

Hydrogen production in fixed-bed reactors with combined reformer-burner modules by steam-ethanol reforming at different temperatures

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Abstract

Use of ethanol is attracting increasing attention both as primary feedstock and as an alternative to increase the feedstock flexibility in a given unit. However, steam reforming of ethanol is not a straight forward process. Equilibrium of the reaction is shifted towards the production of hydrogen even at low temperature. However, in practice, ethanol is also converted to ethylene. The present study is focused primarily upon the production of hydrogen in fixed-bed reactors by steam-ethanol reforming under different temperature conditions. Computational fluid dynamics is used to model fluid flow, heat and mass transfer, and chemical reactions. The governing integral equations are solved for the conservation of mass, momentum, and energy and other scalars such as laminar flow and chemical species. Steady-state analyses are performed using computational fluid dynamics. The reaction rates are computed by the laminar finite-rate model. The present study aims to explore how to effectively produce hydrogen in fixed-bed reactors by steam-ethanol reforming at different temperatures. Particular emphasis is placed upon the effect of temperature on the transport and reaction characteristics of fixed-bed reactors for polymer electrolyte membrane fuel cell applications. The results indicate that under a thermodynamic point of view, high temperatures and steam-ethanol molar ratios promote hydrogen yield. Low ethylene content is obtained at high pressure and low temperature. At high temperatures the contribution of steam reforming reactions results in a marked increasing of overall enthalpy, enhancing process endothermicity, whereas the exothermic contribution of water-gas shift and methanation reactions reduces the external heat supply and the overall energy penalty at lower temperature. Although the equilibrium of the water-gas shift reaction favors the products formation at lower temperatures, reaction kinetics are faster at higher temperatures. The typical products distribution of ethanol steam reforming reaction, according to thermodynamic evaluations, results in considerable hydrogen production rates at higher temperatures and high methane yields at lower temperatures. The majority of supported metals as catalysts expresses better performance at high temperatures, and the production of oxygenated products increases and the formation of coke is thermodynamically favored at low temperatures. Low reaction temperatures generally favor the Boudouard reaction mechanism while methane decomposition is the main route at high temperatures.

Keywords: Hydrogen; Ethanol; Reformers; Burners; Reforming; Combustion

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1. Introduction

Hydrogen is becoming an increasingly desired fuel. One method of obtaining hydrogen is to release it from hydrocarbons [1, 2]. This approach suffers from the simultaneous production of carbon monoxide [3, 4]. Hydrogen containing carbon monoxide impairs the performance of many systems such as ammonia synthesis reactors [5] and low temperature fuel cells [6]. It is therefore desirable to have mechanisms to remove carbon monoxide from hydrogen [7, 8]. One method of accomplishing this removal is the selective oxidation of the carbon monoxide using a fixed-bed catalytic reactor.

Catalytic reactors of the fixed-bed type to selectively oxidize carbon monoxide are well known [7, 8]. These fixed-bed reactors when operated for the selective oxidation of carbon monoxide under varying flow conditions, for example, reduced load conditions in fuel processing for fuel cell applications [9, 10], can actually produce carbon monoxide via the reverse water-gas shift reaction, the reaction occurring when the oxygen concentration within the bed is depleted below a minimum threshold value [11, 12]. Consequently, if oxygen is consumed to this minimal threshold value before the hydrogen containing gas stream exits the catalyst bed, carbon monoxide is reformed in the oxygen depleted zone of the reactor [13, 14]. Addition of additional oxygen into the oxygen depleted zone of the reactor prevents the reverse water-gas shift reaction but at the expense of additional hydrogen consumption and added operational complexity.

The reverse water-gas shift reaction within a fixed-bed, catalytic reactor for the selective oxidation of carbon monoxide can be controlled for a broad range of operating conditions, flow rates, by controlling critical input parameters of the gas stream entering the reactor [15, 16]. An adiabatic reactor is defined as a reactor having no active heat removal device but which may have normal cooling losses associated typically with such reactors [17, 18]. In such a reactor, a temperature rise is observed typically along the length of the reactor for exothermic reactions [19, 20], for example, carbon monoxide oxidation. In an adiabatically operated fixed-bed, catalytic reactor that the inlet temperature of the entering gas stream, and space velocity of

the gas stream in the reactor are determinative of when and to what degree [21, 22], the reverse water-gas shift reaction, if at all, will occur within the catalytic reactor [23, 24]. In essence, when the space velocity is changed due to a change in flow rate, such as during partial load operation, adjustments in the inlet temperature of the gas stream can be used to alter the carbon monoxide formation resulting from the reverse water-gas shift reaction [25, 26]. Under some circumstances, it might be possible to eliminate entirely the reverse water-gas shift reaction and the production of carbon monoxide therefrom.

Use of ethanol is attracting increasing attention both as primary feedstock and as an alternative to increase the feedstock flexibility in a given unit. However, steam reforming of ethanol is not a straight forward process. Equilibrium of the reaction is shifted towards the production of hydrogen even at low temperature. However, in practice, ethanol is also converted to ethylene. Compared to methanol, ethanol offers some well-known advantages, for example, it is non-toxic, can easily be produced from renewable resources, and possesses a higher energy content, which allows a vehicle equipped with such a system to achieve a higher operating range with the same volume of stored fuel. The present study is focused primarily upon the production of hydrogen in fixed-bed reactors by steam-ethanol reforming at different temperatures. Computational fluid dynamics is used to model fluid flow, heat and mass transfer, and chemical reactions. The governing integral equations are solved for the conservation of mass, momentum, and energy and other scalars such as laminar flow and chemical species. Steady-state analyses are performed using computational fluid dynamics. The reaction rates are computed by the laminar finite-rate model. The present study aims to explore how to effectively produce hydrogen in fixed-bed reactors by steam-ethanol reforming at different temperatures. Particular emphasis is placed upon the effect of temperature on the transport and reaction characteristics of fixed-bed reactors for polymer electrolyte membrane fuel cell applications.

2. Design and operation

The fuel cell stack operates on a fuel source comprising hydrogen. Hydrogen can be supplied to the stack via a steam reformer wherein a hydrocarbon fuel, such as natural gas or methane, is contacted with steam and converted in an endothermic process into a synthesis gas comprising a mixture of hydrogen and carbon monoxide and lesser quantities of carbon dioxide and water. The heat required for the endothermic steam reforming is typically generated in an associated burner module, wherein a portion of the hydrocarbon fuel is combusted thereby generating the heat needed for the steam reformer. Generally, the steam reformer employed in the present study comprises a fuel inlet, a steam inlet, and a catalytic reaction zone having disposed therein a substrate onto which a reforming catalyst is supported. Non-limiting examples of suitable substrates include powders, pellets, extrudates, foams, and meshes. The substrate is provided as a mesh constructed in the form of a reticulated net or screen comprising a plurality of pores, cells, or channels having an ultra-short-channel-length. The steam reformer and the burner may be arranged as two concentric cylinders, and the burner occupies the inner cylindrical space and the reformer occupying an annular outer space. The reformer comprises a mesh substrate comprising an array of struts and a plurality of void volumes, the struts having supported thereon particles of catalyst. The mesh is provided as a stack of planar sheets with an inlet at one end of the stack and an outlet at an opposite end of the stack. The mesh may also be provided in a coiled configuration of cylindrical shape having an inner diameter and a larger outer diameter such that reactants flowing there through move along a radial flow path from an inlet along the inner diameter to an outlet along the outer diameter. In any configuration the bulk configuration of the mesh provides for a plurality of void volumes in random order, that is, empty spaces having essentially no regularity along the flow path from inlet to outlet. The mesh substrate is suitably constructed from a metal mesh, a ceramic mesh, or a combination thereof as in a cermet.

The burner is disposed in thermal communication with the steam reformer. A steam reforming catalyst is disposed within the reforming zone, the steam reforming catalyst comprising a porous substrate having an ultra-short-channel-length and having a Group VIII metal deposited thereon. The steam reformer operates on a mixture predominantly comprising the hydrocarbon fuel and steam, with little or no oxidant, in an endothermic steam reforming process. Typically, a burner is integrated with the reformer in a combined steam reformer-burner module, for the purpose of combusting a separate input of hydrocarbon fuel or

combusting a fuel exhaust gas derived from the fuel cell stack, thereby providing heat via combustion to drive the endothermic steam reforming process. The burner provides a primary source of heat to the reformer; whereas heat from the fuel cell stack provides a secondary source of heat to the reformer, due to positioning the reformer within the system as well as capturing excess stack heat in the heat extractor to produce or heat steam for the reformer. This design beneficially allows for high stack fuel utilization, which results in a fuel exhaust gas from the fuel cell stack that is depleted in heat content and is not entirely sufficient to drive the endothermic steam reformer by itself. Excess stack heat of the secondary heat source provides the thermal balance for the reformer in such cases. In another embodiment, the burner is fed with a separate input of hydrocarbon fuel, when needed, to balance overall system requirements, for example, when the fuel cell stack is operating during startup or at high fuel utilization. The burner also functions as a start-up burner providing heat for raising the system components to their desired operating temperatures, particularly, as that pertains to the reforming catalyst and the fuel cell stack. Thus, the burner is utilized during start-up, transients and steady state operation, as desired. During the start-up phase, the temperature of all components including the fuel cell stack and the reforming catalyst must be raised to steady-state operating temperatures. After steady-state temperatures are reached, the steam reformer is advantageously converted to endothermic steam reforming status, wherein heat generated by the fuel cell stack is recuperated for use in the heat extractors and the reformer. The burner, which is needed during endothermic steam reforming, can also be utilized to generate heat during start-up. Furthermore, operation with a high temperature reformer offers the advantage that hydrocarbon-containing impurities in the respective fuel are, to a significant degree, converted in the reformer due to the high operating temperature and do not detrimentally affect downstream components. Extremely long-chained molecules that are not converted are cracked, which reduces their effect on downstream components, and can allow conversion of such cracked constituents in the downstream components.

3. Computational methods

Fluent is a general-purpose computational fluid dynamics software used to model fluid flow, heat and mass transfer, chemical reactions, and more. Fluent offers a modern, user-friendly interface that streamlines the computational fluid dynamics process from pre-processing to post-processing within a single window workflow. Fluent is known for its advanced physics modeling capabilities, which include turbulence modeling, single and multiphase flows, combustion, battery modeling, fluid-structure interaction, and much more. The Fluent solver is used to solve the governing integral equations for the conservation of mass and momentum, and, when appropriate, for energy and other scalars such as laminar flow and chemical species. In both cases, a control-volume-based technique is used that consists of division of the domain into discrete control volumes using a computational grid, integration of the governing equations on the individual control volumes to construct algebraic equations for the discrete dependent variables such as velocities, pressure, temperature, and conserved scalars, and linearization of the discretized equations and solution of the resultant linear equation system to yield updated values of the dependent variables. The two numerical methods employ a similar discretization process, but the approach used to linearize and solve the discretized equations is different. The pressure-based solver employs an algorithm which belongs to a general class of methods called the projection method. In the projection method, wherein the constraint of mass conservation of the velocity field is achieved by solving a pressure equation. The pressure equation is derived from the continuity and the momentum equations in such a way that the velocity field, corrected by the pressure, satisfies the continuity. Since the governing equations are nonlinear and coupled to one another, the solution process involves iterations wherein the entire set of governing equations is solved repeatedly until the solution converges. The pressure-based solver uses a solution algorithm where the governing equations are solved sequentially. Each governing equation, while being solved, is "decoupled" or "segregated" from other equations, hence its name. The segregated algorithm is memory-efficient, since the discretized equations need only be stored in the memory one at a time. However, the solution convergence is relatively slow, inasmuch as the equations are solved in a decoupled manner.

With the segregated algorithm, each iteration consists of the steps outlined below:

- Update fluid properties, for example, density, viscosity, specific heat, including diffusivity based on the current solution.
- Solve the momentum equations, one after another, using the recently updated values of pressure and face mass fluxes.
- Solve the pressure correction equation using the recently obtained velocity field and the mass-flux.
- Correct face mass fluxes, pressure, and the velocity field using the pressure correction obtained.
- Solve the equations for additional scalars, if any, such as turbulent quantities, energy, species, and radiation intensity using the current values of the solution variables.
- Update the source terms arising from the interactions among different phases, for example, source term for the carrier phase due to discrete particles.
- Check for the convergence of the equations.

These steps are continued until the convergence criteria are met.

Fluent uses a control-volume-based technique to convert a general scalar transport equation to an algebraic equation that can be solved numerically. This control volume technique consists of integrating the transport equation about each control volume, yielding a discrete equation that expresses the conservation law on a control-volume basis. When second-order accuracy is desired, quantities at cell faces are computed using a multidimensional linear reconstruction approach. In this approach, higher-order accuracy is achieved at cell faces through a Taylor series expansion of the cell-centered solution about the cell centroid. Gradients are needed not only for constructing values of a scalar at the cell faces, but also for computing secondary diffusion terms and velocity derivatives. The gradient of a given variable is used to discretize the convection and diffusion terms in the flow conservation equations. Gradient limiters, also known as slope limiters, are used on the second-order upwind scheme to prevent spurious oscillations, which would otherwise appear in the solution flow field near shocks, discontinuities, or near rapid local changes in the flow field. The gradient limiter attempts to invoke and enforce the monotonicity principle by prohibiting the linearly reconstructed field variable on the cell faces to exceed the maximum or minimum values of the neighboring cells. Gradient limiters can be categorized into two general groups: non-differentiable limiters and differentiable limiters. Both, the standard limiter and multidimensional limiter are of the non-differentiable form, since they use minimum and maximum types of functions for limiting the solution variables. The third limiter in Fluent, as the name indicates, is a differentiable type of limiter, which uses a smooth function to impose the monotonicity principle. Special practices related to the discretization of the momentum and continuity equations and their solution by means of the pressure-based solver are addressed. These special practices are most easily described by considering the steady-state continuity and momentum equations in integral form. Pressure-velocity coupling is achieved to derive an additional condition for pressure by reformatting the continuity equation. The SIMPLE algorithm uses a relationship between velocity and pressure corrections to enforce mass conservation and to obtain the pressure field. The SIMPLE algorithm substitutes the flux correction equations into the discrete continuity equation to obtain a discrete equation for the pressure correction in the cell.

Steady-state analyses are performed using computational fluid dynamics. Fluent provides comprehensive modeling capabilities for a wide range of incompressible and compressible, laminar and turbulent fluid flow problems. In Fluent, a broad range of mathematical models for transport phenomena, such as heat transfer and chemical reactions, is combined with the ability to model complex geometries. The under-relaxation of variables is used in all cases for some material properties. To permit modeling of fluid flow and related transport phenomena in the steam reformer and burner and the physicochemical processes involved within the system, various useful features are provided. These include porous media, lumped parameter, streamwise-periodic flow and heat transfer, swirl, and moving reference frame models. For all flows, Fluent solves conservation equations for mass and momentum. For flows involving heat transfer or compressibility, an additional equation for energy conservation is solved. For flows involving species mixing or reactions, a species conservation equation is solved or, if the non-premixed combustion model is used, conservation equations for the mixture fraction and its variance are solved. Additional transport equations are also solved when the flow is turbulent. The net transport of energy at inlets consists of both the convection and diffusion

components. The convection component is fixed by the inlet temperature specified. The diffusion component, however, depends on the gradient of the computed temperature field. Thus, the diffusion component and therefore the net inlet transport is not specified a priori.

Fluent can model the mixing and transport of chemical species by solving conservation equations describing convection, diffusion, and reaction sources for each component species. Multiple simultaneous chemical reactions can be modeled, with reactions occurring in the bulk phase, volumetric reactions, and on wall or particle surfaces, and in the porous region. The reaction rates are computed in Fluent by the laminar finite-rate model: The effect of turbulent fluctuations is ignored, and reaction rates are determined by Arrhenius kinetic expressions. The generalized finite-rate formulation is suitable for a wide range of applications including laminar or turbulent reaction systems, and combustion systems with premixed flames. The laminar finite-rate model computes the chemical source terms using Arrhenius expressions, and ignores the effects of turbulent fluctuations. The model is exact for laminar flames, but is generally inaccurate for turbulent flames due to highly non-linear Arrhenius chemical kinetics. The laminar model may, however, be acceptable for combustion with relatively slow chemistry and small turbulence-chemistry interaction. For gas-phase reactions, the reaction rate is defined on a volumetric basis and the rate of creation and destruction of chemical species becomes a source term in the species conservation equations. For surface reactions, the rate of adsorption and desorption is governed by both chemical kinetics and diffusion to and from the surface [27]. Wall surface reactions thus create sources and sinks of chemical species in the gas phase, as well as on the reacting surface [28]. Reactions at surfaces change gas-phase, surface-adsorbed and bulk species [29, 30]. On reacting surfaces, the mass flux of each gas specie due to diffusion and convection to or from the surface is balanced with its rate of consumption or production on the surface [29, 30]. An important step in the setup of the model is to define the materials and their physical properties [31, 32]. Properties are temperature-dependent and composition-dependent, with temperature dependence based on a piecewise-polynomial function and individual component properties computed via kinetic theory [31, 32]. For solid materials, only density, thermal conductivity, and heat capacity are defined. A temperature-dependent function is specified for thermal conductivity and heat capacity.

