

# Designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming

Junjie Chen<sup>1</sup>

<sup>1</sup>Department of Energy and Power Engineering, School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo, Henan, 454000, P.R. China. \*  
Corresponding author, E-mail address: [jchengn@163.com](mailto:jchengn@163.com),  
<https://orcid.org/0000-0001-6708-071X>

February 21, 2023

## Abstract

Endothermic reactions performed in microreactors are driven using heat from an external source. However, the temperature of the gas stream providing the heat is limited by constraints imposed by the materials of construction. The present study is focused primarily upon the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. A symmetry boundary condition is used to model half of each system where symmetry exists. Computations are performed using grids with varying nodal densities to determine the optimum node spacing and density that would give the desired accuracy and minimize computation time. The final grid density is determined when the centerline profiles of temperature and species concentration do not show obvious difference. The second-order upwind scheme is used to discretize the mathematical model, and the semi-implicit method for pressure-linked equations algorithm is employed to solve for the pressure and velocity fields. The convergence is judged upon the residuals of all governing equations. The present study aims to provide a fundamental understanding of the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. Particular emphasis is placed upon the effect of various factors on the thermochemical steam reforming processes in heat integrated reactors. The results indicate that steam reforming produces hydrogen and carbon monoxide when heat is added to a catalytic reactor containing steam and hydrocarbons. Alternating channel parallel plate designs can be applied to thermally coupling endothermic steam reforming with combustion in neighboring channels. Balancing the heat requirements of an endothermic reaction with heat generated by an exothermic reaction flowing parallel to and on the opposite side of a separating plate is extraordinarily difficult since the endothermic reaction is likely to have a very different dependence upon concentration and temperature than the endothermic reaction. A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels. The process gas is raised in temperature and this energy can be utilized by the reforming process. The catalyst coating thickness depends upon the process proceeding within the catalyst matrix. The arrangement leads to improved heat transfer and therefore chemical conversion. Heterogeneous combustion aids in spreading the heat generation along the length of the channel and helps prevent hotspot formation.

**Keywords:** Hydrogen production; Endothermic reactions; Discrete channels; Flow arrangements; Chemical conversion; Heterogeneous combustion

## Designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming

Junjie Chen

Department of Energy and Power Engineering, School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo, Henan, 454000, P.R. China

\* Corresponding author, E-mail address: [jchengn@163.com](mailto:jchengn@163.com), <https://orcid.org/0000-0001-6708-071X>

## Abstract

Endothermic reactions performed in microreactors are driven using heat from an external source. However, the temperature of the gas stream providing the heat is limited by constraints imposed by the materials of construction. The present study is focused primarily upon the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. A symmetry boundary condition is used to model half of each system where symmetry exists. Computations are performed using grids with varying nodal densities to determine the optimum node spacing and density that would give the desired accuracy and minimize computation time. The final grid density is determined when the centerline profiles of temperature and species concentration do not show obvious difference. The second-order upwind scheme is used to discretize the mathematical model, and the semi-implicit method for pressure-linked equations algorithm is employed to solve for the pressure and velocity fields. The convergence is judged upon the residuals of all governing equations. The present study aims to provide a fundamental understanding of the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. Particular emphasis is placed upon the effect of various factors on the thermochemical steam reforming processes in heat integrated reactors. The results indicate that steam reforming produces hydrogen and carbon monoxide when heat is added to a catalytic reactor containing steam and hydrocarbons. Alternating channel parallel plate designs can be applied to thermally coupling endothermic steam reforming with combustion in neighboring channels. Balancing the heat requirements of an endothermic reaction with heat generated by an exothermic reaction flowing parallel to and on the opposite side of a separating plate is extraordinarily difficult since the endothermic reaction is likely to have a very different dependence upon concentration and temperature than the endothermic reaction. A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels. The process gas is raised in temperature and this energy can be utilized by the reforming process. The catalyst coating thickness depends upon the process proceeding within the catalyst matrix. The arrangement leads to improved heat transfer and therefore chemical conversion. Heterogeneous combustion aids in spreading the heat generation along the length of the channel and helps prevent hotspot formation.

**Keywords:** Hydrogen production; Endothermic reactions; Discrete channels; Flow arrangements; Chemical conversion; Heterogeneous combustion

## 1. Introduction

Among the various chemical reactions occurring in industrial reactors, the use of catalytic gas-solid reactions is widespread. A packed bed reactor is commonly used for these types of reactions. Conventional packed bed reactors are associated with various difficulties and disadvantages, including pressure drop, intra particle diffusion limitations, flow channeling, and heat transfer limitations [1, 2]. Structured catalyst reactors are frequently used to address these challenges. These structured catalyst reactors are commonly utilized when there is a need for controlled endothermic or exothermic reactions. However, existing structured catalyst reactors, while demonstrating higher performance in comparison to the packed bed reactors, still have a number of drawbacks, including high cost, weight, thermal resistance, and heat management, among others [3, 4]. Important products of the Fischer-Tropsch reaction include gaseous hydrocarbons, such as lower olefins, paraffins, or alcohols, and liquid hydrocarbons, such as higher olefins, paraffins and alcohols [5, 6]. The Fischer-Tropsch reaction is highly exothermic and therefore effective heat transfer and temperature controls are important prerequisites for the successful operation. Furthermore, the reaction operability range, with pressures between 1-30 bar and temperatures ranging from 200 °C to 350 °C, requires an additional control to prevent formation of local hot spots responsible for the deterioration of the catalyst [7, 8]. Thus, there is a need for very efficient heat transfer during the reaction to prevent metallic catalyst deactivation and formation of undesirable products. Accordingly, there remains a need for a reactor that provides an efficient control over endothermic and exothermic chemical reactions, such as those carried out in the presence of a catalyst. For example, there is a need for a reactor for the Fischer-Tropsch catalytic processing of the synthesis gas that ensures very efficient heat transfer during the catalytic reaction.

