase reactions are implemented, to 18.3% (comprised of gas-phase conversion, 16.8%, and catalytic surface conversion, 1.5%) for cases in which the membrane acts as a fuel conversion catalyst according to R. 3 to R. 5. The CH₄ conversion, $X_{\text{CH}_4}$, is defined as,

$$X_{\text{CH}_4,\text{gas-phase}} = \frac{A_{\text{m,em}} \int_{0}^{t} \dot{y}_{\text{CH}_4,\text{SW,exp}} d\tau_{\text{SW,exp}}}{F_{\text{SW,exp}} \frac{\dot{\xi}_{\text{CH}_4,\text{SW,exp}}}{\rho_{\text{SW,exp}}}}$$

$$X_{\text{CH}_4,\text{catalytic}} = \frac{A_{\text{m,em}} (-\dot{\xi}_{\text{CH}_4})}{F_{\text{SW,exp}} \frac{\dot{\xi}_{\text{CH}_4,\text{SW,exp}}}{\rho_{\text{SW,exp}}}}$$

$$X_{\text{CH}_4,\text{total}} = X_{\text{CH}_4,\text{gas-phase}} + X_{\text{CH}_4,\text{catalytic}}$$

where $A_{\text{m,em}}$ is the membrane area; $F_{\text{SW,exp}}$ is the sweep gas flow rate; $\xi_{\text{CH}_4,\text{SW,exp}}$ is the fuel concentration in the sweep gas; $\rho_{\text{SW,exp}}$ is the molar density of the sweep gas; $\dot{\xi}_{\text{CH}_4}$ and $\dot{\xi}_{\text{CH}_4}$ are CH₄ molar production rate in the gas-phase and catalytic surface, respectively. To elucidate the reason why the reduction in the CH₄ conversion arises, gas-phase species concentrations, temperature and reaction rates are investigated.

The coupling of heterogeneous and homogeneous chemistry influences the gas-phase reaction kinetics. Fig. 2(a) shows that the concentrations of methane and oxygen in the gas-phase are higher in the case for which catalytic surface reactions are taken into account. Even if catalytic fuel conversion processes contribute to methane oxidation and oxygen consumption on the sweep side of the membrane, more fuel and oxidant exist in the gas-phase without being reacted. This is attributed to slower kinetic rates of methane conversion and oxygen consumption reactions in the gas-phase (see reaction expressions below), as shown in Fig. 2(b). Furthermore, in the immediate vicinity of the membrane, the backward reaction of methane conversion, i.e., the reverse direction of R. 6, is favored.
Note that the methane reaction with hydrogen radical, R. 6, is one of key reaction pathways to initiate the homogeneous-phase fuel conversion kinetics, while the oxygen reaction with hydrogen radical, R. 7, is a primary chain-branching reaction to produce more radicals. Since the chain-branching reaction is suppressed, radical concentrations in the gas-phase are lowered, resulting in the lower gas-phase kinetic rates. As a result, the extent of the overall homogeneous-phase reactions is reduced, so is the methane conversion reaction. In addition, the methyl radical produced from the catalytic surface reaction, R. 3, is recombined in the gas-phase to form methane in the presence of hydrogen, i.e., the backward reaction of R. 6. When the reaction zone is established in the immediate neighborhood of the membrane, partial oxidation of methane in the gas-phase takes place, and hence a substantial amount of hydrogen appears near it [17]. When this hydrogen meets the methyl radical produced via heterogeneous chemistry, the reverse direction of the methane conversion reaction becomes dominant, inhibiting the initiation of the homogeneous-phase fuel conversion kinetics. This peculiar phenomenon occurs as the conversion of methane has been considered in the conventional pathway resulting in a methyl radical, i.e., R. 3. If the direct conversion of methane to COx on the membrane surface is accounted for, the effect of catalytic surface reactions on the gas-phase kinetics may change, which will be addressed in the future study.

To examine further the influence of catalytic surface reactions on the homogeneous-phase reaction kinetics, a reaction pathway analysis is conducted. Fig. 3 shows the primary homogeneous-phase reaction pathway for methane when catalytic surface reactions are considered, as compared to the case in which only homogeneous chemistry is accounted for (i.e., arrows in Fig. 3 represent the relative strengths of each pathway). The pathways regarding the reactions with hydroxyl radicals, i.e., H, O and OH, are suppressed, whereas those of methyl radical are strengthened. As discussed above, when catalytic surface reactions are considered, a slower rate of the chain-branching reaction, R. 7, results in lower hydroxyl radical concentrations and hence a drop in the relevant radical reaction rates. Hydroxyl radical reactions play an important role in methane oxidation to form syngas or oxy-fuel combustion products. Thus, reduction in their reaction rates weakens the homogeneous-phase pathways for the formation of partially- or fully-oxidized products. In the meantime, the methyl radical produced from the surface reaction promotes its gas-phase reactions, in particular, the C2 chemistry. As a result of
the interactions between homogeneous and heterogeneous chemistry, the formation of ethane and ethylene is promoted (see Fig. 4) [7], while influencing the kinetics in the gas-phase, which may affect ITM reactor operating regimes, as will be discussed in the following section.