4. Results and discussion

The sensible enthalpy contour plots in the combined steam reformer-burner module are illustrated in Figure 1 under different wall thermal conductivity conditions. Herein, micro-combustors are defined as devices with one or more physical dimensions being below one millimeter. Catalytic combustion is defined as combustion that does not involve flames. The equivalence ratio is defined as the fuel-air ratio normalized by the fuel-air ratio at stoichiometric conditions. Recent efforts have attempted to utilize combustion of hydrocarbons in miniature devices to directly produce heat or power [33, 34]. The devices utilize heat generated from combustion processes [35, 36]. More specifically, these devices typically utilize conventional homogeneous combustion. A major disadvantage of homogeneous combustion is that operating temperatures are necessarily very high [37, 38]. These high temperatures greatly limit material selection, burner life time, require extensive combustor insulation, and lead to significant nitrogen oxides production and emissions [39, 40]. Another disadvantage of homogeneous combustion is that flames quench when confined between walls that are less than about 2.0 mm apart, making it difficult to stabilize and maintain the reaction for long periods of time. These gap sizes can lead to combustors that are relatively bulky in size. A final disadvantage of homogeneous micro-combustion devices is that many of them consist of complicated miniature parts, which are difficult and expensive to fabricate, and so far, have exhibited very low efficiencies. An alternative to homogeneous micro-combustion is to combust the fuel catalytically, without the production of a flame. When implemented in miniature devices, catalytic micro-combustion has the potential to fully utilize the high energy densities of hydrocarbon fuels, but at much lower operating temperatures. Additionally, catalytic systems are typically easier to start, more robust to heat losses, and self-sustained at leaner fuel-air ratios. Finally, since catalytic combustion can be sustained in much smaller channels, catalytical micro-combustors can potentially be designed into more compact geometries than homogeneous combustors. The catalytic burner supports combustion in very shallow gaps and achieves high transport rates and complete conversion of the fuel. In addition, the catalytic burner controls the temperature uniformity by suitable material design

and selection to increase efficiency. Furthermore, the catalytic burner allows control of temperature profiles for improved catalyst life time and performance of fixed-bed reactors for synthesis of chemicals. The water-gas shift reaction can be carried out by means of different catalysts depending on the temperature. Carrying out the water-gas shift reaction at high temperature in a heat exchange steam reformer leads to the immediate benefit of considerable improvement in thermal efficiency. The water-gas shift reaction is carried out at much lower temperatures than the reforming reaction and the water-gas shift catalyst is characterized by its ability to convert carbon monoxide while not producing methane. The ethanol conversion steps into hydrogen by dehydration, hydrogenation, and reforming could in principle be carried out on the same catalyst provided that the polymer carbon forming reactions caused by ethylene is suppressed.

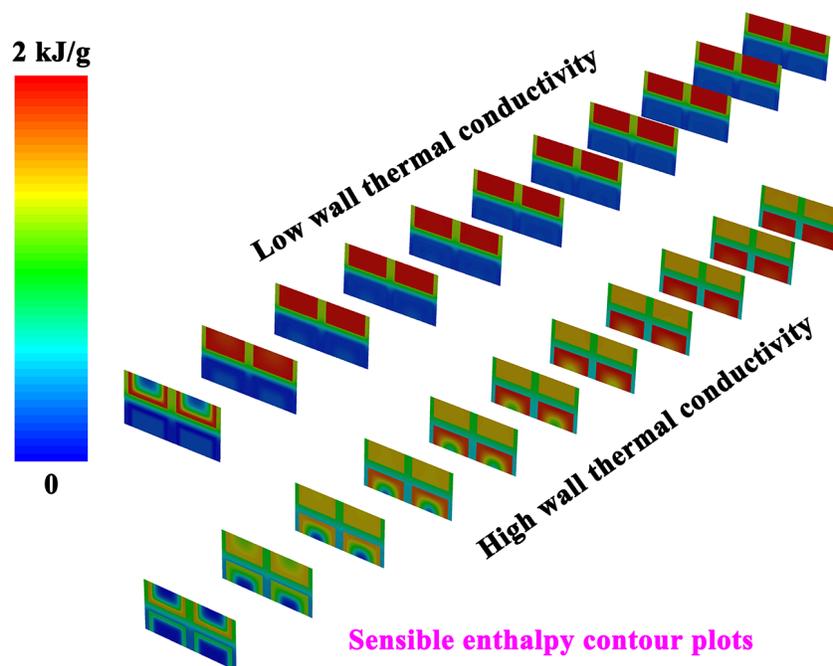


Figure 1. Sensible enthalpy contour plots in the combined steam reformer-burner module under different wall thermal conductivity conditions.

The ethanol molar fraction profiles on the catalyst surface are presented in Figure 2 along the length of the channels in the combined steam reformer-burner module under different temperature conditions. Typical routes for hydrogen production from ethanol include steam reforming, partial oxidation, and oxidative steam reforming. Ethanol steam reforming can potentially produce a high hydrogen amount per mole of converted reactant with no by-product formation other than carbon dioxide. Under a thermodynamic point of view, high temperatures and steam-ethanol molar ratios promote hydrogen yield. Higher hydrogen yield can be reached at higher temperatures. Moderate temperature and high-water content in the reforming mixture can limit carbon monoxide formation, thus avoiding its easy conversion to coke. A reduced content of carbon monoxide in the downstream gas can result in lower impact of further purification stages. In order to achieve a high conversion, the temperature in the reformer must be high. This results in a relatively high carbon monoxide content due to the equilibrium in the water-gas shift reaction established over the reforming catalyst. This device offers significant advantages with respect to the utilization of energy. Due to the very high temperatures in the high temperature steam reformer, the burner may be operated at a comparatively high temperature, since it is able to directly heat the high temperature reformer. At the same time, the feed material, for example, water and ethanol, can be evaporated using the burner exhaust

gas, which is slightly cooler than the above temperature level. The water and the hydrocarbon derivative may be evaporated separately using two separate evaporators. If necessary, the water and the hydrocarbon derivative can also be superheated separately. Appropriate mixing may take place at a position between the metered injection and the high temperature reformer. As an alternative, a pre-mix may be utilized, which is then evaporated and superheated together. This design allows the conversion of methanol, as well as higher alcohols, without any modifications to the arrangement being necessary. Furthermore, operation with a high temperature reformer offers the advantage that hydrocarbon-containing impurities in the respective fuel are, to a significant degree, converted in the reformer due to the high operating temperature and do not detrimentally affect downstream components.

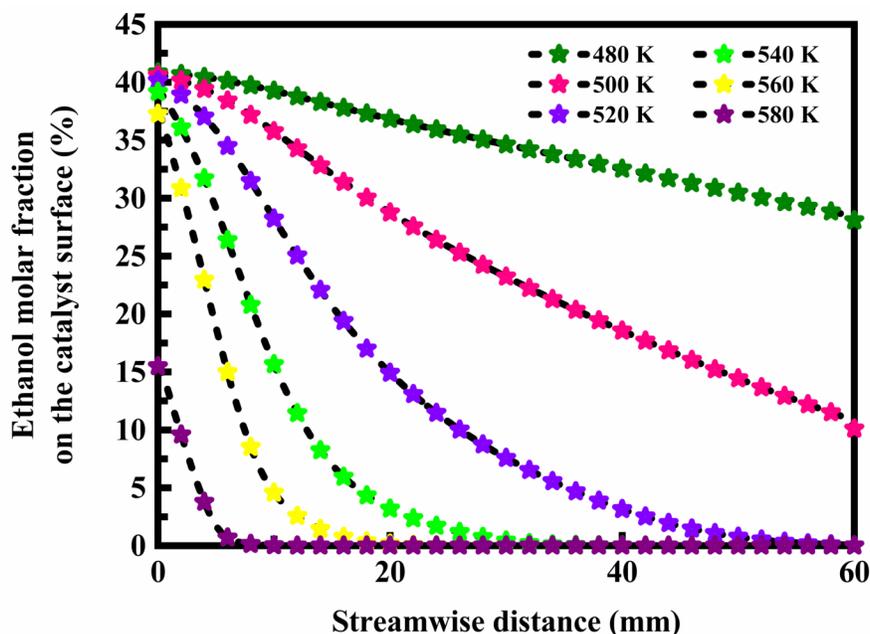


Figure 2. Ethanol molar fraction profiles on the catalyst surface along the length of the channels in the combined steam reformer-burner module under different temperature conditions.

The temperature contour plots in the combined steam reformer-burner module are illustrated in Figure 3 with a highly advantageous parallel heat and fluid flow configuration. Ethylene will even in small amounts rapidly form carbon and thereby carbon polymer on most steam reforming catalysts which causes considerable deactivation. High ethylene contents should therefore be avoided. A dual catalytic system involving the initial conversion of ethanol to ethylene and thereafter to ethane can be used instead and followed by steam reforming of the ethane. In the first catalytic zone, ethanol is converted into ethylene. Furthermore, ethylene reacts with hydrogen to form ethane. Excess hydrogen suppresses the equilibrium concentration of ethylene. Low ethylene content is obtained at high pressure and low temperature. The ethanol reforming process is useful for producing hydrogen for, for instance, fuel cells. Ethanol is steam reformed into hydrogen and carbon dioxide sequentially in a number of steps, each step characterized by a very high selectivity. In the first step ethanol, steam and a hydrogen-comprising stream are transferred to a reactor in which dehydration and hydrogenation reactions take place. Ethanol is dehydrated to ethylene and ethylene is hydrogenated to ethane. Catalysts for the dehydration reaction include a large amount of solid and liquid materials. For solid catalysts primarily acidic catalysts such as alumina, silica alumina, zeolites, zirconia or other solid acids or related compounds, have a high activity for dehydration of ethanol to ethylene. The catalyst of choice is based on alumina although many others are an equally valid choice. Selectivity is relevant with respect to formation of acetaldehyde, which is suppressed by a high hydrogen partial pressure. Diethyl ether may also

be formed. However, this formation may be suppressed by high temperatures. In the second and third step, ethane in the effluent from the dehydration or hydrogenation reaction can be converted into hydrogen by steam reforming of the ethane formed. One option is to use an adiabatic pre-reformer followed by primary steam reforming with addition of heat. The third step is a primary reforming step where methane is steam reformed to carbon monoxide and hydrogen. This step occurs in the primary reformer, also denoted steam reformer, and a major part of the residual methane is converted into carbon oxides, for example, carbon monoxide and carbon dioxide, and hydrogen. The effluent from the primary reformer can also contain some water and methane. This is an endothermic process and the heat required is normally supplied by indirect heat exchange with combusted fuel. Alternatively, if a pressure swing absorber is used for hydrogen purification a waste stream from the pressure swing absorber can also be used for firing. In the fourth step, the carbon monoxide is thus converted into hydrogen according to the water-gas shift reaction.

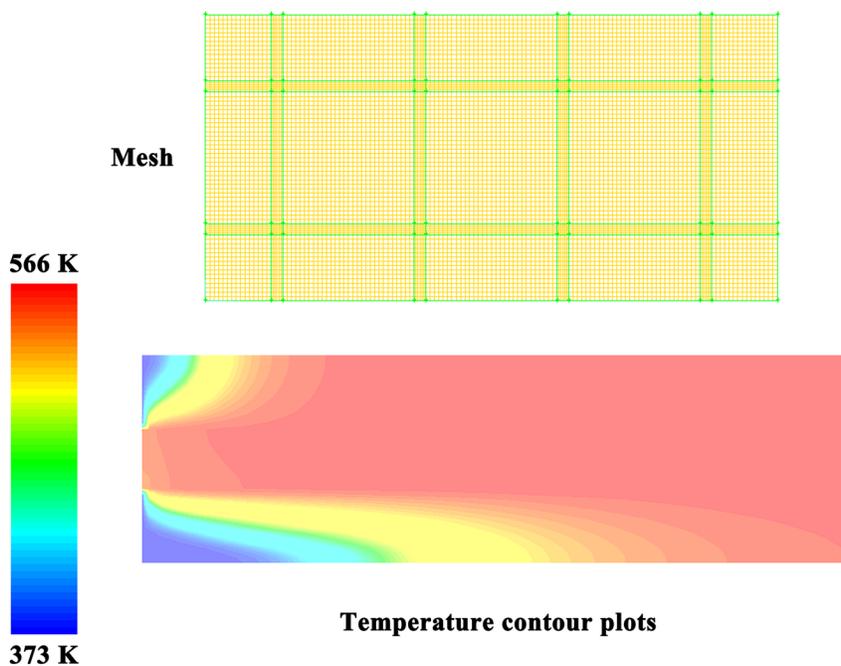


Figure 3. Temperature contour plots in the combined steam reformer-burner module with a highly advantageous parallel heat and fluid flow configuration.

The ethanol molar fraction profiles in the bulk gas phase are presented in Figure 4 along the length of the channels in the combined steam reformer-burner module under different temperature conditions. A stable combustion temperature may be optimized through adjustment of exemplary parameters including: fuel type, equivalence ratio, gap size, flow rate, and wall characteristics. Exemplary such wall characteristics may include: thermal conductivity, thickness, porosity, surface geometry, and non-homogeneity. Due to their dimensions being below the critical quenching distance, these catalytic burners are inherently safe with respect to flash back and explosion. Energy balance on the system evidences that at high temperatures the contribution of steam reforming reactions results in a marked increasing of overall enthalpy, enhancing process endothermicity, whereas the exothermic contribution of water-gas shift and methanation reactions reduces the external heat supply and the overall energy penalty at lower temperature. The auto-thermal point, at which the system is completely thermally self-sustained, depends on feed ratios steam-ethanol and operating pressure. Suppressing the formation of ethylene by hydrogenation of ethylene leads to production of ethane. An excess of hydrogen is required. This results in a reduction in the polymer carbon formation. Hydrogen is therefore added to the first dehydration or hydrogenation step. The product obtained from

the shift step is purified and thereafter separated into hydrogen and water. The hydrogen can serve as a hydrogen-rich anode feed to the fuel cell. The hydrogen recycle ratio is related to the carbon formation. The recycle ratio denotes the fraction or percentage of hydrogen recycled. At a particular value of the recycle ratio, the hydrogen concentration is at such a level that carbon polymer formation ceases to be a significant factor for the performance of the reforming catalyst. The recycle ratio needed to obtain the molar ratio between ethanol and hydrogen depends on where the recycle is taken from. The amount of hydrogen present in the effluent from each process step increases with each process step. Most hydrogen is therefore present in the hydrogen-rich anode feed stream and much less hydrogen is present in the effluent from the pre-reforming step. Recycling an effluent stream from for instance the shift step therefore requires a lower recycle ratio to the dehydration or hydrogenation step as compared to recycling an effluent containing comparatively less hydrogen from the pre-reforming step. Recycling from the pre-reforming step therefore requires a higher recycle ratio in order to provide enough hydrogen to fulfil the required ethanol to hydrogen molar ratio in the dehydration or hydrogenation step.

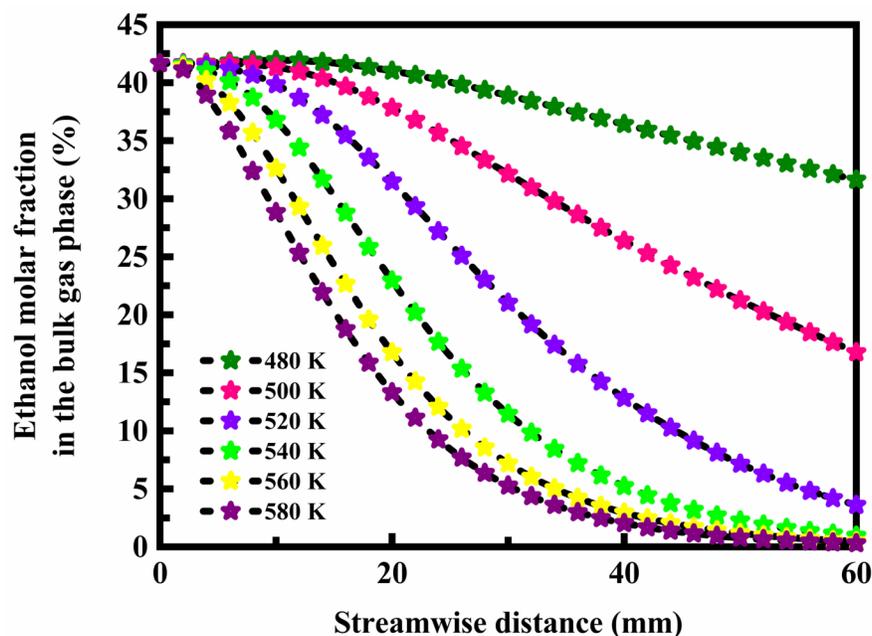


Figure 4. Ethanol molar fraction profiles in the bulk gas phase along the length of the channels in the combined steam reformer-burner module under different temperature conditions.