Natural gas and methane, a major constituent of natural gas, are difficult to economically transport and are not easily converted into liquid fuels or chemicals that are more readily contained and transported. To

facilitate transport, methane is typically converted to synthesis gas which is an intermediate in the conversion of methane to liquid fuels, methanol or other chemicals [9, 10]. Synthesis gas is a mixture of hydrogen and carbon monoxide with a hydrogen to carbon monoxide molar ratio of from about 0.6 to about 6. One chemical reaction effective to convert methane to synthesis gas is steam reforming. Methane is reacted with steam and endothermically converted to a mixture of hydrogen and carbon monoxide [11, 12]. The heat energy to sustain the endothermic reaction is generated by the external combustion of fuel. A second chemical reaction effective to convert methane to synthesis gas is partial oxidation. Methane is reacted with oxygen in an exothermic reaction [13, 14]. Synthesis gas can be produced by combined partial oxidation and steam reforming. The synthesis gas is then converted to liquids by the Fischer-Tropsch process or can be converted to methanol by commercial processes [15, 16]. In the primary steam reforming of fluid hydrocarbons, such as natural gas or methane, the feed material and steam are passed through catalyst-containing vertically hanging reformer tubes maintained at an elevated temperature by radiant heat transfer and by contact with combustion gases in the furnace portion of the tubular reactor. The hot reformer tube effluent may be passed to a waste heat recovery zone for the generation of steam that can be used in the steam reforming operations. Conventional primary steam reforming operations are commonly carried out at temperatures of from about 750 °C to about 850 °C or above [17, 18]. The primary steam reforming is a highly endothermic reaction, and the large amounts of required heat are typically provided by combusting external fuel at close to atmospheric pressures in the reforming furnace. Consequently, the reformer tubes are generally made of high alloy, expensive materials having a limited operating life under such extreme conditions [19, 20]. The reaction temperatures existing inside the reformer tubes are generally lower than about 850 °C so that the effluent gas recovered from the primary reformer typically contains 2-6 percent methane [21, 22]. The effluent from primary reforming is sometimes passed to a secondary reforming zone in which unconverted methane present in the reformed gas mixture is catalytically reacted with air, oxygen or other suitable oxygen-containing gas.

Large quantities of hydrogen, or of an ammonia syngas mixture of hydrogen and nitrogen, are produced either by such steam reforming operations or by partial oxidation reactions. Partial oxidation, like secondary reforming, is an exothermic, autothermal, internal combustion process [23, 24]. While secondary reforming is also a catalytic process, however, the various known partial oxidation processes employ non-catalytic reactions, and thus operate at higher reaction temperatures on the order of about 1300 °C. The significant advantages obtainable by the use of secondary reforming, or by the use of partial oxidation processing, are off-set to some extent by the need to compress the oxygen-containing gas to the desired reaction pressure or higher [25, 26]. Another disadvantage of secondary reforming and of partial oxidation processing is that part of the feed gas is combusted to carbon dioxide and water instead of to desired product. As a result, more natural gas or other feed gas is required to produce a given amount of hydrogen or synthesis gas, although the autothermal processes do not require any fuel. By contrast, the fuel consumption rate for primary reforming is typically between 30 percent and 50 percent of the feed rate [27, 28]. Despite such efforts to improve steam reforming operations, it will be appreciated that there remains a desire to achieve lower steam and fuel requirements and higher thermal efficiencies in such operations [29, 30]. In addition, improved mechanical designs are also desired to reduce the size of the overall reforming systems employed and to achieve other useful purposes, such as a reduction for the thermal stresses to which the primary reformer tubes are subjected [31, 32]. It is also desired to carry out steam reforming operations at higher pressures, as in the range of 20-100 Bar. Such desired improvements also relate to the integration of primary and secondary reforming operations, so as to obtain the benefits of secondary reforming while achieving a more efficient overall reforming operation than has heretofore been possible.

Currently, endothermic reactions performed in microreactors are driven using heat from an external source, such as the effluent from an external combustor. In doing so, the temperature of the gas stream providing the heat is limited by constraints imposed by the materials of construction. Practically, this means that the effluent from an external combustor must be diluted with cool gas to bring the gas temperature down to meet material temperature constraints. This increases the total gas flow rate, raising blower and compressor costs. Moreover, heating the gas stream externally introduces heat losses and expensive high temperature materials to connect the combustor to the microreactor. On the other hand, an integrated combustor can

produce heat for the reaction in close proximity to the reaction zone, thus reducing heat losses and increasing efficiency. Because traditional combustion catalysts are not stable at high temperatures due to noble metal sintering, the integrated combustor must transfer heat at a rate sufficient to keep local temperatures at the catalyst surface below this level or risk rapid catalyst deactivation. The present study is focused primarily upon the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. A symmetry boundary condition is used to model half of each system where symmetry exists. Computations are performed using grids with varying nodal densities to determine the optimum node spacing and density that would give the desired accuracy and minimize computation time. The final grid density is determined when the centerline profiles of temperature and species concentration do not show obvious difference. The second-order upwind scheme is used to discretize the mathematical model, and the semi-implicit method for pressure-linked equations algorithm is employed to solve for the pressure and velocity fields. The simulation convergence is judged upon the residuals of all governing equations. The present study aims to provide a fundamental understanding of the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. Particular emphasis is placed upon the effect of various factors on the thermochemical steam reforming processes in heat integrated reactors.

## 2. Methods

The highly exothermic reactor is illustrated schematically in Figure 1 with a catalytic heat-recirculating reaction chamber. The catalytic heat-recirculating micro-combustors are modeled as parallel plates of infinite width. This study focuses on the heat-recirculating combustor, for which there are two catalytically active inner walls, two outer walls, and one side wall. Unless otherwise stated, all walls are 0.2 millimeters thick. The combustion chamber length is 8.0 millimeters, with a gap size of 0.8 millimeters. This gap size is typical to the geometrical confinements of practical honeycomb combustors. Due to the high aspect ratio of the combustion channel, the combustor is modeled as a two-dimensional system. For the heat-recirculating combustor, pre-mixed methane-air mixtures are sent into the central combustion chamber at ambient temperature, and then the hot products formed are split into two streams that flow into two recirculation chambers, each with a gap size of 0.4 millimeters. The 180° turns occur at 8.0 millimeters. The length of each recirculation chamber is 8.4 millimeters, as a result of the additional space from the turns. Based on these, the length of each outer wall is 8.6 millimeters, and the length of side wall is 2.4 millimeters. Unless otherwise stated, the inlet velocity is 0.8 meters per second, and a uniform inlet velocity profile is assumed. These values represent the nominal operating conditions. The parallel plate geometry implies that the third dimension is much larger than these gap sizes in order to ensure two-dimensional validity. To minimize the computational intensity, only half of the system is modeled by taking properly into account the geometrical symmetry.