Heterogeneous chemistry and the lower gas-phase kinetic rates affect the concentrations of the products. Fig. 5(a) shows the lower concentrations of carbon monoxide and hydrogen, when catalytic surface reactions are introduced. The catalytic oxidation reactions on the membrane surface, R. 4 and R. 5, oxidize them completely to produce carbon dioxide and water, respectively. In addition, since the gas-phase kinetics is somewhat suppressed, their formation from methane through homogeneous chemistry decreases. As a result, lower concentrations of carbon monoxide and hydrogen exist in the gas-phase when both heterogeneous and homogeneous chemistry contributes to fuel conversion. On the other hand, as shown in Fig. 5(b), taking into account surface reactions raises carbon dioxide concentration, but lowers water concentration. The former is explained by the fact that the surface kinetic rate of carbon monoxide oxidation are faster than that of hydrogen oxidation [28]. Furthermore, more carbon monoxide than hydrogen is produced through homogeneous-phase reactions and reaches the membrane surface (see Fig. 5(a)), promoting its catalytic oxidation. This increases the formation of carbon dioxide and hence its concentration in the gas-phase. While catalytic reactions on the membrane surface are predominantly governed by carbon monoxide oxidation, the homogeneous-phase reaction rates are lowered, both of which reduce the production of water in the gas-phase. The coupling of homogeneous-phase and catalytic surface reactions can result in different overall reaction schemes, ranging from partial oxidation of methane to oxy-fuel combustion, and to oxidative coupling of methane.

The catalytic surface reactions enhance the thermal energy transfer from the sweep side towards the membrane and its effect on the gas temperature and the homogeneous-phase reaction kinetics. To examine the reason why the homogeneous-phase kinetic rates are lowered, the reaction zone temperature in the gas-phase for both cases, i.e., with and without heterogeneous chemistry, are compared. Given the same fuel concentration in the sweep gas for both cases, the reaction zone temperature is an important parameter that influences the gas-phase reaction kinetic rates. Fig. 6 shows that accounting for both homogeneous and heterogeneous chemistry lowers the gas temperature. This is attributed to the exothermic reactions being moved from the gas-phase towards the membrane surface. The membrane conducts this reaction heat to the air side and radiates to the reactor walls [17, 27]. Compared to conventional catalytic reactors which are
essentially adiabatic, ITM reactors experience extensive thermal energy transfer through the membrane. When surface reactions take place, hot reactants are adsorbed and converted catalytically on the membrane surface, increasing the thermal energy transfer by species transport and exothermic reactions, which is raised from 9.07 kW/m\(^2\) to 11.6 kW/m\(^2\). The membrane absorbs the heat released from both homogeneous-phase and catalytic surface reactions and transfers it towards the air side and the reactor walls. As a result of catalytic surface reactions, the heat loss from the sweep side increases, which lowers the gas-phase reaction zone temperature. The lower gaseous reaction zone temperature in turn reduces the primary chain-branching reaction, R. 7, which is highly endothermic. Therefore, the rise in the thermal energy transfer from the sweep side to the air side and the reactor walls, attributed to heterogeneous chemistry, lowers homogeneous-phase kinetic rates. When both catalytic surface and homogeneous-phase reactions contribute to fuel conversion on the sweep side, the effect of the thermal energy transfer on the temperature and hence chemical kinetics is significant.

To summarize, the coupling between catalytic surface reactions and gas-phase chemistry raises the thermal energy transfer from the sweep side towards the membrane, which reduces the gas-phase reaction zone temperature. This lowers hydroxyl radical concentrations and the homogeneous kinetic rates, reducing the extent of methane conversion. Moreover, heterogeneous chemistry enhances carbon monoxide and hydrogen oxidation and produces more methyl radical. This alters the homogeneous-phase reaction pathway to promote C\(_2\) chemistry while reducing syngas formation. As a result, the operating modes of the ITM reactor may change from partial oxidation of methane to oxy-fuel combustion, and to oxidative coupling with lower fuel conversion and higher oxygen permeation.

4. **ITM reactor operating regimes**

Given that the coupling of homogeneous-phase and catalytic surface reactions supported by an ITM has a substantial impact on the reaction kinetics, pathway, products and thermal energy transfer and hence fuel conversion and oxygen permeation, operating conditions of ITM reactors should be examined in the presence of both chemistries. To investigate their operating regimes, a parametric study is conducted with respect to key independent parameters affecting fuel conversion, including fuel concentration and temperature. It has been shown that these parameters influence significantly the homogeneous-phase fuel conversion rate and the oxygen permeation rate, when only gas-phase reactions are accounted for [17]. In this study, the fuel concentration is varied from 6% to 75% on a molar basis, and the sweep gas
inlet temperature is changed from 1000K to 1300K, in the presence of homogeneous and heterogeneous chemistry. The fuel concentration and sweep gas inlet temperature are varied simultaneously at the given sweep gas flow rate. These sweep side conditions are selected in order to represent the typical operating conditions of ITM reactors reported in the literature [2].