The hydrogen molar fraction contour plots are illustrated in Figure 5 in the reforming channels of the combined steam reformer-burner module with enhanced heat exchange. At high temperatures, the thermodynamic equilibrium leads to the production of large amounts of carbon monoxide, which poison the electrodes of polymer electrolyte membrane fuel cells. In order to ensure long and efficient use of hydrogen-fueled polymer electrolyte membrane fuel cell, highly pure hydrogen must be delivered. Then, water-gas shift reaction and preferential oxidation of carbon monoxide reaction or pressure swing adsorption steps are required for carbon monoxide removal. During the water-gas shift reaction, carbon monoxide is converted to carbon dioxide and hydrogen through a reaction with steam. Although the equilibrium of the water-gas shift reaction favors the products formation at lower temperatures, reaction kinetics are faster at higher temperatures. Then, the water-gas shift reaction is carried out in the combined steam reformer-burner module in two steps. At first, the reaction is performed at higher temperatures. After this step, the reaction is carried out in the combined steam reformer-burner module at lower temperatures. At the end of the water-gas shift reaction, the carbon monoxide concentration is very low in the combined steam reformer-burner module.

The water-gas shift reaction is followed by preferential oxidation of carbon monoxide reaction or pressure swing adsorption. The concentration of carbon monoxide at the exit of this last step is very low in the combined steam reformer-burner module, which is appropriated to the polymer electrolyte membrane fuel cells. Then, the development of the catalysts that exhibit high performance on the reforming of ethanol at low temperatures, producing low amounts of carbon monoxide and by-products, could reduce the costs associated to the hydrogen purification steps. The feed material, usually water and a hydrocarbon derivative for the production of the hydrogen-containing reformat gas stream are evaporated, and the hot burner exhaust gas is utilized for the evaporation. The feed material vapor is then directed to the high temperature reformer through a superheater, where they are superheated by the hot reformat gas stream being discharged from the steam reformer. The superheater acts as a superheater for the feed material vapor which, in turn, cools the reformat gas stream exiting the high temperature reformer to a temperature level that makes it possible to feed it into the water gas shift stage without any intermediate stages. In the high temperature reformer, the superheated feed material is subjected to steam reforming, and typically high-temperature steam reforming.

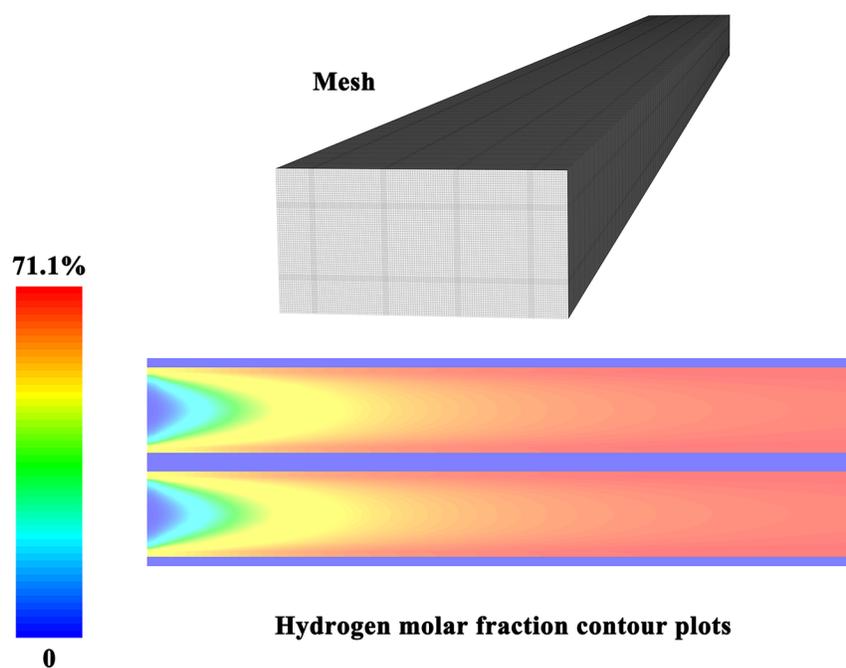


Figure 5. Hydrogen molar fraction contour plots in the reforming channels of the combined steam reformer-burner module with enhanced heat exchange.

The surface-to-bulk concentration ratio profiles are illustrated in Figure 6 along the length of the channels in the combined steam reformer-burner module under different temperature conditions. The typical products distribution of ethanol steam reforming reaction, according to thermodynamic evaluations, results in considerable hydrogen production rates at higher temperatures and high methane yields at lower temperatures. However, depending on the operating conditions selected, for example, temperature, ethanol partial pressure, steam to ethanol molar ratio, and space velocity, and the catalyst used, different reaction pathways can be observed, which reduce the desired product selectivity. In particular, the easy transformation of ethanol to acetaldehyde, ethylene, acetone or other by-products through decomposition, dehydrogenation and dehydration reaction strongly affects hydrogen yields, but above all could represent precursors for carbonaceous compounds that, depositing on the catalyst, determine its irreversible deactivation, and accordingly limiting the application of the process at industrial level. The main pathways responsible for coke deposition include

methane decomposition, Boudouard reaction, and ethylene polymerization. Alternatively, carbon formation from ethylene could occur through decomposition followed by accumulation and polymerization of carbon atoms. In order to keep the carbon monoxide content of the reformat stream as low as possible, since carbon monoxide generally presents a problem for the operation of fuel cells, for example, the carbon monoxide disadvantageously affects the function of the electrodes and membranes in the fuel cells, the temperatures in the reformer during the steam reforming of ethanol are usually approximately 250 °C to 300 °C. Existing systems, however, suffer the disadvantage that they are designed especially for a particular fuel, since the temperatures and catalysts have to be carefully selected in order to achieve an acceptable efficiency and to obtain a stream of reformat gas that meets all requirements, in particular those relating to residual quantities of feed material and carbon monoxide. Accordingly, there remains a need for a device for producing a hydrogen-containing gas for a fuel cell system, which device possesses a simple design, can process various types of fuels, is not affected by contamination with long-chain hydrocarbon compounds in the fuel, and which offers good cold-starting characteristics.

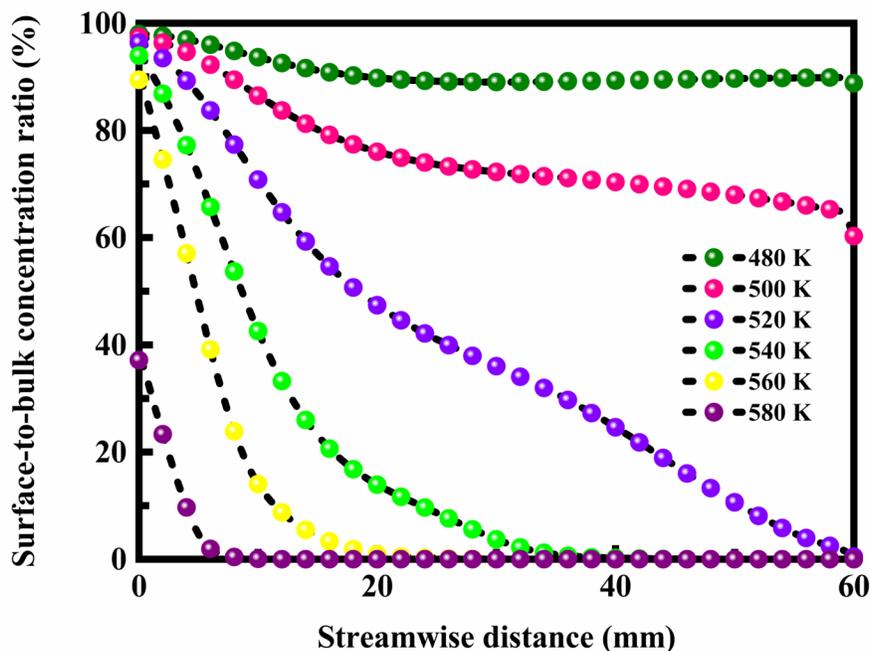


Figure 6. Surface-to-bulk concentration ratio profiles along the length of the channels in the combined steam reformer-burner module under different temperature conditions.

The ethanol molar fraction contour plots are illustrated in Figure 7 in the oxidation and reforming channels arranged in thermal communication of the combined steam reformer-burner module. Steam reforming of ethanol is an endothermic reaction. Then, the addition of energy to the combined reactor system is necessary, which leads to high capital and operation costs [41, 42]. One alternative way of supplying heat to the system is to add oxygen or air to the feedstock and simultaneously to burn a portion of ethanol, reaching the thermal neutrality of the reaction. This process is called autothermal reforming [43, 44]. Nevertheless, several parallels reactions can occur on these two routes, depending on the catalysts and the reaction conditions used, for example, dehydration of ethanol to ethene, followed by polymerization of ethene to form coke, decomposition of ethanol, producing methane, carbon monoxide and hydrogen, and dehydrogenation of ethanol, producing acetaldehyde [45, 46]. The methane can react with water, forming carbon monoxide and hydrogen [47, 48]. The appropriated catalyst for reforming of ethanol in the combined steam reformer-burner module should maximize the hydrogen production and minimize by-products formation. The majority of supported metals as catalysts expresses better performance at high temperatures, and the production of oxygenated products

increases and the formation of coke is thermodynamically favored at low temperatures. The method for producing hydrogen-containing gas from a feed material for a polymer electrolyte membrane fuel cell system comprises the steps of evaporating the feed material to yield a vapor; superheating the vapor to yield a superheated feed material; steam reforming the superheated feed material, wherein the thermal energy required for steam reforming in the combined steam reformer-burner module is provided by a burner that burns a gas stream that contains fuel and oxygen; and reducing the carbon monoxide content of the cooled stream by a water gas shift reaction, wherein the reformat stream is cooled between the steam reforming step and prior to the step of reducing the carbon monoxide content. Also, the method comprises the steps of operating the high temperature reformer as a partial oxidation stage for a period of time immediately following start-up, and then operating the high temperature reformer as a steam reformer once a suitable operating temperature for high temperature reforming is reached. To solve the problem related to a high carbon monoxide content in the reformat gas stream, a water-gas shift stage is included downstream, with respect to the flow direction of the reformats gas stream, of the high temperature reformer, which operates at temperatures that are significantly higher than reformers presently used in gas generation systems of this type. The water-gas shift stage further increases the hydrogen content of the reformat gas stream, and lowers the carbon monoxide content by reacting water and carbon monoxide to form hydrogen and carbon dioxide.

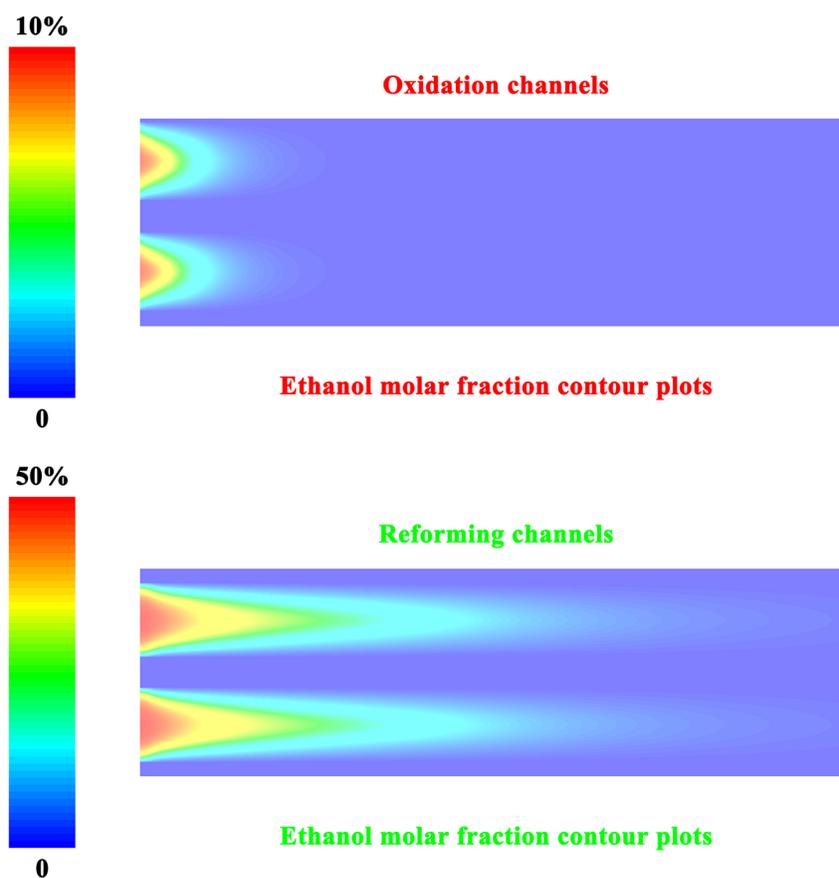


Figure 7. Ethanol molar fraction contour plots in the oxidation and reforming channels arranged in thermal communication of the combined steam reformer-burner module.

The reaction rate profiles on the catalyst surface are presented in Figure 8 along the length of the channels in

the combined steam reformer-burner module under different temperature conditions. Reaction rates increase with increasing catalyst surface area for a given reactor volume. Because of this, high surface areas reactors are constructed. These typically involve particulates in fixed bed reactors. High surface areas provide leaner sustainable combustion, easier startup, potentially higher energy efficiency, and no emissions of unburned hydrocarbons or carbon monoxide. However, most of these particulate bed combustors require pumping the fuel-air mixture directly through the bed, which causes large pressure drops that limit overall system efficiency. The microscale catalytic combustors have a low pressure-drop, and low catalytic surface area. The catalytic surface area available is approximately that of the geometric surface area of the exposed catalyst support. The device has a much higher specific surface area, which can lead to increased performance, especially at high flow rates. The catalytic ethanol reforming is conducted in the presence of steam. The quantity of steam fed to the reactor is selected so as to achieve the optimal steam-ethanol ratios in the feedstock to enhance the yield of the process. The presence of excess steam in the feedstock enables to inhibit carbonaceous compounds formation on the catalyst. The catalyst regeneration is conducted in the presence of superheated steam at high temperature and low pressure. The reforming channels are made flowing with an ethanol rich gaseous stream to generate a mixture of products containing hydrogen. In this way, the overall system is operated continuously. Low reaction temperatures generally favor the Boudouard reaction mechanism while methane decomposition is the main route at high temperatures. Moreover, depending on the reaction temperature, both amorphous and graphitized carbon can be produced. It is therefore necessary to enhance the stability of the catalyst at relatively high operating ethanol partial pressures. The high temperature reformer is heated by a burner that may burn the exhaust gas from the polymer electrolyte membrane fuel cell system and the residual fuel contained therein.

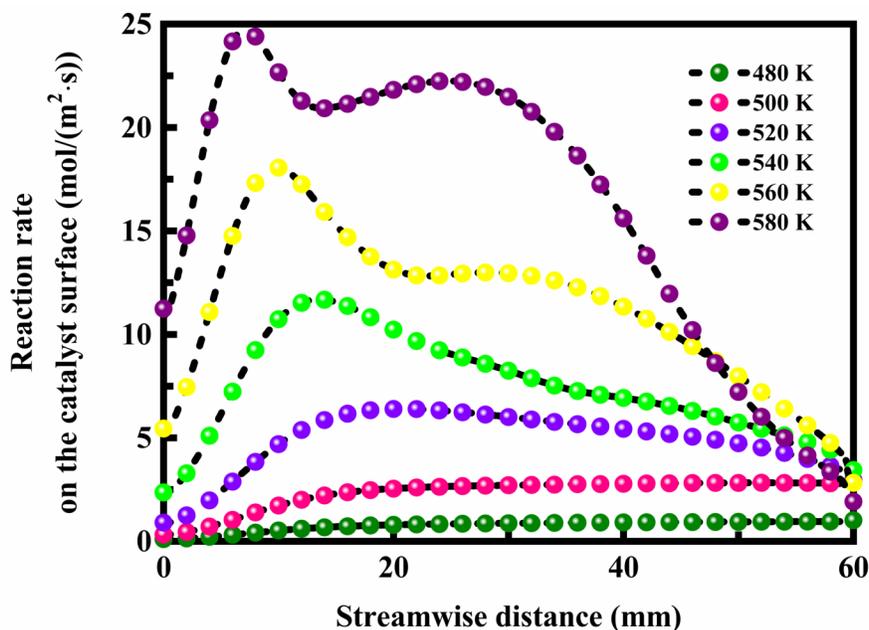


Figure 8. Reaction rate profiles on the catalyst surface along the length of the channels in the combined steam reformer-burner module under different temperature conditions.