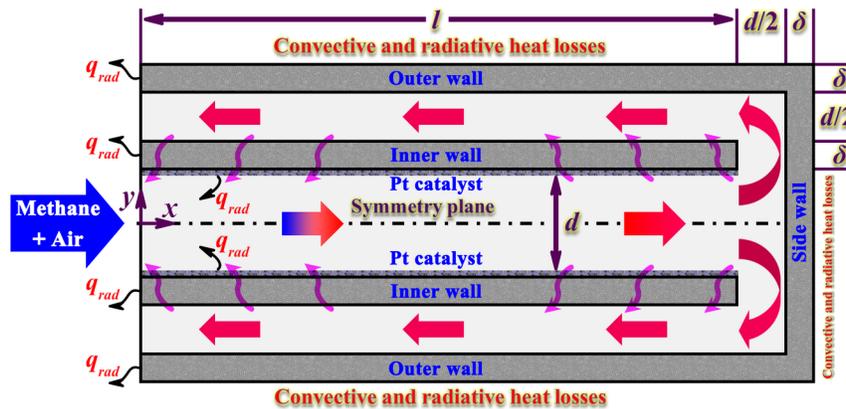


Figure 1. Schematic illustration of the highly exothermic reactor with a catalytic heat-recirculating reaction chamber. The thick arrows indicate the direction of flow, whereas the thin arrows indicate the direction of

heat transfer. All external surfaces exposed to the surroundings are subjected to convective and radiative heat losses. Symmetry allows the simulation of only half of each system.

The highly exothermic reactor is illustrated schematically in Figure 2 with a catalytic single-channel reaction chamber. The catalytic single-channel micro-combustors are modeled as parallel plates of infinite width. For the single-channel combustor, this is a simple geometry, consisting of two walls coated with a catalytically active washcoat. This geometry is used here for comparison purposes. The physical properties of the combustor solid structure, such as the density, specific heat, and wall thermal conductivity, are assumed constant, whereas all fluid properties are temperature-dependent. Specifically, the gaseous species-specific heat is computed using a piecewise polynomial fit of temperature, whereas temperature-dependent species transport properties in the gas phase, such as the species thermal conductivity and viscosity, are computed using the kinetic theory of ideal gases. Fluid transport properties, such as the fluid thermal conductivity, specific heat, and viscosity, are computed by a mass-fraction-weighted average of species properties, depending on the local mixture temperature and composition. The fluid density is determined from the ideal gas law for the local mixture temperature, pressure, and composition. Uniform profiles for the species mass fractions, gas temperature, and axial velocity are specified at the inlet. No-slip boundary conditions are used for both velocity components at the fluid-solid interfaces. A symmetry boundary condition is used to model half of each system where symmetry exists. At the symmetry plane and the outlet, the transverse velocity is set to zero and zero gradient Neumann boundary conditions are used for all other scalars, namely the normal derivatives are set to zero. It is important to note that once the reaction zone shifts approximately past half the length of the combustor, the boundary conditions at the exit may no longer describe the system properly. As a result, the blowout critical conditions are less accurate. To overcome the accuracy problem for a fixed combustor length, one needs to experimentally measure the exit conditions and impose them as boundary conditions.

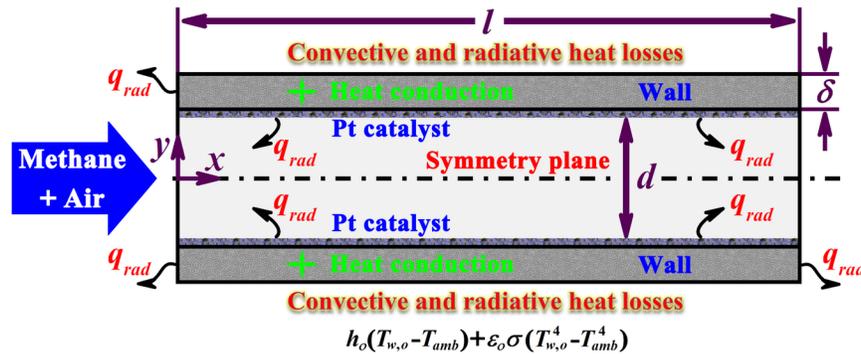


Figure 2. Schematic illustration of the highly exothermic reactor with a catalytic single-channel reaction chamber. The thick arrows indicate the direction of flow, whereas the thin arrows indicate the direction of heat transfer. All external surfaces exposed to the surroundings are subjected to convective and radiative heat losses. Symmetry allows the simulation of only half of each system.

For the single-channel combustor, an orthogonal staggered grid is used to perform these simulations, containing 200 and 80 points in the axial and transverse directions, respectively. The grid is finer where the gradients are steeper, at the entrance and in the vicinity of the active catalytic surface. The solid wall is discretized such that the elements at the fluid-solid interface have the same axial size as the corresponding elements on the fluid sides, resulting in a 200 and 20 grid resolution in the axial and transverse directions, respectively. For the heat-recirculating combustor, a non-uniform grid is used, with elements near the catalytic wall being smaller than those at the symmetry plane, in order to capture more accurately the sharp gradients at the catalytic wall while minimizing the computational intensity. As a result, the grid used contains a 260 and 160 grid resolution in the axial and transverse directions, respectively. Prior to performing these simulations, computations are performed using grids with varying nodal densities to determine the optimum

node spacing and density that would give the desired accuracy and minimize computation time. The final grid density is determined when the centerline profiles of temperature and species concentration do not show obvious difference. Solutions obtained with the above grids are reasonably accurate, and larger grid densities yield no obvious advantage. The second-order upwind scheme is used to discretize the mathematical model, and the semi-implicit method for pressure-linked equations algorithm is employed to solve for the pressure and velocity fields. The simulation convergence is judged upon the residuals of all governing equations. Numerical convergence is in general difficult. In order to assist convergence and compute extinction points, natural parameter continuation is implemented.

The heat integrated reactor with multiple parallel channels is illustrated schematically in Figure 3 for thermochemically producing hydrogen from methanol by steam reforming. The heat integrated reactor can be used to produce hydrogen for fuel cells for the production of electricity. The reactor consists of two sets of flow channels: one where the steam reforming reaction takes place and one where combustion of the same fuel provides the heat necessary to carry out the reaction. Heat is transferred across the channel walls, and the system results in a compact configuration. The two sets of uniform parallel reaction channels are separated by the walls that separate the combustion region from the reforming region, and are in close thermal contact as to facilitate the efficient transfer of heat from the combustion region to the reforming region. In this manner, greater heat integration and utilization is accomplished inside the reactor. The reactor operates in the so-called co-current mode, namely combustion and reforming mixtures flow in the same direction, and the combustion and reforming channels are arranged alternately. Combustion takes place over a structured catalyst comprising copper-oxide and zinc-oxide. Steam reforming is a catalytic reaction and takes place over a structured catalyst comprising copper and zinc-oxide. The washcoat for applying the combustion and reforming catalysts is high surface area aluminum oxide, and it must be in close contact with the channel walls to facilitate efficient heat transfer. On account of the symmetry of the system, only two half combustion and reforming channels associated with the surrounding walls are modeled.