4.1. Homogeneous-phase and catalytic surface reaction regimes

In comparison with non-catalytic fuel reforming or combustion, the temperature in ITM reactors is kept low to protect the membrane, resulting in slower homogeneous-phase chemical kinetics. On the other hand, its temperature is higher than that of conventional catalytic reactors, which may enhance the catalytic surface reaction kinetics. In addition, oxygen permeation does not enable premixing of reactants and oxygen, and a diffusion-controlled reaction zone is established on the sweep side of the membrane. Thus, controlling the chemical kinetics through the fuel concentration and sweep gas temperature is important to fuel conversion rate, reaction products and oxygen permeation rate. Fig. 7(a) and Fig. 7(b) show CH₄ conversion and oxygen permeation rate, respectively, as function of fuel concentration and sweep gas inlet temperature. CH₄ conversion is nearly negligible at sweep gas temperatures below 1100K and grows up to 5% as the temperature is raised to 1200K. Whereas high fuel concentration enables more fuel conversion at temperatures below 1200K, CH₄ conversion increases significantly as the fuel concentration is lowered at the temperature above 1200K. In addition, a small reduction in CH₄ conversion at high temperature and high fuel concentration is observed. In the meantime, the oxygen permeation rate is raised gradually with fuel concentration and sweep gas temperature (except at 1300K, which is explained in [17]), while showing a substantial increase at temperatures above 1200K, which coincides with a high CH₄ conversion at this temperature range. To examine why these operating regimes exist, the contribution of homogeneous-phase and catalytic surface reactions to fuel conversion and oxygen permeation and their coupling are analyzed.

The effect of homogeneous or heterogeneous chemistry on fuel conversion processes is apparent at high temperature but two different limiting ranges of the fuel concentration exist. Fig. 8(a) shows CH₄ conversion attributed to gas-phase reactions as the fuel concentration and temperature are varied. The homogeneous-phase CH₄ conversion is strong for temperatures above 1200K and fuel concentrations below 40%, whereas below this temperature gas-phase conversion is nearly negligible. For fuel concentrations above 60% and gas temperatures above 1200K, homogeneous-phase reactions act adversely and reduce the overall CH₄ conversion. To facilitate the gas-phase chemical kinetics, the sweep gas inlet temperature needs to be raised above a light-off temperature, which is approximately 1200K. As seen in Fig. 8(a), the
homogeneous-phase CH₄ conversion is not substantial below 1200K no matter what fuel concentration is considered. When the sweep gas inlet temperature is raised above the light-off temperature, requisite stoichiometry between the fuel and oxygen should be met to stabilize a homogeneous-phase reaction zone. Since the oxygen permeation rate from typical perovskite membranes is not substantial [1, 2], the fuel concentration in the sweep gas needs to be maintained low to satisfy the stoichiometry required for establishing a diffusion-controlled reaction zone in the gas-phase. If the fuel concentration is raised while maintaining the temperature high, it is not feasible to meet the requisite stoichiometry and establish a finite reaction zone on the sweep side, even though a high fuel concentration may promote the gas-phase chemical kinetics. Consequently, the contribution of homogeneous-phase reactions to CH₄ conversion is significant but limited at low fuel concentration. In addition, at fuel concentration above 60%, a reduction in the homogeneous-phase CH₄ conversion results from a strong influence of heterogeneous chemistry (see Fig. 8(b)), as discussed in Section 3.

As shown in Fig. 8(b), catalytic surface CH₄ conversion is effective for sweep side conditions at which gas-phase reactions are suppressed, i.e., high fuel concentrations above 40% and high temperatures above 1200K. The catalytic CH₄ conversion increases with increasing fuel concentration. Interestingly, when the homogeneous-phase CH₄ conversion reaches its maximum at low fuel concentration and high temperature, the surface CH₄ conversion decreases although a high temperature can enhance the catalytic oxidation kinetics. At sweep gas inlet temperatures below 1100K, the catalytic CH₄ oxidation rate is too slow [28], and oxygen permeation is not sufficient to facilitate fuel conversion even if high fuel concentration reaches the membrane surface. Compared to typical catalysts utilized at low temperature, the heterogeneous reactions activity using an ITM at this low temperature regime is limited. As the sweep gas temperature is raised, catalytic reaction kinetics is promoted, yielding more fuel conversion through heterogeneous chemistry. However, this produces more methyl radical, which is combined to methane (as well as ethane and ethylene) in the presence of hydrogen near the membrane surface, inhibiting the homogeneous-phase CH₄ conversion. On the other hand, at low fuel concentration, it is seen that gas-phase reactions suppress the catalytic surface fuel conversion. To examine why these two regimes exist, we investigate two limiting cases: high and low fuel concentrations for temperatures above 1200K, where homogeneous and heterogeneous reactions, respectively, are dominant and govern the overall fuel conversion.