5. Conclusions

Computational fluid dynamics is used to model fluid flow, heat and mass transfer, and chemical reactions. The governing integral equations are solved for the conservation of mass, momentum, and energy and other scalars such as laminar flow and chemical species. Steady-state analyses are carried out using computational fluid dynamics. The oxidation and reforming reaction rates in the fixed-bed reactor are computed by the

laminar finite-rate model. Particular emphasis is placed upon the effect of temperature on the transport and reaction characteristics of the fixed-bed reactor for polymer electrolyte membrane fuel cell applications. The major conclusions are summarized as follows:

- Under a thermodynamic point of view, high temperatures and steam-ethanol molar ratios promote hydrogen yield.
- Low ethylene content is obtained at high pressure and low temperature.
- At high temperatures the contribution of steam reforming reactions results in a marked increasing of overall enthalpy, enhancing process endothermicity, whereas the exothermic contribution of water-gas shift and methanation reactions reduces the external heat supply and the overall energy penalty at lower temperature.
- Although the equilibrium of the water-gas shift reaction favors the products formation at lower temperatures, reaction kinetics are faster at higher temperatures.
- The typical products distribution of ethanol steam reforming reaction, according to thermodynamic evaluations, results in considerable hydrogen production rates at higher temperatures and high methane yields at lower temperatures.
- The majority of supported metals as catalysts expresses better performance at high temperatures, and the production of oxygenated products increases and the formation of coke is thermodynamically favored at low temperatures.
- Low reaction temperatures generally favor the Boudouard reaction mechanism while methane decomposition is the main route at high temperatures.

References

1. K. Takise, A. Sato, K. Muraguchi, S. Ogo, and Y. Sekine. Steam reforming of aromatic hydrocarbon at low temperature in electric field. *Applied Catalysis A: General* , Volume 573, 2019, Pages 56-63.
2. P.P.S. Quirino, A.F. Amaral, F. Manenti, and K.V. Pontes. Mapping and optimization of an industrial steam methane reformer by the design of experiments (DOE). *Chemical Engineering Research and Design* , Volume 184, 2022, Pages 349-365.
3. O. Ovalle-Encinia and J.Y.S. Lin. Water-gas shift reaction in ceramic-carbonate dual-phase membrane reactor at high temperatures and pressures. *Chemical Engineering Journal* , Volume 448, 2022, Article Number: 137652.
4. M.I. Ariëns, L.G.A. van de Water, A.I. Dugulan, E. Brück, and E.J.M. Hensen. Copper promotion of chromium-doped iron oxide water-gas shift catalysts under industrially relevant conditions. *Journal of Catalysis* , Volume 405, 2022, Pages 391-403.
5. A. Shamiri and N. Aliabadi. Modeling and performance improvement of an industrial ammonia synthesis reactor. *Chemical Engineering Journal Advances* , Volume 8, 2021, Article Number: 100177.
6. P.H.A. Nóbrega. A review of physics-based low-temperature proton-exchange membrane fuel cell models for system-level water and thermal management studies. *Journal of Power Sources* , Volume 558, 2023, Article Number: 232585.
7. R. Huang, C. Lim, M.G. Jang, J.Y. Hwang, and J.W. Han. Exsolved metal-boosted active perovskite oxide catalyst for stable water gas shift reaction. *Journal of Catalysis* , Volume 400, 2021, Pages 148-159.
8. M. Shekhar, W.-S. Lee, M.C. Akatay, L. Maciel, W. Tang, J.T. Miller, E.A. Stach, M. Neurock, W.N. Delgass, and F.H. Ribeiro. Water-gas shift reaction over supported Au nanoparticles. *Journal of Catalysis* , Volume 405, 2022, Pages 475-488.
9. J.S. Moura, J. da S.L. Fonseca, N. Bion, F. Epron, T. de F. Silva, C.G. Maciel, J.M. Assaf, and M. do C. Rangel. Effect of lanthanum on the properties of copper, cerium and zirconium catalysts for preferential oxidation of carbon monoxide. *Catalysis Today* , Volume 228, 2014, Pages 40-50.
10. P.V. Gosavi and R.B. Biniwale. Catalytic preferential oxidation of carbon monoxide over platinum supported on lanthanum ferrite-ceria catalysts for cleaning of hydrogen. *Journal of Power Sources* , Volume 222, 2013, Pages 1-9.
11. P.C. Hulteberg, J.G.M. Brandin, F.A. Silversand, and M. Lundberg. Preferential oxidation of carbon

- monoxide on mounted and unmounted noble-metal catalysts in hydrogen-rich streams. *International Journal of Hydrogen Energy* , Volume 30, Issue 11, 2005, Pages 1235-1242.
12. C. Kwak, T.-J. Park, and D.J. Suh. Preferential oxidation of carbon monoxide in hydrogen-rich gas over platinum-cobalt-alumina aerogel catalysts. *Chemical Engineering Science* , Volume 60, Issue 5, 2005, Pages 1211-1217.
 13. F. Mariño, C. Descorme, and D. Duprez. Noble metal catalysts for the preferential oxidation of carbon monoxide in the presence of hydrogen (PROX). *Applied Catalysis B: Environmental* , Volume 54, Issue 1, 2004, Pages 59-66.
 14. E. Quinet, F. Morfin, F. Diehl, P. Avenier, V. Caps, and J.-L. Rousset. Hydrogen effect on the preferential oxidation of carbon monoxide over alumina-supported gold nanoparticles. *Applied Catalysis B: Environmental* , Volume 80, Issues 3-4, 2008, Pages 195-201.
 15. W. Li, F.J Gracia, and E.E Wolf. Selective combinatorial catalysis; challenges and opportunities: The preferential oxidation of carbon monoxide. *Catalysis Today* , Volume 81, Issue 3, 2003, Pages 437-447.
 16. H. Igarashi, H. Uchida, and M. Watanabe. Analyses of the preferential oxidation of carbon monoxide in hydrogen-rich gas over noble metal catalysts supported on mordenite. *Studies in Surface Science and Catalysis* , Volume 132, 2001, Pages 953-958.
 17. S.J. Wajc. Analytical solutions for adiabatic reactor problems. *Industrial & Engineering Chemistry Fundamentals* , Volume 8, Issue 3, 1969, Pages 593-594.
 18. J.M. Douglas and L.C. Eagleton. Analytical solutions for some adiabatic reactor problems. *Industrial & Engineering Chemistry Fundamentals* , Volume 1, Issue 2, 1962, Pages 116-119.
 19. L. Pirro, A. Obradović, B.D. Vandegehuchte, G.B. Marin, and J.W. Thybaut. Model-based catalyst selection for the oxidative coupling of methane in an adiabatic fixed-bed reactor. *Industrial & Engineering Chemistry Research* , Volume 57, Issue 48, 2018, Pages 16295-16307.
 20. W.L. Luyben. Control of outlet temperature in adiabatic tubular reactors. *Industrial & Engineering Chemistry Research* , Volume 39, Issue 5, 2000, Pages 1271-1278.
 21. S. Wedel and D. Luss. Steady-state multiplicity features of an adiabatic fixed-bed reactor with Langmuir-Hinshelwood kinetics; carbon monoxide or carbon dioxide methanation. *Industrial & Engineering Chemistry Fundamentals* , Volume 23, Issue 3, 1984, Pages 280-288.
 22. R.B. Menendez, C. Graschinsky, and N.E. Amadeo. Sorption-enhanced ethanol steam reforming process in a fixed-bed reactor. *Industrial & Engineering Chemistry Research* , Volume 57, Issue 34, 2018, 11547-11553.
 23. D. Luss. Temperature fronts and patterns in catalytic systems. *Industrial & Engineering Chemistry Research* , Volume 36, Issue 8, 1997, Pages 2931-2944.
 24. C.P.P. Singh and D.N. Saraf. Simulation of low-temperature water-gas shift reactor. *Industrial & Engineering Chemistry Process Design and Development* , Volume 19, Issue 3, 1980, Pages 393-396.
 25. G. Barbieri, A. Brunetti, T. Granato, P. Bernardo, and E. Drioli. Engineering evaluations of a catalytic membrane reactor for the water gas shift reaction. *Industrial & Engineering Chemistry Research* , Volume 44, Issue 20, 2005, Pages 7676-7683.
 26. P.V. Kherdekar, S. Roy, and D. Bhatia. Engineering evaluations of a catalytic dynamic modeling and optimization of a fixed-bed reactor for the partial water-gas shift reaction. *Industrial & Engineering Chemistry Research* , Volume 60, Issue 25, 2021, Pages 9022-9036.
 27. S.M. Senkan, L.B. Evans, and J.B. Howard. An analysis of the tube-wall reactor under diffusion limiting conditions. *Industrial & Engineering Chemistry Process Design and Development* , Volume 15, Issue 1, 1976, Pages 184-187.
 28. J.M.V. Castillo, T. Sato, and N. Itoh. Microkinetic analysis of the methane steam reforming on a Ru-supported catalytic wall reactor. *Industrial & Engineering Chemistry Research* , Volume 56, Issue 31, 2017, Pages 8815-8822.
 29. C. Ledesma, J. Yang, D. Chen, and A. Holmen. Recent approaches in mechanistic and kinetic studies of catalytic reactions using SSITKA technique. *ACS Catalysis* , Volume 4, Issue 12, 2014, Pages 4527-4547.
 30. M. Stamatakis and D.G. Vlachos. Unraveling the complexity of catalytic reactions via kinetic Monte

Carlo simulation: Current status and frontiers. *ACS Catalysis* , Volume 2, Issue 12, 2012, Pages 2648-2663.

31. V. Kumar, P. Gupta, and K.D.P. Nigam. Fluid flow and heat transfer in curved tubes with temperature-dependent properties. *Industrial & Engineering Chemistry Research* , Volume 46, Issue 10, 2007, Pages 3226-3236.
32. T.E. Daubert. Evaluated equation forms for correlating thermodynamic and transport properties with temperature. *Industrial & Engineering Chemistry Research* , Volume 37, Issue 8, 1998, Pages 3260-3267.
33. C.H. Marton, G.S. Haldeman, and K.F. Jensen. Portable thermoelectric power generator based on a microfabricated silicon combustor with low resistance to flow. *Industrial & Engineering Chemistry Research* , Volume 50, Issue 14, 2011, Pages 8468-8475.
34. S. Prakash, R. Akberov, D. Agonafer, A.D. Armijo, and M.A. Shannon. Influence of boundary conditions on sub-millimeter combustion. *Energy & Fuels* , Volume 23, Issue 7, 2009, Pages 3549-3557.
35. N. Yedala and N.S. Kaisare. Modeling of thermal integration of a catalytic microcombustor with a thermoelectric for power generation applications. *Energy & Fuels* , Volume 35, Issue 6, 2021, Pages 5141-5152.
36. D.G. Norton, E.D. Wetzel, and D.G. Vlachos. Fabrication of single-channel catalytic microburners: Effect of confinement on the oxidation of hydrogen-air mixtures. *Industrial & Engineering Chemistry Research* , Volume 43, Issue 16, 2004, Pages 4833-4840.
37. D.G. Norton, E.D. Wetzel, and D.G. Vlachos. Thermal management in catalytic microreactors. *Industrial & Engineering Chemistry Research* , Volume 45, Issue 1, 2006, Pages 76-84.
38. A.B. Mhadeshwar and D.G. Vlachos. A catalytic reaction mechanism for methane partial oxidation at short contact times, reforming, and combustion, and for oxygenate decomposition and oxidation on platinum. *Industrial & Engineering Chemistry Research* , Volume 46, Issue 16, 2007, Pages 5310-5324.
39. S.R. Deshmukh and D.G. Vlachos. CFD simulations of coupled, countercurrent combustor-reformer microdevices for hydrogen production. *Industrial & Engineering Chemistry Research* , Volume 44, Issue 14, 2005, Pages 4982-4992.
40. G.D. Stefanidis and D.G. Vlachos. Controlling homogeneous chemistry in homogeneous-heterogeneous reactors: Application to propane combustion. *Industrial & Engineering Chemistry Research* , Volume 48, Issue 13, 2009, Pages 5962-5968.
41. Y. Sekine, K. Urasaki, S. Kado, M. Matsukata, and E. Kikuchi. Nonequilibrium pulsed discharge: a novel method for steam reforming of hydrocarbons or alcohols. *Energy & Fuels* , Volume 18, Issue 2, 2004, Pages 455-459.
42. P.V. Mathure, S. Ganguly, A.V. Patwardhan, and R.K. Saha. Steam reforming of ethanol using a commercial nickel-based catalyst. *Industrial & Engineering Chemistry Research* , Volume 46, Issue 25, 2007, Pages 8471-8479.
43. J. Kniep, M. Anderson, and Y.S. Lin. Autothermal reforming of methane in a proton-conducting ceramic membrane reactor. *Industrial & Engineering Chemistry Research* , Volume 50, Issue 22, 2011, Pages 12426-12432.
44. D. Scognamiglio, L. Russo, P.L. Maffettone, L. Salemme, M. Simeone, and S. Crescitelli. Modeling temperature profiles of a catalytic autothermal methane reformer with nickel catalyst. *Industrial & Engineering Chemistry Research* , Volume 48, Issue 4, 2009, Pages 1804-1815.
45. E. Lopez, V. Gepert, A. Gritsch, U. Nieken, and G. Eigenberger. Ethanol steam reforming thermally coupled with fuel combustion in a parallel plate reactor. *Industrial & Engineering Chemistry Research* , Volume 51, Issue 11, 2012, Pages 4143-4151.
46. Z. Ferencz, A. Erdőhelyi, K. Baán, A. Oszkó, L. Óvári, Z. Kónya, C. Papp, H.-P. Steinrück, and J. Kiss. Effects of support and Rh additive on Co-based catalysts in the ethanol steam reforming reaction. *ACS Catalysis* , Volume 4, Issue 4, 2014, Pages 1205-1218.
47. G. Kolios, A. Gritsch, B. Glöckler, G. Sorescu, and J. Frauhammer. Novel reactor concepts for thermally efficient methane steam reforming: modeling and simulation. *Industrial & Engineering Chemistry Research* , Volume 43, Issue 16, 2004, Pages 4796-4808.

48. L. Basini and L. Piovesan. Reduction on synthesis gas costs by decrease of steam-carbon and oxygen-carbon ratios in the feedstock. *Industrial & Engineering Chemistry Research* , Volume 37, Issue 1, 1998, Pages 258-266.

Hydrogen production in fixed-bed reactors with combined reformer-burner modules by steam-ethanol reforming at different temperatures

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Abstract

Use of ethanol is attracting increasing attention both as primary feedstock and as an alternative to increase the feedstock flexibility in a given unit. However, steam reforming of ethanol is not a straight forward process. Equilibrium of the reaction is shifted towards the production of hydrogen even at low temperature. However, in practice, ethanol is also converted to ethylene. The present study is focused primarily upon the production of hydrogen in fixed-bed reactors by steam-ethanol reforming under different temperature conditions. Computational fluid dynamics is used to model fluid flow, heat and mass transfer, and chemical reactions. The governing integral equations are solved for the conservation of mass, momentum, and energy and other scalars such as laminar flow and chemical species. Steady-state analyses are performed using computational fluid dynamics. The reaction rates are computed by the laminar finite-rate model. The present study aims to explore how to effectively produce hydrogen in fixed-bed reactors by steam-ethanol reforming at different temperatures. Particular emphasis is placed upon the effect of temperature on the transport and reaction characteristics of fixed-bed reactors for polymer electrolyte membrane fuel cell applications. The results indicate that under a thermodynamic point of view, high temperatures and steam-ethanol molar ratios promote hydrogen yield. Low ethylene content is obtained at high pressure and low temperature. At high temperatures the contribution of steam reforming reactions results in a marked increasing of overall enthalpy, enhancing process endothermicity, whereas the exothermic contribution of water-gas shift and methanation reactions reduces the external heat supply and the overall energy penalty at lower temperature. Although the equilibrium of the water-gas shift reaction favors the products formation at lower temperatures, reaction kinetics are faster at higher temperatures. The typical products distribution of ethanol steam reforming reaction, according to thermodynamic evaluations, results in considerable hydrogen production rates at higher temperatures and high methane yields at lower temperatures. The majority of supported metals as catalysts expresses better performance at high temperatures, and the production of oxygenated products increases and the formation of coke is thermodynamically favored at low temperatures. Low reaction temperatures generally favor the Boudouard reaction mechanism while methane decomposition is the main route at high temperatures.

Keywords: Hydrogen; Ethanol; Reformers; Burners; Reforming; Combustion

1. Introduction

Hydrogen is becoming an increasingly desired fuel. One method of obtaining hydrogen is to release it from hydrocarbons [1, 2]. This approach suffers from the simultaneous production of carbon monoxide [3, 4]. Hydrogen containing carbon monoxide impairs the performance of many systems such as ammonia synthesis reactors [5] and low temperature fuel cells [6]. It is therefore desirable to have mechanisms to remove carbon monoxide from hydrogen [7, 8]. One method of accomplishing this removal is the selective oxidation of the carbon monoxide using a fixed-bed catalytic reactor.