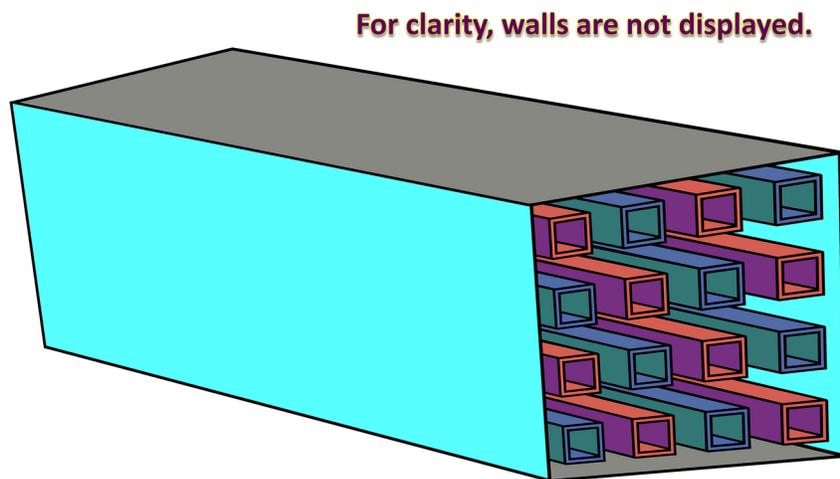


Figure 3. Schematic illustration of the heat integrated reactor with multiple parallel channels for thermochemically producing hydrogen from methanol by steam reforming.

The computational domain of the heat integrated reactor is illustrated schematically in Figure 4 for thermochemically producing hydrogen from methanol by steam reforming. A methanol-steam mixture is supplied to the reforming channels to be reformed, and a methanol-air mixture is supplied to the combustion channels to be combusted. The temperatures and pressures of the two streams entering the combustion channels and the reforming channels, respectively, are the same. The temperature of the two streams is 373 K at the flow inlets. The system operates at a pressure of up to 1.5 MPa. Typically, high pressure combustion is

widely practiced, although combustion can take place at low or near-atmospheric pressure. Steam reforming can take place at pressures somewhat above atmospheric to moderately high, up to 5.0 MPa. The channel walls should be of sufficient strength to allow for the pressure differential between the two streams entering the reactor. The composition of the mixture entering the combustion channels should be such as to ensure complete combustion of the fuel. Although a stoichiometric ratio of fuel to air is sufficient, an equivalence ratio of 0.8 is employed with the present study. The composition of the mixture entering the reforming channels is determined by the stoichiometries of the reforming reaction for the given fuel. It is typical practice to provide a higher than stoichiometric steam-to-fuel ratio to minimize possible side reactions that can cause carbon formation to the detriment of the catalyst and the reactor. A steam-to-carbon molar ratio of 1.4 is employed with the present study. The fluids flow essentially parallel to the axes of the channels. The velocity of the fluid flowing into the reforming channels is 2.0 meters per second at the flow inlets. In contrast, the velocity of the fluid flowing into the combustion channels varies depending on the desired design requirements. Theoretically, the washcoats can be of any shape. The washcoats can be shaped into any of various configurations, but they must be designed to increase the area available for heat exchange, thereby minimizing the length of the channels and the associated pressure drop. The mass transfer coefficient can be estimated from the relation between the pore Reynolds and Schmidt numbers and the asymptotic Sherwood number. The local mass transport coefficient is dependent upon the local velocity of the fluid, reaction rate, and local pore structure. The term bulk flow region refers to open areas or open channels within the reaction chamber. A contiguous bulk flow region allows rapid gas flow through the reaction chamber without large pressure drops. Equilibrium conversion is defined in the classical manner, where the maximum attainable conversion is a function of the reactor temperature, pressure, and feed composition. For the case of hydrocarbon steam reforming reactions, the equilibrium conversion increases with increasing temperature and decreases with increasing pressure.

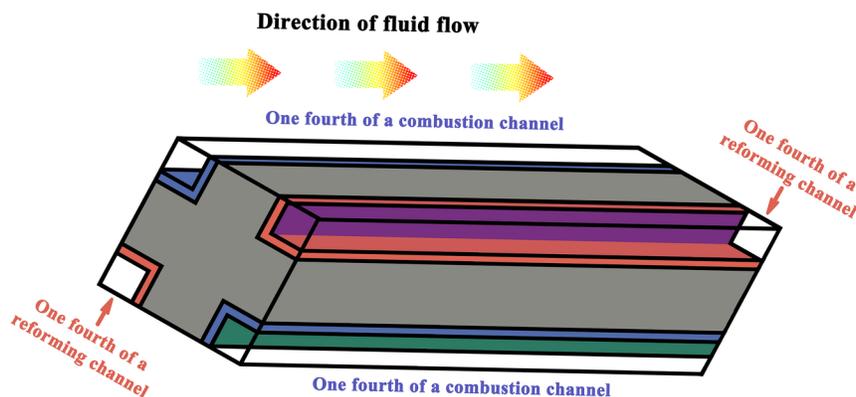


Figure 4. Schematic illustration of the computational domain of the heat integrated reactor for thermochemically producing hydrogen from methanol by steam reforming.

### 3. Results and discussion

The contour plots of temperature, methanol mole fraction, and hydrogen mole fraction under nominal operating conditions are presented in Figure 5 for the heat integrated reactor. Chemical reactions that produce heat and those that take up heat form two very important classes of reactions. Some highly exothermic reactions, reactions with a large but negative heat of reaction, require heat to be removed from a system to prevent overheating. One example is the partial oxidation of ethylene to produce ethylene oxide, an important intermediate in the production of ethylene glycol. This reaction oxidizes ethylene over a catalyst to produce ethylene oxide and heat. If the reaction temperature is too high, ethylene oxide will decompose to carbon dioxide and water. In order to reduce degradation into undesired products, the reaction temperature must be held under control by removing heat produced by the partial oxidation. Conversely, endothermic