At low fuel concentration and high temperature when homogeneous-phase reactions dominate the overall CH₄ conversion, heterogeneous chemistry has negligible impacts on fuel conversion and oxygen permeation. The sweep gas
conditions for this gas-phase reaction regime referred to in [27], which include a methane concentration of 6% on a molar basis with the remainder being carbon dioxide and a sweep gas inlet temperature of 1300 K, corresponding to the largest CH\textsubscript{4} conversion in Fig. 7(a) and Fig. 8(a). Under these conditions, it has been shown that the extent of homogeneous-phase reactions is significant leading to substantial fuel conversion in the gas-phase and the enhancement of oxygen permeation [17, 27], when only homogeneous-phase reactions were modeled. When catalytic surface reactions are also considered, the change in CH\textsubscript{4} conversion and oxygen permeation rate are negligible. As shown in Fig. 9(a), since the reactants, i.e., methane, carbon monoxide and hydrogen, are predominantly oxidized through homogeneous-phase reactions, they hardly reach the membrane surface. Note that the homogeneous-phase reaction zone (characterized by the location of the maximum temperature) is stabilized approximately 4 mm away from the membrane. For these sweep side conditions, homogeneous chemistry predominantly governs fuel oxidation. This is consistent with the results from conventional catalytic reactors with which it has been demonstrated that the chemical reactions in the gas-phase dominate fuel conversion, even though the surface catalytic reactions can take place [34, 35]. In addition, as the reaction zone is established at a distance from the membrane, the mass transport of reactants towards the catalytic membrane surface is limited, suppressing the effect of heterogeneous chemistry on fuel conversion. Fig. 9(b), showing the location of the homogeneous-phase reaction zone with respect to the membrane as the fuel concentration and sweep gas inlet temperature are varied, confirms this effect of limited species transport on catalytic surface reactions. The reaction zone location relative to the membrane is consistent with the trend of the reduction in the catalytic surface CH\textsubscript{4} conversion (compare Fig. 8(b) and Fig. 9(b)). The discussion regarding the reaction zone location and species transport towards the membrane surface is detailed in [17].

At high fuel concentration and high temperature when a homogeneous-phase reaction zone is not established, heterogeneous chemistry contributes to the enhancement of fuel conversion, but the coupling of gas-phase and catalytic surface reactions reduces its contribution to the CH\textsubscript{4} conversion. To examine the effect of surface reactions when a gas-phase reaction zone is not stabilized, we consider the case of a temperature of 1300 K and a fuel concentration of 75%. Fig. 10(a) shows that the reactants (CH\textsubscript{4} and products of its partial oxidation) reach the membrane surface, enabling catalytic oxidation reactions, but no finite gas-phase reaction zone exists, if compared to Fig. 9(a). Note that hydrogen and carbon monoxide are produced from pyrolysis of methane and carbon dioxide, respectively. At given conditions, the catalytic CH\textsubscript{4} conversion of 8% is obtained, which is substantially smaller than that attributed to the onset of gas-phase reactions [17, 26].
Because of the low catalytic activity of perovskite membranes [3, 4, 28], its contribution to fuel conversion is small in comparison with the impact of homogeneous chemistry. Furthermore, the overall CH$_4$ conversion reduces to 3.83% due to the coupling of homogeneous-phase and catalytic surface reactions, recombining methyl radical to methane, i.e., backward reaction of R. 6, and prohibiting gas-phase reactions. Fig. 10(b) shows the proportion of methyl radical, which is produced from catalytic surface reactions, recombined to ethylene and methane in the gas-phase, as the sweep gas temperature is raised while maintaining the fuel concentration at 75%. As the extent of catalytic reactions increases, represented by the catalytic production rate of methyl radical, the formation rate of ethylene is also raised, which indicates the oxidative coupling of methane. However, when the sweep gas inlet temperature is raised to 1300K, a large portion of methyl radical is recombined to methane in the gas-phase, inhibiting the initiation of homogeneous-phase fuel conversion processes. This reduces the enhancement of overall fuel conversion by catalytic surface reactions and lowers the overall CH$_4$ conversion at high fuel concentration and high temperature when heterogeneous chemistry governs the overall fuel conversion processes (see Fig. 7(a)).