Catalytic reactors of the fixed-bed type to selectively oxidize carbon monoxide are well known [7, 8]. These fixed-bed reactors when operated for the selective oxidation of carbon monoxide under varying flow conditions, for example, reduced load conditions in fuel processing for fuel cell applications [9, 10], can actually produce carbon monoxide via the reverse water-gas shift reaction, the reaction occurring when the oxygen concentration within the bed is depleted below a minimum threshold value [11, 12]. Consequently, if oxygen is consumed to this minimal threshold value before the hydrogen containing gas stream exits the catalyst bed, carbon monoxide is reformed in the oxygen depleted zone of the reactor [13, 14]. Addition of additional oxygen into the oxygen depleted zone of the reactor prevents the reverse water-gas shift reaction but at the expense of additional hydrogen consumption and added operational complexity.

The reverse water-gas shift reaction within a fixed-bed, catalytic reactor for the selective oxidation of carbon monoxide can be controlled for a broad range of operating conditions, flow rates, by controlling critical input parameters of the gas stream entering the reactor [15, 16]. An adiabatic reactor is defined as a reactor having no active heat removal device but which may have normal cooling losses associated typically with such reactors [17, 18]. In such a reactor, a temperature rise is observed typically along the length of the reactor for exothermic reactions [19, 20], for example, carbon monoxide oxidation. In an adiabatically operated fixed-bed, catalytic reactor that the inlet temperature of the entering gas stream, and space velocity of the gas stream in the reactor are determinative of when and to what degree [21, 22], the reverse water-gas shift reaction, if at all, will occur within the catalytic reactor [23, 24]. In essence, when the space velocity is changed due to a change in flow rate, such as during partial load operation, adjustments in the inlet temperature of the gas stream can be used to alter the carbon monoxide formation resulting from the reverse water-gas shift reaction [25, 26]. Under some circumstances, it might be possible to eliminate entirely the reverse water-gas shift reaction and the production of carbon monoxide therefrom.

Use of ethanol is attracting increasing attention both as primary feedstock and as an alternative to increase the feedstock flexibility in a given unit. However, steam reforming of ethanol is not a straight forward process. Equilibrium of the reaction is shifted towards the production of hydrogen even at low temperature. However, in practice, ethanol is also converted to ethylene. Compared to methanol, ethanol offers some well-known advantages, for example, it is non-toxic, can easily be produced from renewable resources, and possesses a higher energy content, which allows a vehicle equipped with such a system to achieve a higher operating range with the same volume of stored fuel. The present study is focused primarily upon the production of hydrogen in fixed-bed reactors by steam-ethanol reforming at different temperatures. Computational fluid dynamics is used to model fluid flow, heat and mass transfer, and chemical reactions. The governing integral equations are solved for the conservation of mass, momentum, and energy and other scalars such as laminar flow and chemical species. Steady-state analyses are performed using computational fluid dynamics. The reaction rates are computed by the laminar finite-rate model. The present study aims to explore how to effectively produce hydrogen in fixed-bed reactors by steam-ethanol reforming at different temperatures. Particular emphasis is placed upon the effect of temperature on the transport and reaction characteristics of fixed-bed reactors for polymer electrolyte membrane fuel cell applications.

2. Design and operation

The fuel cell stack operates on a fuel source comprising hydrogen. Hydrogen can be supplied to the stack via a steam reformer wherein a hydrocarbon fuel, such as natural gas or methane, is contacted with steam and converted in an endothermic process into a synthesis gas comprising a mixture of hydrogen and carbon monoxide and lesser quantities of carbon dioxide and water. The heat required for the endothermic steam reforming is typically generated in an associated burner module, wherein a

portion of the hydrocarbon fuel is combusted thereby generating the heat needed for the steam reformer. Generally, the steam reformer employed in the present study comprises a fuel inlet, a steam inlet, and a catalytic reaction zone having disposed therein a substrate onto which a reforming catalyst is supported. Non-limiting examples of suitable substrates include powders, pellets, extrudates, foams, and meshes. The substrate is provided as a mesh constructed in the form of a reticulated net or screen comprising a plurality of pores, cells, or channels having an ultra-short-channel-length. The steam reformer and the burner may be arranged as two concentric cylinders, and the burner occupies the inner cylindrical space and the reformer occupying an annular outer space. The reformer comprises a mesh substrate comprising an array of struts and a plurality of void volumes, the struts having supported thereon particles of catalyst. The mesh is provided as a stack of planar sheets with an inlet at one end of the stack and an outlet at an opposite end of the stack. The mesh may also be provided in a coiled configuration of cylindrical shape having an inner diameter and a larger outer diameter such that reactants flowing there through move along a radial flow path from an inlet along the inner diameter to an outlet along the outer diameter. In any configuration the bulk configuration of the mesh provides for a plurality of void volumes in random order, that is, empty spaces having essentially no regularity along the flow path from inlet to outlet. The mesh substrate is suitably constructed from a metal mesh, a ceramic mesh, or a combination thereof as in a cermet.

The burner is disposed in thermal communication with the steam reformer. A steam reforming catalyst is disposed within the reforming zone, the steam reforming catalyst comprising a porous substrate having an ultra-short-channel-length and having a Group VIII metal deposited thereon. The steam reformer operates on a mixture predominantly comprising the hydrocarbon fuel and steam, with little or no oxidant, in an endothermic steam reforming process. Typically, a burner is integrated with the reformer in a combined steam reformer-burner module, for the purpose of combusting a separate input of hydrocarbon fuel or combusting a fuel exhaust gas derived from the fuel cell stack, thereby providing heat via combustion to drive the endothermic steam reforming process. The burner provides a primary source of heat to the reformer; whereas heat from the fuel cell stack provides a secondary source of heat to the reformer, due to positioning the reformer within the system as well as capturing excess stack heat in the heat extractor to produce or heat steam for the reformer. This design beneficially allows for high stack fuel utilization, which results in a fuel exhaust gas from the fuel cell stack that is depleted in heat content and is not entirely sufficient to drive the endothermic steam reformer by itself. Excess stack heat of the secondary heat source provides the thermal balance for the reformer in such cases. In another embodiment, the burner is fed with a separate input of hydrocarbon fuel, when needed, to balance overall system requirements, for example, when the fuel cell stack is operating during startup or at high fuel utilization. The burner also functions as a start-up burner providing heat for raising the system components to their desired operating temperatures, particularly, as that pertains to the reforming catalyst and the fuel cell stack. Thus, the burner is utilized during start-up, transients and steady state operation, as desired. During the start-up phase, the temperature of all components including the fuel cell stack and the reforming catalyst must be raised to steady-state operating temperatures. After steady-state temperatures are reached, the steam reformer is advantageously converted to endothermic steam reforming status, wherein heat generated by the fuel cell stack is recuperated for use in the heat extractors and the reformer. The burner, which is needed during endothermic steam reforming, can also be utilized to generate heat during start-up. Furthermore, operation with a high temperature reformer offers the advantage that hydrocarbon-containing impurities in the respective fuel are, to a significant degree, converted in the reformer due to the high operating temperature and do not detrimentally affect downstream components. Extremely long-chained molecules that are not converted are cracked, which reduces their effect on downstream components, and can allow conversion of such cracked constituents in the downstream components.

3. Computational methods

Fluent is a general-purpose computational fluid dynamics software used to model fluid flow, heat and mass transfer, chemical reactions, and more. Fluent offers a modern, user-friendly interface that streamlines the computational fluid dynamics process from pre-processing to post-processing within a single window workflow. Fluent is known for its advanced physics modeling capabilities, which include turbulence modeling, single and multiphase flows, combustion, battery modeling, fluid-structure interaction, and much more. The Fluent solver is used to solve the governing integral equations for the conservation of mass and momentum, and, when appropriate, for energy and other scalars such as laminar flow and chemical species. In both cases, a control-volume-based technique is used that consists of division of the domain into discrete control volumes using a computational grid, integration of the governing equations on the individual control volumes to construct algebraic equations for the discrete dependent variables such as velocities, pressure, temperature, and conserved scalars, and linearization of the discretized equations and solution of the resultant linear equation system to yield updated values of the dependent variables. The two numerical methods employ a similar discretization process, but the approach used to linearize and solve the discretized equations is different. The pressure-based solver employs an algorithm which belongs to a general class of methods called the projection method. In the projection method, wherein the constraint of mass conservation of the velocity field is achieved by solving a pressure equation. The pressure equation is derived from the continuity and the momentum equations in such a way that the velocity field, corrected by the pressure, satisfies the continuity. Since the governing equations are nonlinear and coupled to one another, the solution process involves iterations wherein the entire set of governing equations is solved repeatedly until the solution converges. The pressure-based solver uses a solution algorithm where the governing equations are solved sequentially. Each governing equation, while being solved, is "decoupled" or "segregated" from other equations, hence its name. The segregated algorithm is memory-efficient, since the discretized equations need only be stored in the memory one at a time. However, the solution convergence is relatively slow, inasmuch as the equations are solved in a decoupled manner.

With the segregated algorithm, each iteration consists of the steps outlined below:

- Update fluid properties, for example, density, viscosity, specific heat, including diffusivity based on the current solution.
- Solve the momentum equations, one after another, using the recently updated values of pressure and face mass fluxes.
- Solve the pressure correction equation using the recently obtained velocity field and the mass-flux.
- Correct face mass fluxes, pressure, and the velocity field using the pressure correction obtained.
- Solve the equations for additional scalars, if any, such as turbulent quantities, energy, species, and radiation intensity using the current values of the solution variables.
- Update the source terms arising from the interactions among different phases, for example, source term for the carrier phase due to discrete particles.
- Check for the convergence of the equations.

These steps are continued until the convergence criteria are met.

Fluent uses a control-volume-based technique to convert a general scalar transport equation to an algebraic equation that can be solved numerically. This control volume technique consists of integrating the transport equation about each control volume, yielding a discrete equation that expresses the conservation law on a control-volume basis. When second-order accuracy is desired, quantities at cell faces are computed using a multidimensional linear reconstruction approach. In this approach, higher-order accuracy is achieved at cell faces through a Taylor series expansion of the cell-centered solution about the cell centroid. Gradients are needed not only for constructing values of a scalar at the

cell faces, but also for computing secondary diffusion terms and velocity derivatives. The gradient of a given variable is used to discretize the convection and diffusion terms in the flow conservation equations. Gradient limiters, also known as slope limiters, are used on the second-order upwind scheme to prevent spurious oscillations, which would otherwise appear in the solution flow field near shocks, discontinuities, or near rapid local changes in the flow field. The gradient limiter attempts to invoke and enforce the monotonicity principle by prohibiting the linearly reconstructed field variable on the cell faces to exceed the maximum or minimum values of the neighboring cells. Gradient limiters can be categorized into two general groups: non-differentiable limiters and differentiable limiters. Both, the standard limiter and multidimensional limiter are of the non-differentiable form, since they use minimum and maximum types of functions for limiting the solution variables. The third limiter in Fluent, as the name indicates, is a differentiable type of limiter, which uses a smooth function to impose the monotonicity principle. Special practices related to the discretization of the momentum and continuity equations and their solution by means of the pressure-based solver are addressed. These special practices are most easily described by considering the steady-state continuity and momentum equations in integral form. Pressure-velocity coupling is achieved to derive an additional condition for pressure by reformatting the continuity equation. The SIMPLE algorithm uses a relationship between velocity and pressure corrections to enforce mass conservation and to obtain the pressure field. The SIMPLE algorithm substitutes the flux correction equations into the discrete continuity equation to obtain a discrete equation for the pressure correction in the cell.

Steady-state analyses are performed using computational fluid dynamics. Fluent provides comprehensive modeling capabilities for a wide range of incompressible and compressible, laminar and turbulent fluid flow problems. In Fluent, a broad range of mathematical models for transport phenomena, such as heat transfer and chemical reactions, is combined with the ability to model complex geometries. The under-relaxation of variables is used in all cases for some material properties. To permit modeling of fluid flow and related transport phenomena in the steam reformer and burner and the physicochemical processes involved within the system, various useful features are provided. These include porous media, lumped parameter, streamwise-periodic flow and heat transfer, swirl, and moving reference frame models. For all flows, Fluent solves conservation equations for mass and momentum. For flows involving heat transfer or compressibility, an additional equation for energy conservation is solved. For flows involving species mixing or reactions, a species conservation equation is solved or, if the non-premixed combustion model is used, conservation equations for the mixture fraction and its variance are solved. Additional transport equations are also solved when the flow is turbulent. The net transport of energy at inlets consists of both the convection and diffusion components. The convection component is fixed by the inlet temperature specified. The diffusion component, however, depends on the gradient of the computed temperature field. Thus, the diffusion component and therefore the net inlet transport is not specified a priori.

Fluent can model the mixing and transport of chemical species by solving conservation equations describing convection, diffusion, and reaction sources for each component species. Multiple simultaneous chemical reactions can be modeled, with reactions occurring in the bulk phase, volumetric reactions, and on wall or particle surfaces, and in the porous region. The reaction rates are computed in Fluent by the laminar finite-rate model: The effect of turbulent fluctuations is ignored, and reaction rates are determined by Arrhenius kinetic expressions. The generalized finite-rate formulation is suitable for a wide range of applications including laminar or turbulent reaction systems, and combustion systems with premixed flames. The laminar finite-rate model computes the chemical source terms using Arrhenius expressions, and ignores the effects of turbulent fluctuations. The model is exact for laminar flames, but is generally inaccurate for turbulent flames due to highly non-linear Arrhenius chemical kinetics. The laminar model may, however, be acceptable for combustion with

relatively slow chemistry and small turbulence-chemistry interaction. For gas-phase reactions, the reaction rate is defined on a volumetric basis and the rate of creation and destruction of chemical species becomes a source term in the species conservation equations. For surface reactions, the rate of adsorption and desorption is governed by both chemical kinetics and diffusion to and from the surface [27]. Wall surface reactions thus create sources and sinks of chemical species in the gas phase, as well as on the reacting surface [28]. Reactions at surfaces change gas-phase, surface-adsorbed and bulk species [29, 30]. On reacting surfaces, the mass flux of each gas specie due to diffusion and convection to or from the surface is balanced with its rate of consumption or production on the surface [29, 30]. An important step in the setup of the model is to define the materials and their physical properties [31, 32]. Properties are temperature-dependent and composition-dependent, with temperature dependence based on a piecewise-polynomial function and individual component properties computed via kinetic theory [31, 32]. For solid materials, only density, thermal conductivity, and heat capacity are defined. A temperature-dependent function is specified for thermal conductivity and heat capacity.

4. Results and discussion

The sensible enthalpy contour plots in the combined steam reformer-burner module are illustrated in Figure 1 under different wall thermal conductivity conditions. Herein, micro-combustors are defined as devices with one or more physical dimensions being below one millimeter. Catalytic combustion is defined as combustion that does not involve flames. The equivalence ratio is defined as the fuel-air ratio normalized by the fuel-air ratio at stoichiometric conditions. Recent efforts have attempted to utilize combustion of hydrocarbons in miniature devices to directly produce heat or power [33, 34]. The devices utilize heat generated from combustion processes [35, 36]. More specifically, these devices typically utilize conventional homogeneous combustion. A major disadvantage of homogeneous combustion is that operating temperatures are necessarily very high [37, 38]. These high temperatures greatly limit material selection, burner life time, require extensive combustor insulation, and lead to significant nitrogen oxides production and emissions [39, 40]. Another disadvantage of homogeneous combustion is that flames quench when confined between walls that are less than about 2.0 mm apart, making it difficult to stabilize and maintain the reaction for long periods of time. These gap sizes can lead to combustors that are relatively bulky in size. A final disadvantage of homogeneous micro-combustion devices is that many of them consist of complicated miniature parts, which are difficult and expensive to fabricate, and so far, have exhibited very low efficiencies. An alternative to homogeneous micro-combustion is to combust the fuel catalytically, without the production of a flame. When implemented in miniature devices, catalytic micro-combustion has the potential to fully utilize the high energy densities of hydrocarbon fuels, but at much lower operating temperatures. Additionally, catalytic systems are typically easier to start, more robust to heat losses, and self-sustained at leaner fuel-air ratios. Finally, since catalytic combustion can be sustained in much smaller channels, catalytical micro-combustors can potentially be designed into more compact geometries than homogeneous combustors. The catalytic burner supports combustion in very shallow gaps and achieves high transport rates and complete conversion of the fuel. In addition, the catalytic burner controls the temperature uniformity by suitable material design and selection to increase efficiency. Furthermore, the catalytic burner allows control of temperature profiles for improved catalyst life time and performance of fixed-bed reactors for synthesis of chemicals. The water-gas shift reaction can be carried out by means of different catalysts depending on the temperature. Carrying out the water-gas shift reaction at high temperature in a heat exchange steam reformer leads to the immediate benefit of considerable improvement in thermal efficiency. The water-gas shift reaction is carried out at much lower temperatures than the reforming reaction and the water-gas shift catalyst is characterized by its ability to convert carbon monoxide while not producing methane. The ethanol conversion steps into

hydrogen by dehydration, hydrogenation, and reforming could in principle be carried out on the same catalyst provided that the polymer carbon forming reactions caused by ethylene is suppressed.