reactions, those with a positive heat of reaction, do not produce heat but require heat for the reaction to proceed. Steam reforming of hydrocarbons is an endothermic reaction of considerable interest for hydrogen production as a fuel for fuel cells. Steam reforming produces hydrogen and carbon monoxide when heat is added to a catalytic reactor containing steam and hydrocarbons. Although exothermic and endothermic reactions are easy to implement, to do so with a compact and simple reactor design is challenging due to the limitations of heat transfer between the reaction and the outside of the reactor. One aspect in building compact reactors with adequate thermal exchange requires a provision for high interfacial area between the reaction stream and the reactor body. Microchannel technology is capable of high heat and mass transfer coefficients between a bulk reaction fluid and the catalytic heat exchange surface. Alternating channel parallel plate designs can be applied to thermally coupling endothermic steam reforming with combustion in neighboring channels. Such designs enable orders of magnitude size reduction over conventional shell-and-tube steam reformers. Enclosed parallel flow channels are typically formed by stacking plates separated by spacers, and fitting the stack with appropriate headers so that alternating channels contain the reforming reaction with exothermic combustion in the intermediate channels. Microchannel reactors exchange heat between chemically reacting fluid streams where flow is parallel to and on opposite sides of a thermally conductive separating plate. In this design, enclosed channels are formed by stacking plates separated by spacers, and the stack is fitted with appropriate headers so that alternating channels contain the reaction fluid with heat exchange fluid in the intermediate channels. The reaction channels can be filled with catalyst, and the heat exchange channels can have a structured packing to increase the heat exchange area. Another approach to increasing the surface area for reaction on each side of the separating plate is to add fins or other surface features. Indeed, this approach is adopted in plate-type reactor designs. Although somewhat successful, the design still adds complexity and the alternating coupled reaction chambers continue to restrict the overall size of each chamber. All of these examples share the same general flow geometry where thermal energy transfers between chemically reacting fluid streams that flow parallel to and on opposite sides of a separating plate.

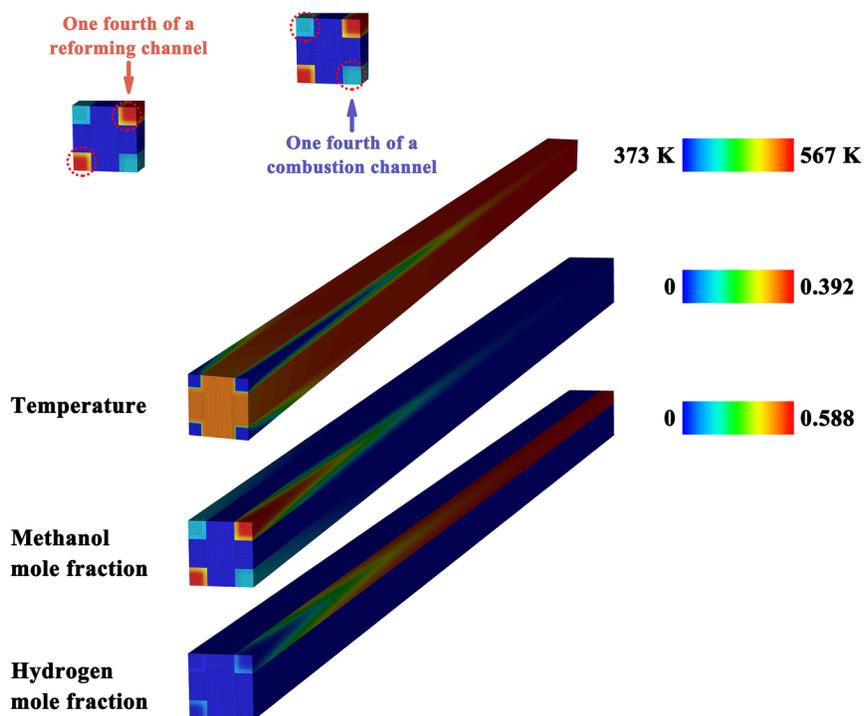


Figure 5. Contour plots of temperature, methanol mole fraction, and hydrogen mole fraction under nominal

operating conditions for the heat integrated reactor.

The contour plots of water mole fraction, oxygen mole fraction, and carbon dioxide mole fraction under nominal operating conditions are presented in Figure 6 for the heat integrated reactor. A reaction chamber has dimensions of height, width and length. The length of the reaction chamber is typically longer. Typically, the sides of the reaction chamber are defined by reaction chamber walls. These walls are preferably made of a hard material such as a ceramic, an iron-based alloy, or high temperature nickel-based superalloys. More preferably, the reaction chamber walls are comprised of stainless steel which is durable and has good thermal conductivity. In addition to thermal transfer between adjacent reaction chambers, in some cases, a reaction chamber can be in thermal contact with a microchannel heat exchanger. This combination of reaction chambers and heat exchangers can result in high rates of thermal transfer. The catalyst could also be applied by other methods such as wash coating. On metal surfaces, it is preferred to first apply a buffer layer by chemical vapor deposition or thermal oxidation, which improves adhesion of subsequent wash coats. Preferred reactors and methods of conducting reactions in integrated reactors can be characterized by their properties. The devices may be made of materials such as plastic, metal, ceramic and composites, depending on the desired characteristics. Walls separating the device from the environment may be thermally insulating. However, the walls separating adjacent exothermic and endothermic reaction chambers should be thermally conductive. Introduction of laterally distributed combustion fuel and air in co-flow with endothermic reactant flow concentrates the heat transfer at the endothermic reactor inlet, where the concentration gradient is highest, thus obtaining superior results over systems that distribute the combustion fuel evenly over the entire surface of the combustion catalyst. Although the examples with distributed combustion still exhibit excellent heat flux in comparison to conventional steam reformers. The present design could use alternate exothermic reactions, such as oxidation reactions, including partial oxidation reaction, to drive an endothermic reaction. During operation, a reactant enters a combustion or reaction chamber in a bulk flow path flowing past and in contact with a porous material or porous catalyst. A portion of the reactant molecularly transversely diffuses into the porous catalyst and reacts to form a product or products, and then the products diffuse transversely into the bulk flow path and out of the reactor. A short heat transport distance is desired for good performance. These short heat transport distances, combined with preferred reactor configurations, can provide surprisingly high volumetric productivity and low pressure drop. The reactor designs suffer from a fundamental limitation resulting from the flow configuration in which a reacting stream flows parallel to a heat transfer surface through which the majority of heat is transferred perpendicular to the direction of fluid flow. Regardless of the reaction taking place in the reaction channels, its reaction rate will vary along the flow length of that channel due to changes in concentration and temperature. Balancing the heat requirements of an endothermic reaction with heat generated by an exothermic reaction flowing parallel to and on the opposite side of a separating plate is extraordinarily difficult since the endothermic reaction is likely to have a very different dependence upon concentration and temperature than the endothermic reaction. Along the flow length of the plate that divides these reactions, the heat flux through the plate that is perpendicular to fluid flow will vary due to temperature and reaction rate differences along the flow length of the plate. Since the thermally coupled reactions are so closely coupled, neither reaction can run at a significantly different reaction rate at any point along the channel length. Thus, each reaction will exhibit a peak in reaction rate at nearly the same position within the reactor with slower reaction rates before and after this peak, which leads to the need for a long reactor channel to ensure complete conversion. A specific example of this reaction rate problem encountered in the parallel flow arrangement is demonstrated by attempts to drive endothermic steam reforming with exothermic combustion in microchannel and alternating parallel plate reactors. A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels. Thus, the stacked reactor becomes an alternating series of endothermic and exothermic reactors separated by thin heat exchange walls. Unfortunately, the combustion reaction is difficult to control with convenient combustion catalysts and fuels, and most of the combustion occurs near the fuel inlet. This uneven combustion results in uneven heat transfer to the endothermic reaction and poor overall reactor performance. The geometry allows intimate thermal contact whilst keeping the streams from becoming mixed. The reactor body is constructed by modification of a substantially rigid and essentially nonporous monolith honeycomb. Prior to modification the monolith consists of a honeycombed