### 4.2. Thermal energy transfer from the sweep to the feed side

Thermal energy transfer towards the membrane and the air side depends on the extent of catalytic surface reactions and the onset of gas-phase chemical reactions. Along with oxygen permeation, i.e., mass transfer, through the membrane, this thermal energy transport is an important feature of ITM reactors. Fig. 11 shows that this energy flux increases in general as the fuel concentration and sweep gas temperature are raised, following the trend of the surface CH$_4$ conversion shown in Fig. 8(b), with an exception at low fuel concentration and high temperature. As discussed in Section 3, heterogeneous chemistry results in extensive thermal energy transfer due to exothermic reactions and mass transfer between the gas-phase and surface species. Consequently, the amount of thermal energy transfer is raised, according to the sweep side conditions favorable promoting catalytic oxidation reactions, such as high fuel concentration and sweep gas temperature. The exception at low fuel concentration and high temperature is explained by the onset of homogeneous chemistry (see Fig. 8(a)). Heat released from homogeneous-phase reactions raises the gas temperature and is transferred towards the membrane mainly by conductive heat transfer, indicated by a sharp temperature gradient near the membrane shown in Fig. 9(a). Although this rise in heat transfer is substantial, it is not as large as that attributed to catalytic oxidation reactions. Heat released from exothermic catalytic oxidation reactions on the membrane surface is transferred by the membrane to the air side. Along with the chemical effect of catalytic reactions coupled with homogeneous chemistry, this
lowers the gas-phase reaction kinetic rates and further suppresses the homogeneous-phase fuel conversion reactions, as both fuel concentration and sweep gas temperature are raised. The result confirms that the influence of thermal energy transfer is significant when ITM reactors feature catalytic surface fuel conversion, as well as homogeneous-phase chemical reactions.

4.3. **Influences on the oxygen permeation rate**

Catalytic surface reactions are effective in reducing the oxygen concentration on the sweep side and raising the permeation flux. If we can identify which chemistry is more effective in lowering the oxygen concentration on the sweep side, we may acquire a better understanding of the oxygen permeation trends shown in Fig. 7(b). Fig. 12(a) shows the variation in the bulk oxygen concentration on the sweep side as a function of the fuel concentration and its inlet temperature. The oxygen concentration decreases gradually with fuel concentration and sweep gas temperature, while showing a substantial reduction beyond 1200K. The reduction is more significant at high fuel concentration. The variation is comparable to that of the oxygen permeation rate. Although gas-phase fuel conversion is not initiated below 1200K (see Fig. 8(a)), oxygen ion concentration on the sweep side is lowered, attributed to the catalytic surface reactions (see Fig. 8(b)). Beyond 1200 K, homogeneous-phase reactions at low fuel concentration (see Fig. 8(a)) and catalytic oxidation reactions at high fuel concentration (see Fig. 8(b)) are effective in consuming the oxygen permeated from the air side. This effect is more evident for high fuel concentrations, where heterogeneous chemistry governs the overall fuel conversion processes, indicating that oxygen consumption through surface reactions is faster or more effective to reduce the oxygen concentration on the sweep side. The catalytic fuel conversion reactions, i.e., R. 3 to R. 5, compete with the oxygen surface exchange reactions, i.e., the backward reactions of R. 1 and R. 2, on the membrane surface. When operating conditions are in favor of heterogeneous chemistry, such as high fuel concentration and sweep gas temperature, catalytic oxidation reactions consume oxygen immediately on the membrane surface, inhibiting it from being released to the gas-phase. Although the contribution of heterogeneous chemistry to the CH₄ conversion is weaker than that of homogeneous-phase reactions, its influence on the oxygen permeation rate is more significant.

The influence of heterogeneous chemistry on the oxygen permeation rate is strong when permeation is limited by either bulk diffusion or oxygen surface exchange. To examine further, we compare the results obtained from the current study to the case when only gas-phase reactions are considered. The high fuel concentrations of 50% and 75% are considered in order to emphasize the effect of catalytic fuel conversion (i.e., gas-phase reactions are insignificant), while
the inlet temperature is varied from 1000 K to 1300 K. Fig. 12(b) shows that the increase of the oxygen permeation, attributed to heterogeneous chemistry, is significant at low (i.e., 1000 K ~ 1100 K) and high (i.e., 1200 K ~ 1300 K) temperature. In addition, the enhancement is larger for high fuel concentrations. As discussed in [26], in a non-reactive environment (e.g., without employing heterogeneous chemistry seen in Fig. 12(b)), oxygen permeation is limited by oxygen surface exchange at low temperature, whereas bulk diffusion limits it at high temperature. Oxygen consumption on the membrane surface reduces the resistance of surface exchange at low temperature and that of bulk diffusion at high temperature, resulting in a higher oxygen permeation rate. As a result, the dependency of oxygen permeation on temperature is raised. Moreover, a high fuel concentration promotes the catalytic fuel conversion kinetics and emphasizes the role of heterogeneous chemistry. However, when both resistances are not rate-limiting at intermediate temperature (i.e., 1100 K ~ 1200 K), the enhancing effect of catalytic surface reactions on oxygen permeation is reduced. Only if one of the permeation resistances is significant and rate-limiting, the catalytic activity of perovskite membranes effectively influences oxygen permeation.