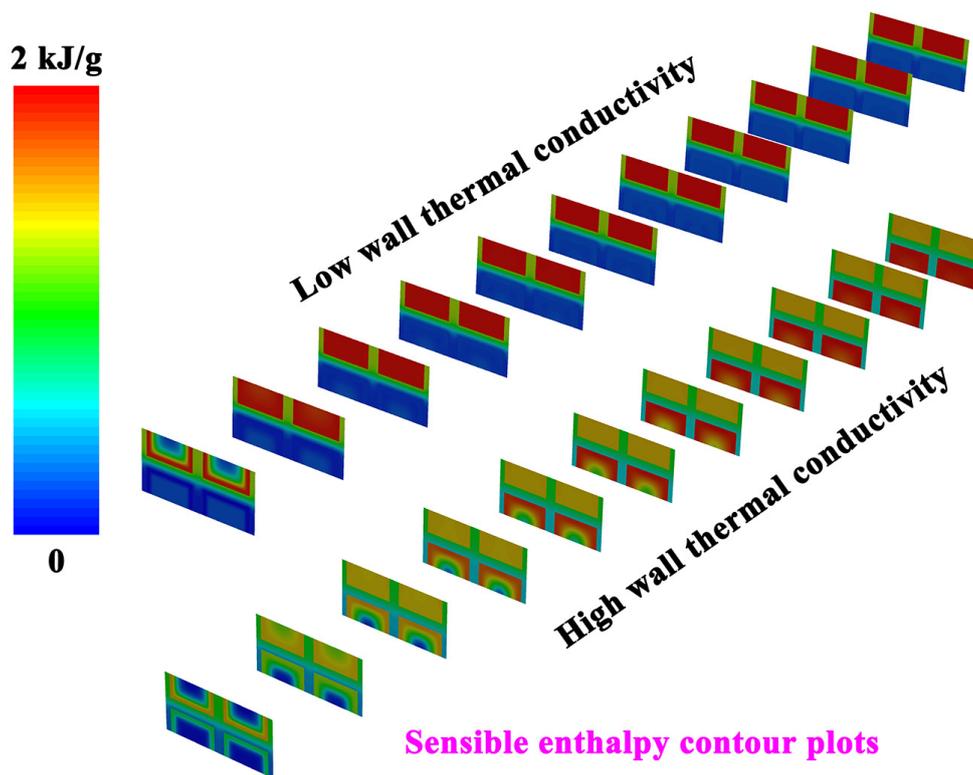


Figure 1. Sensible enthalpy contour plots in the combined steam reformer-burner module under different wall thermal conductivity conditions.

The ethanol molar fraction profiles on the catalyst surface are presented in Figure 2 along the length of the channels in the combined steam reformer-burner module under different temperature conditions. Typical routes for hydrogen production from ethanol include steam reforming, partial oxidation, and oxidative steam reforming. Ethanol steam reforming can potentially produce a high hydrogen amount per mole of converted reactant with no by-product formation other than carbon dioxide. Under a thermodynamic point of view, high temperatures and steam-ethanol molar ratios promote hydrogen yield. Higher hydrogen yield can be reached at higher temperatures. Moderate temperature and high-water content in the reforming mixture can limit carbon monoxide formation, thus avoiding its easy conversion to coke. A reduced content of carbon monoxide in the downstream gas can result in lower impact of further purification stages. In order to achieve a high conversion, the temperature in the reformer must be high. This results in a relatively high carbon monoxide content due to the equilibrium in the water-gas shift reaction established over the reforming catalyst. This device offers significant advantages with respect to the utilization of energy. Due to the very high temperatures in the high temperature steam reformer, the burner may be operated at a comparatively high temperature, since it is able to directly heat the high temperature reformer. At the same time, the feed material, for example, water and ethanol, can be evaporated using the burner exhaust gas, which is slightly cooler than the above temperature level. The water and the hydrocarbon derivative may be evaporated separately using two separate evaporators. If necessary, the water and the hydrocarbon derivative can also be superheated separately. Appropriate mixing may take place at a position between the metered injection and the high temperature reformer. As an alternative, a pre-mix may be utilized, which is then evaporated and superheated together. This design allows the conversion of methanol, as well as higher alcohols, without any modifications to the arrangement being necessary. Furthermore, operation with a high temperature reformer offers the advantage that hydrocarbon-containing impurities

in the respective fuel are, to a significant degree, converted in the reformer due to the high operating temperature and do not detrimentally affect downstream components.

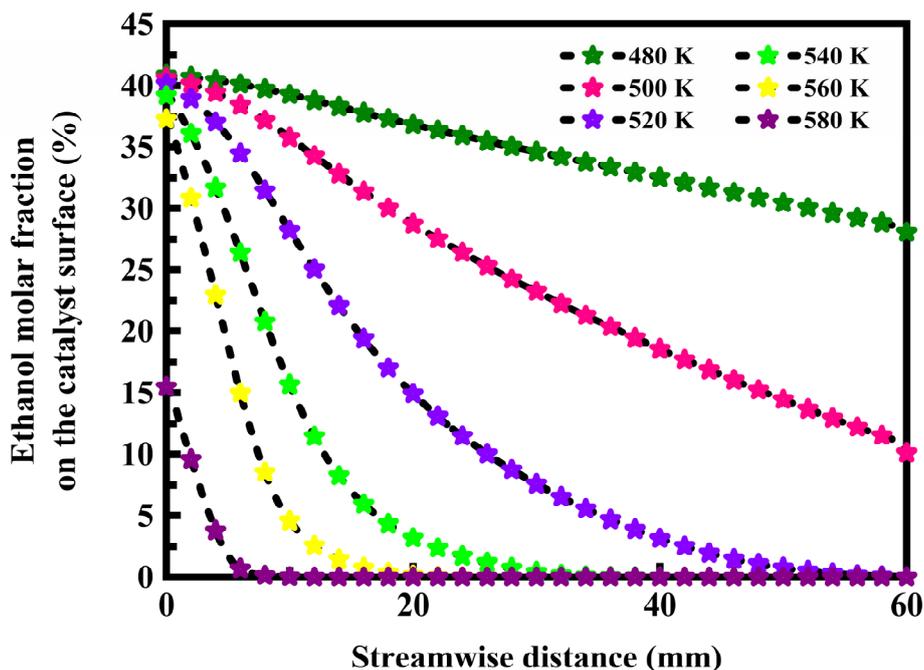


Figure 2. Ethanol molar fraction profiles on the catalyst surface along the length of the channels in the combined steam reformer-burner module under different temperature conditions.

The temperature contour plots in the combined steam reformer-burner module are illustrated in Figure 3 with a highly advantageous parallel heat and fluid flow configuration. Ethylene will even in small amounts rapidly form carbon and thereby carbon polymer on most steam reforming catalysts which causes considerable deactivation. High ethylene contents should therefore be avoided. A dual catalytic system involving the initial conversion of ethanol to ethylene and thereafter to ethane can be used instead and followed by steam reforming of the ethane. In the first catalyst zone, ethanol is converted into ethylene. Furthermore, ethylene reacts with hydrogen to form ethane. Excess hydrogen suppresses the equilibrium concentration of ethylene. Low ethylene content is obtained at high pressure and low temperature. The ethanol reforming process is useful for producing hydrogen for, for instance, fuel cells. Ethanol is steam reformed into hydrogen and carbon dioxide sequentially in a number of steps, each step characterized by a very high selectivity. In the first step ethanol, steam and a hydrogen-comprising stream are transferred to a reactor in which dehydration and hydrogenation reactions take place. Ethanol is dehydrated to ethylene and ethylene is hydrogenated to ethane. Catalysts for the dehydration reaction include a large amount of solid and liquid materials. For solid catalysts primarily acidic catalysts such as alumina, silica alumina, zeolites, zirconia or other solid acids or related compounds, have a high activity for dehydration of ethanol to ethylene. The catalyst of choice is based on alumina although many others are an equally valid choice. Selectivity is relevant with respect to formation of acetaldehyde, which is suppressed by a high hydrogen partial pressure. Diethyl ether may also be formed. However, this formation may be suppressed by high temperatures. In the second and third step, ethane in the effluent from the dehydration or hydrogenation reaction can be converted into hydrogen by steam reforming of the ethane formed. One option is to use an adiabatic pre-reformer followed by primary steam reforming with addition of heat. The third step is a primary reforming step where methane is steam reformed to carbon monoxide and hydrogen. This step occurs in the primary reformer, also denoted steam reformer, and a major part of the residual methane is converted into carbon oxides, for example, carbon monoxide and carbon dioxide, and hydrogen. The effluent from the primary reformer can also contain some water and methane. This is an endothermic

process and the heat required is normally supplied by indirect heat exchange with combusted fuel. Alternatively, if a pressure swing absorber is used for hydrogen purification a waste stream from the pressure swing absorber can also be used for firing. In the fourth step, the carbon monoxide is thus converted into hydrogen according to the water-gas shift reaction.

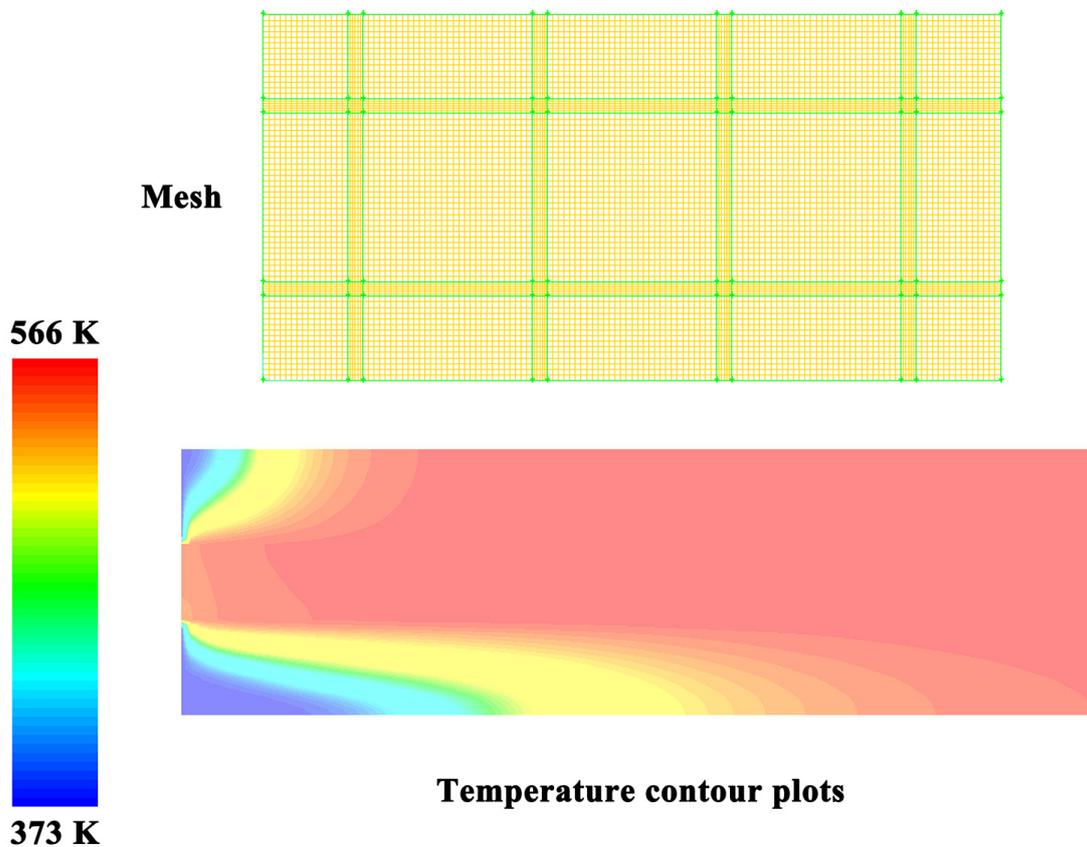


Figure 3. Temperature contour plots in the combined steam reformer-burner module with a highly advantageous parallel heat and fluid flow configuration.

The ethanol molar fraction profiles in the bulk gas phase are presented in Figure 4 along the length of the channels in the combined steam reformer-burner module under different temperature conditions. A stable combustion temperature may be optimized through adjustment of exemplary parameters including: fuel type, equivalence ratio, gap size, flow rate, and wall characteristics. Exemplary such wall characteristics may include: thermal conductivity, thickness, porosity, surface geometry, and non-homogeneity. Due to their dimensions being below the critical quenching distance, these catalytic burners are inherently safe with respect to flash back and explosion. Energy balance on the system evidences that at high temperatures the contribution of steam reforming reactions results in a marked increasing of overall enthalpy, enhancing process endothermicity, whereas the exothermic contribution of water-gas shift and methanation reactions reduces the external heat supply and the overall energy penalty at lower temperature. The auto-thermal point, at which the system is completely thermally self-sustained, depends on feed ratios steam-ethanol and operating pressure. Suppressing the formation of ethylene by hydrogenation of ethylene leads to production of ethane. An excess of hydrogen is required. This results in a reduction in the polymer carbon formation. Hydrogen is therefore added to the first dehydration or hydrogenation step. The product obtained from the shift step is purified and thereafter separated into hydrogen and water. The hydrogen can serve as a hydrogen-rich anode feed to the fuel cell. The hydrogen recycle ratio is related to the carbon formation. The recycle ratio denotes the fraction or percentage of hydrogen recycled. At a particular value of the recycle ratio, the hydrogen concentration is at such a level that carbon polymer formation ceases to be a significant factor for the performance of the reforming catalyst. The recycle ratio needed to obtain the molar ratio between

ethanol and hydrogen depends on where the recycle is taken from. The amount of hydrogen present in the effluent from each process step increases with each process step. Most hydrogen is therefore present in the hydrogen-rich anode feed stream and much less hydrogen is present in the effluent from the pre-reforming step. Recycling an effluent stream from for instance the shift step therefore requires a lower recycle ratio to the dehydration or hydrogenation step as compared to recycling an effluent containing comparatively less hydrogen from the pre-reforming step. Recycling from the pre-reforming step therefore requires a higher recycle ratio in order to provide enough hydrogen to fulfil the required ethanol to hydrogen molar ratio in the dehydration or hydrogenation step.

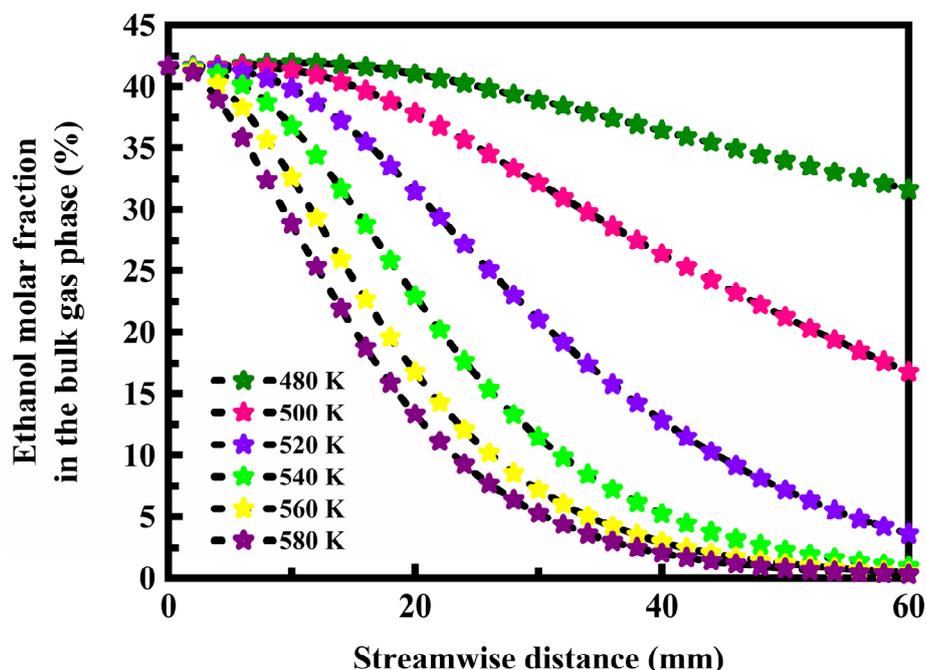


Figure 4. Ethanol molar fraction profiles in the bulk gas phase along the length of the channels in the combined steam reformer-burner module under different temperature conditions.