body having a matrix of thin walls defining a multiplicity of discrete channels which pass through the body of the structure from one face to the opposing face. The monolith is modified in such a way as to produce a rigid body containing at least two discrete process flow paths which have a number of dividing walls in common. A channel is defined as any individual passageway through the monolith body and a flow path is the group of channels used for a single reaction. The inlets to the first reaction flow paths and the inlets to the second reaction flow paths are in the inlet manifold such that the reactants run in a co-current configuration. The reactants also leave the reactor in the same outlet manifold via the first reaction outlets and the second reaction outlets. The fuel processor is described using the steam reformation of methane and oxidation of methane reactions to illustrate the concept. The inlets and outlets may be arranged for a countercurrent flow of the reactants.

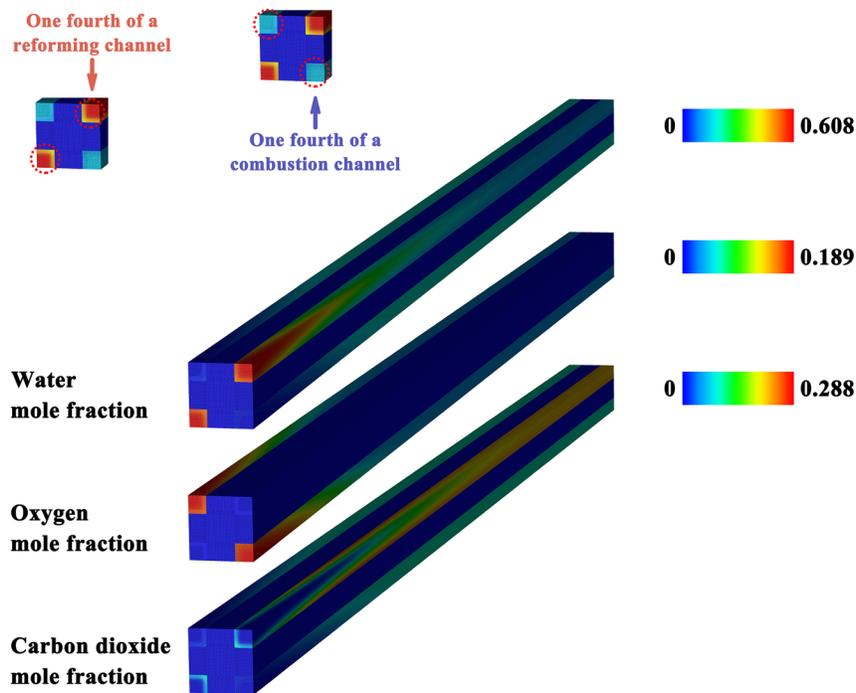


Figure 6. Contour plots of water mole fraction, oxygen mole fraction, and carbon dioxide mole fraction under nominal operating conditions for the heat integrated reactor.

The Nusselt number profiles along the length of the heat integrated reactor are presented in Figure 7 under nominal operating conditions for thermochemically producing hydrogen from methanol by steam reforming. Many chemical processes utilize catalysts to enhance chemical conversion behavior. A catalyst promotes the rate of chemical conversion but does not affect the energy transformations which occur during the reaction. Often catalytic processes are conducted within tubes which are packed with a suitable catalytic substance. The process gas flows within the tube and contacts the catalytic packing where reaction proceeds. The tube is placed within a hot environment such as a furnace such that the energy for the process can be supplied through the tube wall via conduction. The mechanism for heat transfer with this arrangement is rather tortuous as heat must first be transferred through the outer boundary layer of the tube, conducted through the often-heavy gauge wall of the tube and then pass through the inner boundary layer into the process gas. The process gas is raised in temperature and this energy can be utilized by the process for chemical reaction. The process engineer is often caused to compromise between the pressure drop within the tube reactor with the overall heat transfer and catalytic effectiveness. The inner heat transfer coefficient can be effectively increased by raising the superficial velocity of the process gas. The higher gas velocity therefore improves the