5. CONCLUSIONS

Numerical simulations were conducted to elucidate ITM reactor operating regimes and examine the effect of catalytic fuel oxidation reactions supported by an ITM and their coupling with homogeneous-phase chemistry on the oxygen permeation rate and CH$_4$ conversion. In our previous studies, we developed a spatially resolved physical model that incorporates heterogeneous chemistry, accounting for oxygen surface exchange and catalytic oxidation for methane, carbon monoxide and hydrogen, and a detailed homogeneous-phase chemical kinetic mechanism, both of which are coupled with oxygen permeation. The numerical model relates the air and sweep gas sides by matching the oxygen flux and heat flux across the membrane. In this study, this model was used to investigate the coupling of homogeneous-phase and surface catalytic reactions and their influence on oxygen permeation and fuel conversion.

It was shown that under sweep side conditions resulting in the fuel conversion process being governed by homogeneous and heterogeneous reactions, their coupling is significant and affects the reaction kinetics, pathway, products and thermal energy transfer substantially. Since the membrane is not adiabatic and rather conducts heat towards the air side, the thermal energy transfer from the sweep side to the air side is important in determining the reaction zone temperature on
the sweep side. Surface catalytic reactions move the exothermic oxidation reactions towards the membrane, which lowers the gas temperature on the sweep side and hence homogeneous-phase chemical kinetic rates. The products from surface catalytic reactions influence the homogeneous-phase reaction pathway enhancing methyl radical reactions but suppressing hydroxyl radical reactions. These reduce the overall CH₄ conversion, whereas catalytic surface reactions raise the oxygen permeation rate slightly. In addition, the products are comprised of lower carbon monoxide and hydrogen but higher carbon dioxide concentrations, in comparison with the case for which only homogeneous chemistry was taken into account. For the sweep stream conditions considered, the overall reaction scheme is changed from partial oxidation of methane to oxidative coupling and oxy-fuel combustion.

Given the significance of the coupling between homogeneous-phase and surface catalytic reactions and their interactions with oxygen permeation, ITM reactor operating regimes were re-examined. A sensitivity analysis with respect to fuel concentration and temperature was conducted. It was shown that temperatures above 1200 K are required to facilitate fuel conversion reactions in the gas-phase and on the catalytic membrane surface. While homogeneous chemistry is effective at low fuel concentrations below 40%, heterogeneous chemistry plays an important role in the CH₄ conversion at high fuel concentrations above 60% (with the remainder being carbon dioxide). In the gas-phase reaction regime, the reactants are predominantly oxidized through homogeneous chemistry, and hence the role of surface catalytic reactions in determining the CH₄ conversion and oxygen permeation rate is limited. In contrast, in the surface reaction regime, heterogeneous chemistry contributes to a small enhancement of oxygen permeation and fuel conversion. Due to the low catalytic activity of perovskite membranes, its effect on the oxygen permeation and CH₄ conversion is not as substantial as that of the onset of homogeneous chemistry observed in the gas-phase reaction regime. Catalytic surface reactions enhance the permeation rate only if the resistance of either surface exchange or bulk diffusion is rate-limiting at low or high temperature, respectively. Moreover, variations in the thermal energy transfer and the oxygen concentration on the sweep side follow the trend of surface catalytic fuel conversion, indicating that heterogeneous chemistry influences them significantly.

6. ACKNOWLEDGEMENTS
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7. NOMENCLATURE

\( V \) \quad \text{Convective mass flux (}\ y\text{-direction; normal to the membrane)} [kg/m\(^2\)/s]

\( D_k \) \quad \text{Diffusion coefficient of bulk species } k [m\(^2\)/s]

\( \varphi \) \quad \text{Dynamic viscosity [kg/m/s]}

\( \varepsilon \) \quad \text{Emissivity}

\( \rho \) \quad \text{Gas-phase density [kg/m\(^3\)]}

\( Y_k \) \quad \text{Mass fraction of gas-phase species } k

\( D_{km} \) \quad \text{Mixture-averaged diffusion coefficient [m\(^2\)/s]}

\( \bar{W} \) \quad \text{Mixture molecular weight [kg/kmol]}

\( c_p \) \quad \text{Mixture specific heat [J/kg/K]}

\( \bar{\rho}_{m \ em} \) \quad \text{Molar density of the membrane [kmol/m\(^3\)]}

\( \bar{h}_k \) \quad \text{Molar enthalpy of species } k [J/kmol]

\( C_k \) \quad \text{Molar fraction of bulk species } k

\( \omega_k \) \quad \text{Molar production rate of gas-phase species } k \text{ through homogeneous chemistry [kmol/m\(^3\)/s]}

\( \dot{s}_k \) \quad \text{Molar surface production rate of species } k \text{ through heterogeneous chemistry [kmol/m\(^2\)/s]}

\( W_k \) \quad \text{Molecular weight of gas-phase species } k [kg/kmol]

\( N_b \) \quad \text{Number of bulk species}

\( N_g \) \quad \text{Number of gas-phase species}

\( N_s \) \quad \text{Number of surface species}

\( A_x \) \quad \text{Scaled parallel pressure gradient [kg/m\(^3\)/s\(^2\)]}

\( U \) \quad \text{Scaled parallel velocity (}\ x\text{-direction; parallel to the membrane)} [1/s]