The hydrogen molar fraction contour plots are illustrated in Figure 5 in the reforming channels of the combined steam reformer-burner module with enhanced heat exchange. At high temperatures, the thermodynamic equilibrium leads to the production of large amounts of carbon monoxide, which poison the electrodes of polymer electrolyte membrane fuel cells. In order to ensure long and efficient use of hydrogen-fueled polymer electrolyte membrane fuel cell, highly pure hydrogen must be delivered. Then, water-gas shift reaction and preferential oxidation of carbon monoxide reaction or pressure swing adsorption steps are required for carbon monoxide removal. During the water-gas shift reaction, carbon monoxide is converted to carbon dioxide and hydrogen through a reaction with steam. Although the equilibrium of the water-gas shift reaction favors the products formation at lower temperatures, reaction kinetics are faster at higher temperatures. Then, the water-gas shift reaction is carried out in the combined steam reformer-burner module in two steps. At first, the reaction is performed at higher temperatures. After this step, the reaction is carried out in the combined steam reformer-burner module at lower temperatures. At the end of the water-gas shift reaction, the carbon monoxide concentration is very low in the combined steam reformer-burner module. The water-gas shift reaction is followed by preferential oxidation of carbon monoxide reaction or pressure swing adsorption. The concentration of carbon monoxide at the exit of this last step is very low in the combined steam reformer-burner module, which is appropriated to the polymer electrolyte membrane fuel cells. Then, the development of the catalysts that exhibit high performance on the reforming of ethanol at low temperatures, producing low amounts of carbon monoxide and by-products, could reduce the costs associated to the hydrogen purification steps. The feed material, usually water and a

hydrocarbon derivative for the production of the hydrogen-containing reformat gas stream are evaporated, and the hot burner exhaust gas is utilized for the evaporation. The feed material vapor is then directed to the high temperature reformer through a superheater, where they are superheated by the hot reformat gas stream being discharged from the steam reformer. The superheater acts as a superheater for the feed material vapor which, in turn, cools the reformat gas stream exiting the high temperature reformer to a temperature level that makes it possible to feed it into the water gas shift stage without any intermediate stages. In the high temperature reformer, the superheated feed material is subjected to steam reforming, and typically high-temperature steam reforming.

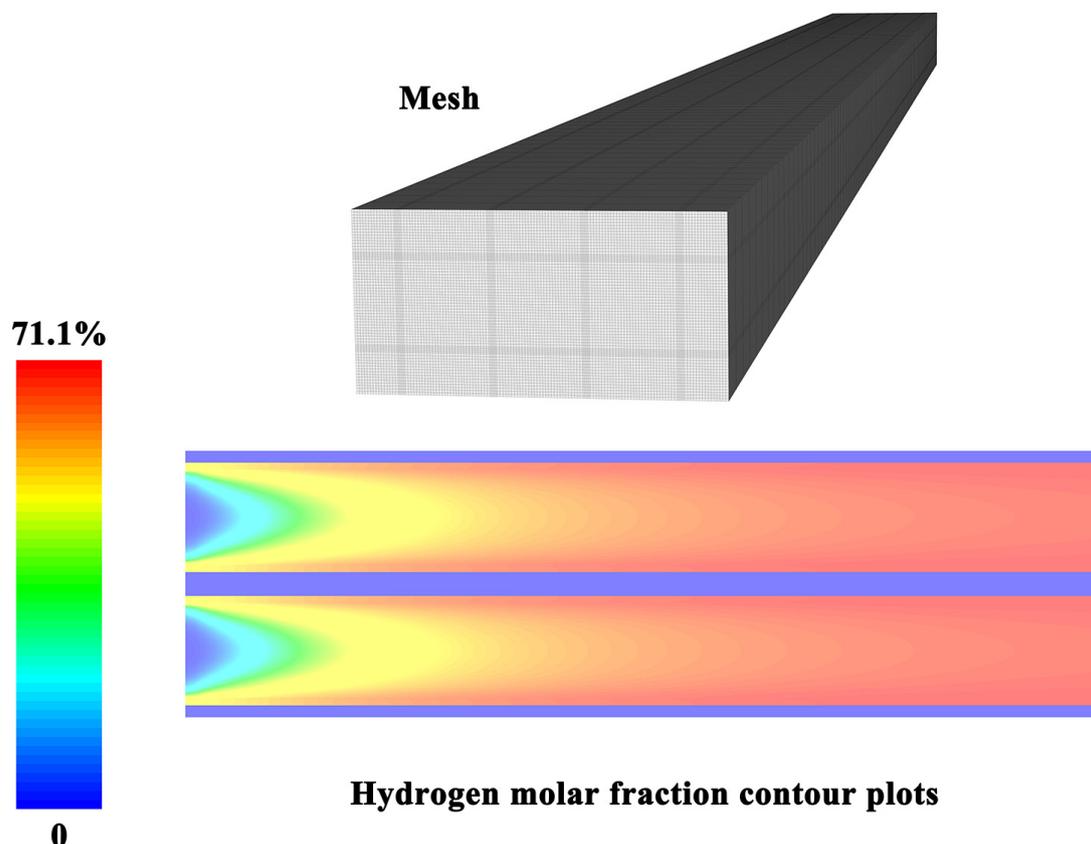


Figure 5. Hydrogen molar fraction contour plots in the reforming channels of the combined steam reformer-burner module with enhanced heat exchange.

The surface-to-bulk concentration ratio profiles are illustrated in Figure 6 along the length of the channels in the combined steam reformer-burner module under different temperature conditions. The typical products distribution of ethanol steam reforming reaction, according to thermodynamic evaluations, results in considerable hydrogen production rates at higher temperatures and high methane yields at lower temperatures. However, depending on the operating conditions selected, for example, temperature, ethanol partial pressure, steam to ethanol molar ratio, and space velocity, and the catalyst used, different reaction pathways can be observed, which reduce the desired product selectivity. In particular, the easy transformation of ethanol to acetaldehyde, ethylene, acetone or other by-products through decomposition, dehydrogenation and dehydration reaction strongly affects hydrogen yields, but above all could represent precursors for carbonaceous compounds that, depositing on the catalyst, determine its irreversible deactivation, and accordingly limiting the application of the process at industrial level. The main pathways responsible for coke deposition include methane decomposition, Boudouard reaction, and ethylene polymerization. Alternatively, carbon formation from ethylene could occur through decomposition followed by accumulation and polymerization of carbon atoms. In order to keep the carbon monoxide content of the reformat stream as low as possible, since carbon monoxide generally presents a problem for the operation of fuel cells, for example, the carbon

monoxide disadvantageously affects the function of the electrodes and membranes in the fuel cells, the temperatures in the reformer during the steam reforming of ethanol are usually approximately 250 °C to 300 °C. Existing systems, however, suffer the disadvantage that they are designed especially for a particular fuel, since the temperatures and catalysts have to be carefully selected in order to achieve an acceptable efficiency and to obtain a stream of reformat gas that meets all requirements, in particular those relating to residual quantities of feed material and carbon monoxide. Accordingly, there remains a need for a device for producing a hydrogen-containing gas for a fuel cell system, which device possesses a simple design, can process various types of fuels, is not affected by contamination with long-chain hydrocarbon compounds in the fuel, and which offers good cold-starting characteristics.

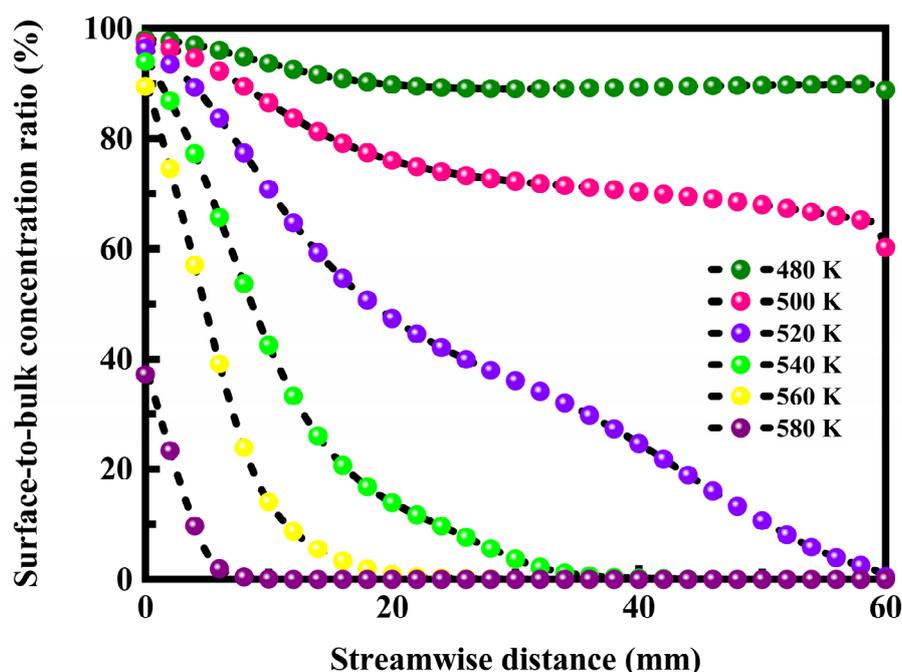


Figure 6. Surface-to-bulk concentration ratio profiles along the length of the channels in the combined steam reformer-burner module under different temperature conditions.

The ethanol molar fraction contour plots are illustrated in Figure 7 in the oxidation and reforming channels arranged in thermal communication of the combined steam reformer-burner module. Steam reforming of ethanol is an endothermic reaction. Then, the addition of energy to the combined reactor system is necessary, which leads to high capital and operation costs [41, 42]. One alternative way of supplying heat to the system is to add oxygen or air to the feedstock and simultaneously to burn a portion of ethanol, reaching the thermal neutrality of the reaction. This process is called autothermal reforming [43, 44]. Nevertheless, several parallel reactions can occur on these two routes, depending on the catalysts and the reaction conditions used, for example, dehydration of ethanol to ethene, followed by polymerization of ethene to form coke, decomposition of ethanol, producing methane, carbon monoxide and hydrogen, and dehydrogenation of ethanol, producing acetaldehyde [45, 46]. The methane can react with water, forming carbon monoxide and hydrogen [47, 48]. The appropriated catalyst for reforming of ethanol in the combined steam reformer-burner module should maximize the hydrogen production and minimize by-products formation. The majority of supported metals as catalysts expresses better performance at high temperatures, and the production of oxygenated products increases and the formation of coke is thermodynamically favored at low temperatures. The method for producing hydrogen-containing gas from a feed material for a polymer electrolyte membrane fuel cell system comprises the steps of evaporating the feed material to yield a vapor; superheating the vapor to yield a superheated feed material; steam reforming the superheated feed material, wherein the thermal energy required for steam reforming in the combined steam reformer-burner module is provided by a

burner that burns a gas stream that contains fuel and oxygen; and reducing the carbon monoxide content of the cooled stream by a water gas shift reaction, wherein the reformat stream is cooled between the steam reforming step and prior to the step of reducing the carbon monoxide content. Also, the method comprises the steps of operating the high temperature reformer as a partial oxidation stage for a period of time immediately following start-up, and then operating the high temperature reformer as a steam reformer once a suitable operating temperature for high temperature reforming is reached. To solve the problem related to a high carbon monoxide content in the reformat gas stream, a water-gas shift stage is included downstream, with respect to the flow direction of the reformats gas stream, of the high temperature reformer, which operates at temperatures that are significantly higher than reformers presently used in gas generation systems of this type. The water-gas shift stage further increases the hydrogen content of the reformat gas stream, and lowers the carbon monoxide content by reacting water and carbon monoxide to form hydrogen and carbon dioxide.

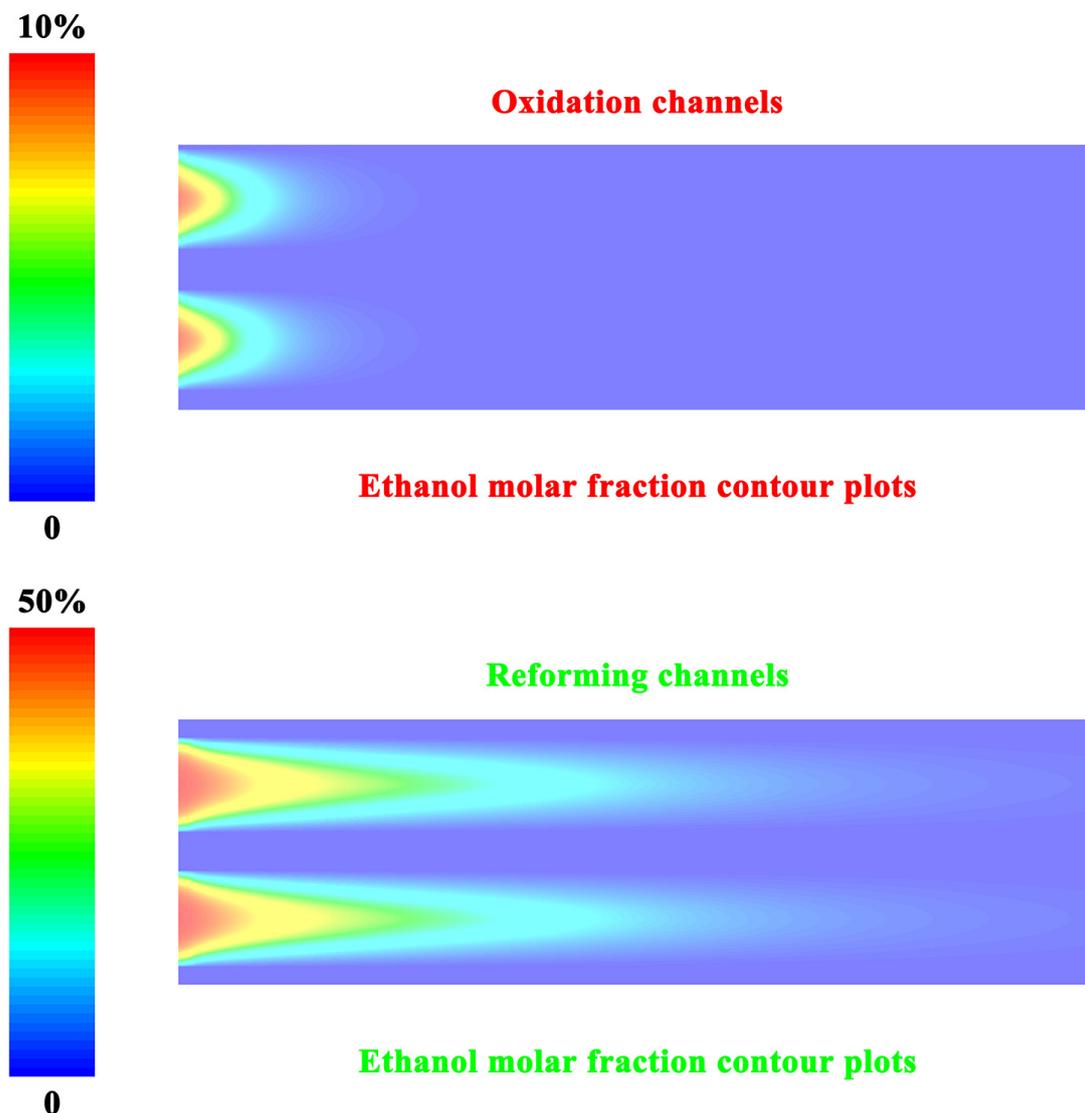


Figure 7. Ethanol molar fraction contour plots in the oxidation and reforming channels arranged in thermal communication of the combined steam reformer-burner module.

The reaction rate profiles on the catalyst surface are presented in Figure 8 along the length of the channels in the combined steam reformer-burner module under different temperature conditions. Reaction rates increase with increasing catalyst surface area for a given reactor volume. Because of this, high surface areas reactors are constructed. These typically involve particulates in fixed bed reactors. High surface areas provide leaner sustainable combustion, easier startup, potentially higher energy

efficiency, and no emissions of unburned hydrocarbons or carbon monoxide. However, most of these particulate bed combustors require pumping the fuel-air mixture directly through the bed, which causes large pressure drops that limit overall system efficiency. The microscale catalytic combustors have a low pressure-drop, and low catalytic surface area. The catalytic surface area available is approximately that of the geometric surface area of the exposed catalyst support. The device has a much higher specific surface area, which can lead to increased performance, especially at high flow rates. The catalytic ethanol reforming is conducted in the presence of steam. The quantity of steam fed to the reactor is selected so as to achieve the optimal steam-ethanol ratios in the feedstock to enhance the yield of the process. The presence of excess steam in the feedstock enables to inhibit carbonaceous compounds formation on the catalyst. The catalyst regeneration is conducted in the presence of superheated steam at high temperature and low pressure. The reforming channels are made flowing with an ethanol rich gaseous stream to generate a mixture of products containing hydrogen. In this way, the overall system is operated continuously. Low reaction temperatures generally favor the Boudouard reaction mechanism while methane decomposition is the main route at high temperatures. Moreover, depending on the reaction temperature, both amorphous and graphitized carbon can be produced. It is therefore necessary to enhance the stability of the catalyst at relatively high operating ethanol partial pressures. The high temperature reformer is heated by a burner that may burn the exhaust gas from the polymer electrolyte membrane fuel cell system and the residual fuel contained therein.