thermal effectiveness of the system. However, higher gas velocities increase the system's pressure drop and results in increased compressor sizes and associated operating costs. A reactor must be of sufficient length to allow a reaction to proceed to the required conversion [33, 34]. Utilizing high gas velocities typically results in reactors with large length to width ratios which again results in systems with high pressure drops [35, 36]. The smaller the characteristic dimension of the catalyst particle the higher is the utilization of the catalyst [37, 38]. This is sometimes expressed as a higher effectiveness factor [39, 40]. However, beds formed from small particles exhibit higher pressure drops than similar beds formed from larger particle. So, an engineer designs a system with expectable compromises between heat transfer, catalyst utilization, system conversion, and pressure drop. Therefore, a reactor for conducting catalytic processes which can promote overall heat transfer and levels of conversion whilst minimizing pressure drop is desired. The dividing walls must be of sufficient strength to maintain the integrity of channels. The minimum wall thickness therefore depends upon material of construction. The wall thickness is in the range of about 0.5 millimeter to 5 millimeters and more particularly in the range of about 0.5 millimeter to 2 millimeters. The wall will act as a thermal barrier to heat transfer, however, as the wall is very thin its resistance is small. The heat for the reaction is supplied directly through the wall from the oxidation channels occurring on the opposing side of the dividing wall. As the heat transfer characteristics are highly independent of the bulk reactants velocity, a velocity can be chosen to ensure that the reactants exiting the reactor has attained the desired level of conversion or indeed reached any equilibrium. It is interesting to note that in such an arrangement it is desirable to operate the reactants in a co-current flow arrangement. This ensures that the area with the greatest heat generation is adjacent to the area with the greatest heat requirement. However, cases may exist where a countercurrent flow arrangement is desirable. The system can be used to for a number of reactions as a wide range of process conditions are possible. A number of techniques are available in which to deposit an active catalyst onto the wall of the monolith. One such technique is that of the washcoat as is used in catalytic converters. Others include the sol-gel technique, metal sputtering, or the grinding of commercial catalyst pellets followed by attachment through the use of a cement or sol-gel. Many of the coating techniques allow different thicknesses of coating to be applied. It may also be possible to increase or decrease the thickness of the coating along the channel length. This technique can be used enhance the kinetics in the downstream sections of the channel. The thickness of the catalyst coating depends upon the process proceeding within the catalyst matrix. The products of some processes are highly dependent upon the catalyst thickness. In this case, the thickness should be no larger than the characteristic length beyond which the product spectrum degrades. For some processes the catalyst thickness has no effect on the product spectrum, an example of which is the steam reforming of methane. In this case the catalyst thicknesses can be of any dimension. However, excessively thick coatings are avoided as the catalyst interior performs little reaction due to diffusion limitations and acts as a thermal barrier. Many catalysts are prone to deactivation due to diffusion of an impurity into the catalyst. In cases where the catalyst is supported on a metallic surface, the source of the impurity is often the metal surface itself. Metals have low diffusion coefficients, however, as the catalyst is in intimate contact with the support over extended periods and at elevated temperature, small amounts of the metallic substrate will diffuse into the catalyst structure. A common example of this effect is the poisoning of nickel-based steam reforming catalysts with iron. It is possible to minimize this effect by using a dense and nonporous barrier coating located between the metal surfaces and the active catalyst. However, this problem can be circumnavigated through the use of ceramic structures.

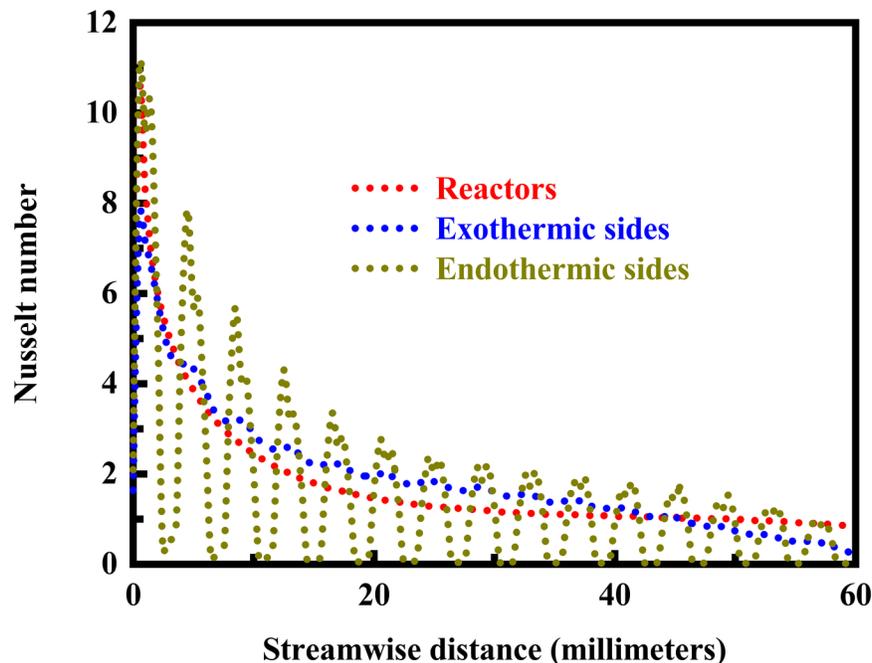


Figure 7. Nusselt number profiles along the length of the heat integrated reactor under nominal operating conditions for thermochemically producing hydrogen from methanol by steam reforming.

The Sherwood number profiles along the length of the heat integrated reactor are presented in Figure 8 under nominal operating conditions for thermochemically producing hydrogen from methanol by steam reforming. An advantage of the arrangement is the low thermal inertia of the system. This allows the reactor to operate with inherently fast thermal response and is particularly advantageous during startup. The low thermal inertia will minimize startup time to the order of minutes from the order of hours, which is typical for large packed tube technology. With suitable ancillary equipment, the system can be operated with a level of control and operating flexibility not encountered in traditional steam reformers. Another deficiency of traditional heat transfer equipment is start-up time and thermal response to transients. As reactors are traditionally large and heavy, they have significant thermal inertia. Therefore, the system takes significant time to re-equilibrate from any change in load or process operating conditions. Therefore, a reactor with enhanced response characteristics particularly for rapid start up is desired. The design consists of multiple packed tubes, of small diameter, being placed in intimate contact with a heat generating flame. The arrangement leads to improved heat transfer and therefore chemical conversion. However, the packed tube results in a significant pressure drop and the author states the process is still heat transfer limited. Therefore, a reactor design which minimizes the process side pressure drop and does not suffer from heat transfer limitation is required. It is proposed that the arrangement can either be used as a heat exchanger, where energy is transferred from one stream to another via conduction through the wall or it is suitable as a chemical reactor where the second set of channels allow the introduction of a heat transfer fluid [41, 42]. It is noted that the reaction can be a catalytic process and the catalytically active material can be coated onto the monolith passage walls to minimize pressure drop [43, 44]. In this arrangement the heat transfer from the process catalyst to the dividing wall will be highly efficient, however, the uptake of the energy by the heat transfer fluid will suffer from all of the limitations of traditional heat transfer operations [45, 46]. In this case the boundary layer will provide a significant resistance to heat transfer and will severely limit the rate of the process [47, 48]. The high velocities will reduce the characteristic thickness of the boundary layer and ensure that a sufficient mass of heat transfer fluid is available to absorb the heat of reaction without significantly changing temperature. These requirements will lead to excessive pressure drop through the coolant channels.