\( c_{p,k} \) \quad \text{Specific heat of species } k [J/kg/K]
$\sigma$  Stefan-Boltzmann constant [W/m$^2$/K$^4$]

$Z_k$  Surface site occupancy of surface species $k$

$T$  Temperature [K]

$\lambda$  Thermal conductivity [W/m/K]

$D_k^T$  Thermal diffusion coefficient [kg/m/s]

$\Gamma$  Total available surface site density [kmol/m$^2$]

Subscripts

in  Inlet

mem  Membrane

air  Air (feed) side of membrane

sweep  Sweep gas (permeate) side of membrane

$\infty$  Surrounding walls

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<th>Geometry</th>
<th>Thermo-dynamic state</th>
<th>Membrane materials</th>
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<tbody>
<tr>
<td>Akin and Lin [18]</td>
<td>$CO + 0.5O_2 \rightarrow CO_2$ (equilibrium)</td>
<td>Continuously stirred tank reactor</td>
<td>Bulk</td>
<td>LSCF, BYS</td>
</tr>
<tr>
<td>Rui et al. [19]</td>
<td>$CO + 0.5O_2 \rightarrow CO_2$ (kinetically controlled)</td>
<td>Continuously stirred tank reactor</td>
<td>Bulk</td>
<td>LSCF, BYS</td>
</tr>
<tr>
<td>Ben-Mansour et al. [13]</td>
<td>One-step CH$_4$ reaction with O$_2$ (kinetically controlled)</td>
<td>Axisymmetric tubular reactor</td>
<td>Local</td>
<td>BSCF</td>
</tr>
<tr>
<td>Habib et al. [14]</td>
<td>One-step CH$_4$ reaction with O$_2$ (kinetically controlled)</td>
<td>Multi-channel reactor</td>
<td>Local</td>
<td>LSCF</td>
</tr>
<tr>
<td>Nemitallah et al. [15]</td>
<td>$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$</td>
<td>2D stagnation flow reactor</td>
<td>Local</td>
<td>LSCF</td>
</tr>
<tr>
<td>Nemitallah et al. [16]</td>
<td>$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$</td>
<td>Monolith structure reactor</td>
<td>Local</td>
<td>LSCF</td>
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<td>Wang and Lin [20]</td>
<td>$CH_4 + \frac{x}{2}O_2 \rightarrow CO_2$</td>
<td>Continuously stirred tank reactor</td>
<td>Bulk</td>
<td>YSZ, Ti-doped YSZ</td>
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<td>Tan et al. [12]</td>
<td>$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (kinetically controlled)</td>
<td>Packed hollow fiber membrane reactor</td>
<td>Bulk</td>
<td>LSCF</td>
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<td>Zhang et al. [21]</td>
<td>$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$ $CO + 0.5O_2 \leftrightarrow CO_2$ $H_2 + 0.5O_2 \leftrightarrow H_2O$ (equilibrium)</td>
<td>Shell-and-tube reactor</td>
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<td>Rui et al. [22, 23]</td>
<td>$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$ $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$ $CO + H_2O \leftrightarrow CO_2 + H_2$ $CO + 0.5O_2 \leftrightarrow CO_2$ $H_2 + 0.5O_2 \leftrightarrow H_2O$ (kinetically controlled)</td>
<td>Packed tubular reactor</td>
<td>Bulk</td>
<td>LSCF with Ni/Al$_2$O$_3$</td>
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<tr>
<td>Jin et al. [24] Tan et al. [25]</td>
<td>$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$ $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ (kinetically controlled)</td>
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<td>Bulk</td>
<td>LSCF with Ni/Al$_2$O$_3$</td>
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<table>
<thead>
<tr>
<th>Governing equations</th>
</tr>
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<tbody>
<tr>
<td><strong>Continuity</strong></td>
</tr>
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<td>( \frac{\partial \rho}{\partial t} + \frac{\partial \rho \mathbf{U}}{\partial y} + \rho \mathbf{U} \cdot \nabla \mathbf{U} = -\rho \frac{\partial \mathbf{T}}{\partial t} - \sum_{k=1}^{N_g} \rho \mathbf{W}_k \cdot \frac{\partial \mathbf{Y}_k}{\partial t} + \frac{\partial \mathbf{Y}}{\partial y} + \rho \mathbf{J} = 0 )</td>
</tr>
<tr>
<td><strong>Momentum</strong></td>
</tr>
<tr>
<td>( \rho \frac{\partial \mathbf{U}}{\partial t} + \frac{\partial \rho \mathbf{U}^2}{\partial y} + \mathbf{A}_z - \frac{\partial}{\partial y} \left( \Phi \frac{\partial \mathbf{U}}{\partial y} \right) = 0 )</td>