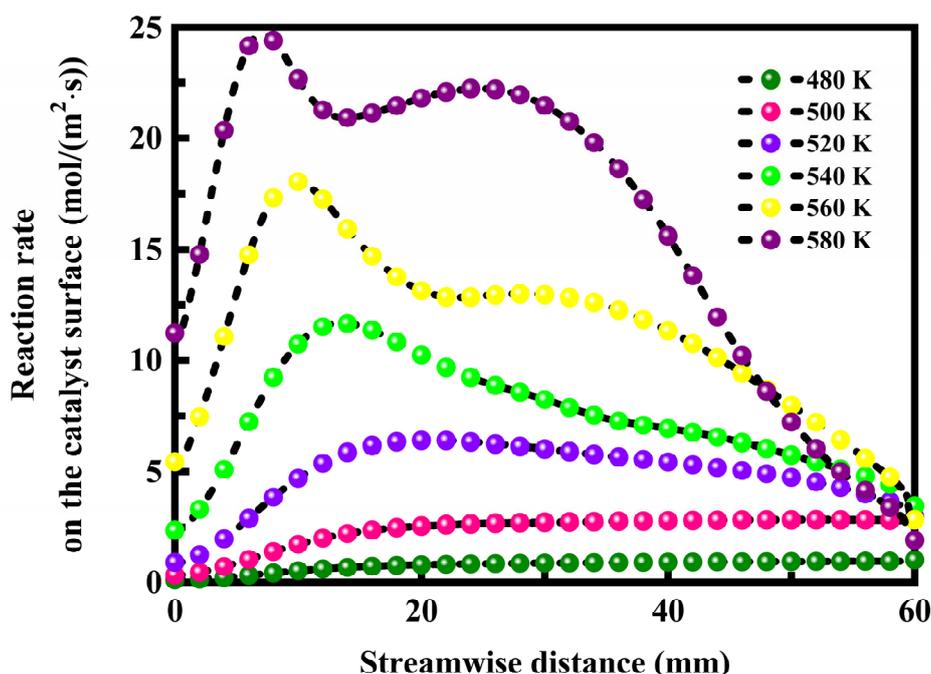


Figure 8. Reaction rate profiles on the catalyst surface along the length of the channels in the combined steam reformer-burner module under different temperature conditions.

5. Conclusions

Computational fluid dynamics is used to model fluid flow, heat and mass transfer, and chemical reactions. The governing integral equations are solved for the conservation of mass, momentum, and energy and other scalars such as laminar flow and chemical species. Steady-state analyses are carried out using computational fluid dynamics. The oxidation and reforming reaction rates in the fixed-bed reactor are computed by the laminar finite-rate model. Particular emphasis is placed upon the effect of temperature on the transport and reaction characteristics of the fixed-bed reactor for polymer electrolyte membrane fuel cell applications. The major conclusions are summarized as follows:

- Under a thermodynamic point of view, high temperatures and steam-ethanol molar ratios promote

hydrogen yield.

- Low ethylene content is obtained at high pressure and low temperature.
- At high temperatures the contribution of steam reforming reactions results in a marked increasing of overall enthalpy, enhancing process endothermicity, whereas the exothermic contribution of water-gas shift and methanation reactions reduces the external heat supply and the overall energy penalty at lower temperature.
- Although the equilibrium of the water-gas shift reaction favors the products formation at lower temperatures, reaction kinetics are faster at higher temperatures.
- The typical products distribution of ethanol steam reforming reaction, according to thermodynamic evaluations, results in considerable hydrogen production rates at higher temperatures and high methane yields at lower temperatures.
- The majority of supported metals as catalysts expresses better performance at high temperatures, and the production of oxygenated products increases and the formation of coke is thermodynamically favored at low temperatures.
- Low reaction temperatures generally favor the Boudouard reaction mechanism while methane decomposition is the main route at high temperatures.

References

- [1] K. Takise, A. Sato, K. Muraguchi, S. Ogo, and Y. Sekine. Steam reforming of aromatic hydrocarbon at low temperature in electric field. *Applied Catalysis A: General*, Volume 573, 2019, Pages 56-63.
- [2] P.P.S. Quirino, A.F. Amaral, F. Manenti, and K.V. Pontes. Mapping and optimization of an industrial steam methane reformer by the design of experiments (DOE). *Chemical Engineering Research and Design*, Volume 184, 2022, Pages 349-365.
- [3] O. Ovalle-Encinia and J.Y.S. Lin. Water-gas shift reaction in ceramic-carbonate dual-phase membrane reactor at high temperatures and pressures. *Chemical Engineering Journal*, Volume 448, 2022, Article Number: 137652.
- [4] M.I. Ariëns, L.G.A. van de Water, A.I. Dugulan, E. Brück, and E.J.M. Hensen. Copper promotion of chromium-doped iron oxide water-gas shift catalysts under industrially relevant conditions. *Journal of Catalysis*, Volume 405, 2022, Pages 391-403.
- [5] A. Shamiri and N. Aliabadi. Modeling and performance improvement of an industrial ammonia synthesis reactor. *Chemical Engineering Journal Advances*, Volume 8, 2021, Article Number: 100177.
- [6] P.H.A. Nóbrega. A review of physics-based low-temperature proton-exchange membrane fuel cell models for system-level water and thermal management studies. *Journal of Power Sources*, Volume 558, 2023, Article Number: 232585.
- [7] R. Huang, C. Lim, M.G. Jang, J.Y. Hwang, and J.W. Han. Exsolved metal-boosted active perovskite oxide catalyst for stable water gas shift reaction. *Journal of Catalysis*, Volume 400, 2021, Pages 148-159.
- [8] M. Shekhar, W.-S. Lee, M.C. Akatay, L. Maciel, W. Tang, J.T. Miller, E.A. Stach, M. Neurock, W.N. Delgass, and F.H. Ribeiro. Water-gas shift reaction over supported Au nanoparticles. *Journal of Catalysis*, Volume 405, 2022, Pages 475-488.
- [9] J.S. Moura, J. da S.L. Fonseca, N. Bion, F. Epron, T. de F. Silva, C.G. Maciel, J.M. Assaf, and M. do C. Rangel. Effect of lanthanum on the properties of copper, cerium and zirconium catalysts for preferential oxidation of carbon monoxide. *Catalysis Today*, Volume 228, 2014, Pages 40-50.
- [10] P.V. Gosavi and R.B. Biniwale. Catalytic preferential oxidation of carbon monoxide over platinum

- supported on lanthanum ferrite-ceria catalysts for cleaning of hydrogen. *Journal of Power Sources*, Volume 222, 2013, Pages 1-9.
- [11] P.C. Hulteberg, J.G.M. Brandin, F.A. Silversand, and M. Lundberg. Preferential oxidation of carbon monoxide on mounted and unmounted noble-metal catalysts in hydrogen-rich streams. *International Journal of Hydrogen Energy*, Volume 30, Issue 11, 2005, Pages 1235-1242.
- [12] C. Kwak, T.-J. Park, and D.J. Suh. Preferential oxidation of carbon monoxide in hydrogen-rich gas over platinum-cobalt-alumina aerogel catalysts. *Chemical Engineering Science*, Volume 60, Issue 5, 2005, Pages 1211-1217.
- [13] F. Mariño, C. Descorme, and D. Duprez. Noble metal catalysts for the preferential oxidation of carbon monoxide in the presence of hydrogen (PROX). *Applied Catalysis B: Environmental*, Volume 54, Issue 1, 2004, Pages 59-66.
- [14] E. Quinet, F. Morfin, F. Diehl, P. Avenier, V. Caps, and J.-L. Rousset. Hydrogen effect on the preferential oxidation of carbon monoxide over alumina-supported gold nanoparticles. *Applied Catalysis B: Environmental*, Volume 80, Issues 3-4, 2008, Pages 195-201.
- [15] W. Li, F.J. Gracia, and E.E. Wolf. Selective combinatorial catalysis; challenges and opportunities: The preferential oxidation of carbon monoxide. *Catalysis Today*, Volume 81, Issue 3, 2003, Pages 437-447.
- [16] H. Igarashi, H. Uchida, and M. Watanabe. Analyses of the preferential oxidation of carbon monoxide in hydrogen-rich gas over noble metal catalysts supported on mordenite. *Studies in Surface Science and Catalysis*, Volume 132, 2001, Pages 953-958.
- [17] S.J. Wajc. Analytical solutions for adiabatic reactor problems. *Industrial & Engineering Chemistry Fundamentals*, Volume 8, Issue 3, 1969, Pages 593-594.
- [18] J.M. Douglas and L.C. Eagleton. Analytical solutions for some adiabatic reactor problems. *Industrial & Engineering Chemistry Fundamentals*, Volume 1, Issue 2, 1962, Pages 116-119.
- [19] L. Pirro, A. Obradović, B.D. Vandegheuchte, G.B. Marin, and J.W. Thybaut. Model-based catalyst selection for the oxidative coupling of methane in an adiabatic fixed-bed reactor. *Industrial & Engineering Chemistry Research*, Volume 57, Issue 48, 2018, Pages 16295-16307.
- [20] W.L. Luyben. Control of outlet temperature in adiabatic tubular reactors. *Industrial & Engineering Chemistry Research*, Volume 39, Issue 5, 2000, Pages 1271-1278.
- [21] S. Wedel and D. Luss. Steady-state multiplicity features of an adiabatic fixed-bed reactor with Langmuir-Hinshelwood kinetics; carbon monoxide or carbon dioxide methanation. *Industrial & Engineering Chemistry Fundamentals*, Volume 23, Issue 3, 1984, Pages 280-288.
- [22] R.B. Menendez, C. Graschinsky, and N.E. Amadeo. Sorption-enhanced ethanol steam reforming process in a fixed-bed reactor. *Industrial & Engineering Chemistry Research*, Volume 57, Issue 34, 2018, 11547-11553.
- [23] D. Luss. Temperature fronts and patterns in catalytic systems. *Industrial & Engineering Chemistry Research*, Volume 36, Issue 8, 1997, Pages 2931-2944.
- [24] C.P.P. Singh and D.N. Saraf. Simulation of low-temperature water-gas shift reactor. *Industrial & Engineering Chemistry Process Design and Development*, Volume 19, Issue 3, 1980, Pages 393-396.
- [25] G. Barbieri, A. Brunetti, T. Granato, P. Bernardo, and E. Drioli. Engineering evaluations of a catalytic membrane reactor for the water gas shift reaction. *Industrial & Engineering Chemistry Research*, Volume 44, Issue 20, 2005, Pages 7676-7683.
- [26] P.V. Kherdekar, S. Roy, and D. Bhatia. Engineering evaluations of a catalytic dynamic modeling and optimization of a fixed-bed reactor for the partial water-gas shift reaction. *Industrial & Engineering Chemistry Research*, Volume 60, Issue 25, 2021, Pages 9022-9036.
- [27] S.M. Senkan, L.B. Evans, and J.B. Howard. An analysis of the tube-wall reactor under diffusion

- limiting conditions. *Industrial & Engineering Chemistry Process Design and Development*, Volume 15, Issue 1, 1976, Pages 184-187.
- [28] J.M.V. Castillo, T. Sato, and N. Itoh. Microkinetic analysis of the methane steam reforming on a Ru-supported catalytic wall reactor. *Industrial & Engineering Chemistry Research*, Volume 56, Issue 31, 2017, Pages 8815-8822.
- [29] C. Ledesma, J. Yang, D. Chen, and A. Holmen. Recent approaches in mechanistic and kinetic studies of catalytic reactions using SSITKA technique. *ACS Catalysis*, Volume 4, Issue 12, 2014, Pages 4527-4547.
- [30] M. Stamatakis and D.G. Vlachos. Unraveling the complexity of catalytic reactions via kinetic Monte Carlo simulation: Current status and frontiers. *ACS Catalysis*, Volume 2, Issue 12, 2012, Pages 2648-2663.
- [31] V. Kumar, P. Gupta, and K.D.P. Nigam. Fluid flow and heat transfer in curved tubes with temperature-dependent properties. *Industrial & Engineering Chemistry Research*, Volume 46, Issue 10, 2007, Pages 3226-3236.
- [32] T.E. Daubert. Evaluated equation forms for correlating thermodynamic and transport properties with temperature. *Industrial & Engineering Chemistry Research*, Volume 37, Issue 8, 1998, Pages 3260-3267.
- [33] C.H. Marton, G.S. Haldeman, and K.F. Jensen. Portable thermoelectric power generator based on a microfabricated silicon combustor with low resistance to flow. *Industrial & Engineering Chemistry Research*, Volume 50, Issue 14, 2011, Pages 8468-8475.
- [34] S. Prakash, R. Akberov, D. Agonafer, A.D. Armijo, and M.A. Shannon. Influence of boundary conditions on sub-millimeter combustion. *Energy & Fuels*, Volume 23, Issue 7, 2009, Pages 3549-3557.
- [35] N. Yedala and N.S. Kaisare. Modeling of thermal integration of a catalytic microcombustor with a thermoelectric for power generation applications. *Energy & Fuels*, Volume 35, Issue 6, 2021, Pages 5141-5152.
- [36] D.G. Norton, E.D. Wetzel, and D.G. Vlachos. Fabrication of single-channel catalytic microburners: Effect of confinement on the oxidation of hydrogen-air mixtures. *Industrial & Engineering Chemistry Research*, Volume 43, Issue 16, 2004, Pages 4833-4840.
- [37] D.G. Norton, E.D. Wetzel, and D.G. Vlachos. Thermal management in catalytic microreactors. *Industrial & Engineering Chemistry Research*, Volume 45, Issue 1, 2006, Pages 76-84.
- [38] A.B. Mhadeshwar and D.G. Vlachos. A catalytic reaction mechanism for methane partial oxidation at short contact times, reforming, and combustion, and for oxygenate decomposition and oxidation on platinum. *Industrial & Engineering Chemistry Research*, Volume 46, Issue 16, 2007, Pages 5310-5324.
- [39] S.R. Deshmukh and D.G. Vlachos. CFD simulations of coupled, countercurrent combustor-reformer microdevices for hydrogen production. *Industrial & Engineering Chemistry Research*, Volume 44, Issue 14, 2005, Pages 4982-4992.
- [40] G.D. Stefanidis and D.G. Vlachos. Controlling homogeneous chemistry in homogeneous-heterogeneous reactors: Application to propane combustion. *Industrial & Engineering Chemistry Research*, Volume 48, Issue 13, 2009, Pages 5962-5968.
- [41] Y. Sekine, K. Urasaki, S. Kado, M. Matsukata, and E. Kikuchi. Nonequilibrium pulsed discharge: a novel method for steam reforming of hydrocarbons or alcohols. *Energy & Fuels*, Volume 18, Issue 2, 2004, Pages 455-459.
- [42] P.V. Mathure, S. Ganguly, A.V. Patwardhan, and R.K. Saha. Steam reforming of ethanol using a commercial nickel-based catalyst. *Industrial & Engineering Chemistry Research*, Volume 46, Issue 25, 2007, Pages 8471-8479.

- [43]J. Kniep, M. Anderson, and Y.S. Lin. Autothermal reforming of methane in a proton-conducting ceramic membrane reactor. *Industrial & Engineering Chemistry Research*, Volume 50, Issue 22, 2011, Pages 12426-12432.
- [44]D. Scognamiglio, L. Russo, P.L. Maffettone, L. Salemme, M. Simeone, and S. Crescitelli. Modeling temperature profiles of a catalytic autothermal methane reformer with nickel catalyst. *Industrial & Engineering Chemistry Research*, Volume 48, Issue 4, 2009, Pages 1804-1815.
- [45]E. Lopez, V. Geper, A. Gritsch, U. Nieken, and G. Eigenberger. Ethanol steam reforming thermally coupled with fuel combustion in a parallel plate reactor. *Industrial & Engineering Chemistry Research*, Volume 51, Issue 11, 2012, Pages 4143-4151.
- [46]Z. Ferencz, A. Erdőhelyi, K. Baán, A. Oszkó, L. Óvári, Z. Kónya, C. Papp, H.-P. Steinrück, and J. Kiss. Effects of support and Rh additive on Co-based catalysts in the ethanol steam reforming reaction. *ACS Catalysis*, Volume 4, Issue 4, 2014, Pages 1205-1218.
- [47]G. Kolios, A. Gritsch, B. Glöckler, G. Sorescu, and J. Frauhammer. Novel reactor concepts for thermally efficient methane steam reforming: modeling and simulation. *Industrial & Engineering Chemistry Research*, Volume 43, Issue 16, 2004, Pages 4796-4808.
- [48]L. Basini and L. Piovesan. Reduction on synthesis gas costs by decrease of steam-carbon and oxygen-carbon ratios in the feedstock. *Industrial & Engineering Chemistry Research*, Volume 37, Issue 1, 1998, Pages 258-266.