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<tr>
<td><strong>Gas-phase species</strong></td>
</tr>
<tr>
<td>( \rho \frac{\partial \mathbf{Y}_k}{\partial t} + \frac{\partial \mathbf{Y}_k}{\partial y} + \frac{\partial j_k^g}{\partial y} - \omega_k \mathbf{W}_k = 0 )</td>
</tr>
<tr>
<td>where, ( j_k^g = -\rho D_{em} \left( \frac{\partial \mathbf{y}_k}{\partial y} + \frac{\mathbf{v}_k \cdot \nabla \mathbf{W}}{\mathbf{W}} \right) - \frac{\mathbf{v}_k \cdot \nabla \mathbf{T}}{\mathbf{T}} )</td>
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<tr>
<td><strong>Surface species</strong></td>
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<tr>
<td>( \frac{\partial \mathbf{Z}_k}{\partial t} - \mathbf{s}_k = 0 )</td>
</tr>
<tr>
<td><strong>Bulk species</strong></td>
</tr>
<tr>
<td>( \int \mathbf{\rho}_m \mathbf{C}_k \mathbf{d} \mathbf{y} - \int \mathbf{s}_k \mathbf{d} \mathbf{A} + \int \mathbf{j}_k^b \mathbf{d} \mathbf{A} = 0 )</td>
</tr>
<tr>
<td>where, ( j_k^b = -\mathbf{\rho}_m D_k \mathbf{\partial c}_k / \partial y )</td>
</tr>
<tr>
<td><strong>Energy</strong></td>
</tr>
<tr>
<td>( \frac{\partial \mathbf{T}}{\partial t} + \frac{\partial \mathbf{T}}{\partial y} + \frac{1}{c_p} \sum_{k=1}^{N_g} \mathbf{h}<em>k \omega_k + \sum</em>{k=1}^{N_g} j_k^g c_{p,k} \frac{\partial \mathbf{T}}{\partial y} - \frac{\partial}{\partial y} \left( \mathbf{\lambda} \frac{\partial \mathbf{T}}{\partial y} \right) = 0 )</td>
</tr>
<tr>
<td><strong>Pressure curvature</strong></td>
</tr>
<tr>
<td>( \frac{\partial \mathbf{A}_x}{\partial y} = 0 )</td>
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<tr>
<td><strong>Boundary conditions</strong></td>
</tr>
<tr>
<td><strong>Inlets</strong></td>
</tr>
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<td>( \mathbf{V}<em>n = \mathbf{V}</em>{at} , \mathbf{V}_{aw} \mathbf{eep} )</td>
</tr>
<tr>
<td>( \mathbf{U}_n = 0 )</td>
</tr>
<tr>
<td>( \mathbf{Y}<em>{k,n} = \mathbf{Y}</em>{k,at} , \mathbf{Y}_{k,aw} \mathbf{eep} )</td>
</tr>
<tr>
<td>( \mathbf{T}<em>n = \mathbf{T}</em>{at} , \mathbf{T}_{aw} \mathbf{eep} )</td>
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<tr>
<td><strong>Membrane surfaces</strong></td>
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<tr>
<td>( \mathbf{V}<em>{m,em} = \sum</em>{k=1}^{N_g} \mathbf{s}_k \mathbf{W}_k )</td>
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<tr>
<td>( \mathbf{U}_{m,em} = 0 )</td>
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<tr>
<td>( j_{k,m,em} + \mathbf{Y}<em>{k,m,em} \mathbf{V}</em>{m,em} = \mathbf{s}_k \mathbf{W}_k )</td>
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<tr>
<td>( \mathbf{Q}<em>{aw,em} - \mathbf{Q}</em>{aw} - 2 \sigma \mathbf{e}<em>{m,em} (\mathbf{T}</em>{mem} - \mathbf{T}<em>{at}) \sum</em>{k=1}^{N_g} \mathbf{h}_k \mathbf{s}_k = 0 )</td>
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<tr>
<td>where, ( \mathbf{Q}<em>{aw} = -\mathbf{\lambda} \mathbf{V}</em>{aw} + \sum_{k=1}^{N_g} \left( j_{k,m,em} + \mathbf{Y}<em>{k,m,em} \mathbf{V}</em>{m,em} \right) \mathbf{h}_k )</td>
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<td>and ( \mathbf{Q}<em>{aw,em} = \mathbf{\lambda} \mathbf{V}</em>{aw} - \sum_{k=1}^{N_g} \left( j_{k,m,em} + \mathbf{Y}<em>{k,m,em} \mathbf{V}</em>{m,em} \right) \mathbf{h}_k )</td>
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Table 3

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<th>Sweep gas variables</th>
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<td>Fuel concentration (remainder being carbon dioxide)</td>
<td>[%]</td>
<td>25</td>
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<tr>
<td>Inlet temperature</td>
<td>[K]</td>
<td>1300</td>
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<tr>
<td>Flow rate</td>
<td>[m$^3$/s]</td>
<td>$4.39 \times 10^{-4}$</td>
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