Therefore, a reactor design which minimizes the heat transfer fluid side pressure drop is required. Combining endothermic and exothermic reactions on opposing sides of dividing walls of adjacent channels can serve as an efficient method of heat transfer. It is proposed that steam reforming of a hydrocarbon be performed by one layer and the energy for this process be supplied by a hydrocarbon oxidative process being promoted in the subsequent layer. Various hybrids of this theme are proposed. However, as the heat is supplied by an autothermal reaction, oxygen must be supplied along with the fuel stream. As well as the oxygen, associated nitrogen is present. This nitrogen acts to absorb process energy which lowers the thermal efficiency of the process as well as diluting the desired product, hydrogen. The presence of the nitrogen increases the load on downstream partial oxidation units which act to oxidize carbon monoxide to carbon dioxide. The nitrogen also reduces the streams suitability for use in fuel cells. Therefore, a reactor which can supply sufficient energy to an endothermic reaction without mixing the streams is needed. It should be noted that an advantage is the ability to use low calorific fuel for the exothermic reaction. Such fuel is not ideally suited to homogeneous combustion and results in a highly unstable flame. Heterogeneous combustion aids in spreading the heat generation along the length of the channel and helps prevent hotspot formation. The use of low caloric value gas allows the use of certain waste streams as the fuel to supply the heat. Examples of such streams include the off-gas stream from a fuel cell, the gaseous components from a Fischer-Tropsch synthesis. It should be further noted that the heat generation rate per unit area is approximately matched to the heat requirement in the adjacent channel. This can be achieved by controlling the catalyst thickness in each channel. A trial-and-error process may be required to obtain the optimum catalyst thicknesses for some processes. If the processes are not thermally matched, the overall efficiency of the reactor will be reduced. Suitable metals include copper, aluminum, stainless steel, iron, titanium, and mixtures or alloys thereof.

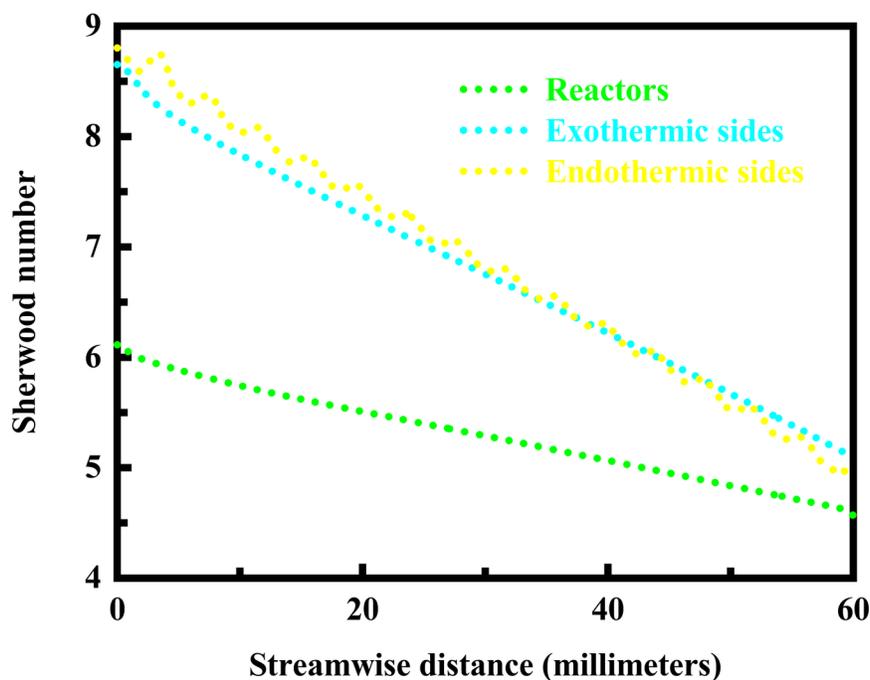


Figure 8. Sherwood number profiles along the length of the heat integrated reactor under nominal operating conditions for thermochemically producing hydrogen from methanol by steam reforming.

#### 4. Conclusions

Computations are performed using grids with varying nodal densities to determine the optimum node spacing and density that would give the desired accuracy and minimize computation time. The final grid density

is determined when the centerline profiles of temperature and species concentration do not show obvious difference. The second-order upwind scheme is used to discretize the mathematical model, and the semi-implicit method for pressure-linked equations algorithm is employed to solve for the pressure and velocity fields. The simulation convergence is judged upon the residuals of all governing equations. Particular emphasis is placed upon the effect of various factors on the thermochemical steam reforming processes in heat integrated reactors. The major conclusions are summarized as follows:

- Steam reforming produces hydrogen and carbon monoxide when heat is added to a catalytic reactor containing steam and hydrocarbons.
- Alternating channel parallel plate designs can be applied to thermally coupling endothermic steam reforming with combustion in neighboring channels.
- Balancing the heat requirements of an endothermic reaction with heat generated by an exothermic reaction flowing parallel to and on the opposite side of a separating plate is extraordinarily difficult since the endothermic reaction is likely to have a very different dependence upon concentration and temperature than the endothermic reaction.
- A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels.
- The process gas is raised in temperature and this energy can be utilized by the reforming process.
- The catalyst coating thickness depends upon the process proceeding within the catalyst matrix.
- The arrangement leads to improved heat transfer and therefore chemical conversion.
- Heterogeneous combustion aids in spreading the heat generation along the length of the channel and helps prevent hotspot formation.

## References

1. M. Menzinger, V. Yakhnin, A. Jaree, P.L. Silveston, and R.R. Hudgins. Dynamic responses of packed bed reactors. *Chemical Engineering Science* , Volume 59, Issue 19, 2004, Pages 4011-4022.
2. G. Langhendries, G.V. Baron, and P.A. Jacobs. Selective and efficient hydrocarbon oxidation in a packed bed membrane reactor. *Chemical Engineering Science* , Volume 54, Issue 10, 1999, Pages 1467-1472.
3. V. Höller, I. Yuranov, L. Kiwi-Minsker, and A. Renken. Structured multiphase reactors based on fibrous catalysts: Nitrite hydrogenation as a case study. *Catalysis Today* , Volume 69, Issues 1-4, 2001, Pages 175-181.
4. P. Aguiar, N. Lapeña-Rey, D. Chadwick, and L. Kershenbaum. Improving catalyst structures and reactor configurations for autothermal reaction systems: Application to solid oxide fuel cells. *Chemical Engineering Science* , Volume 56, Issue 2, 2001, Pages 651-658.
5. R. Carli, C.L. Bianchi, R. Bernasconi, G. Frontini, and V. Ragaini. Fisher-Tropsch synthesis on ruthenium supported titanium silicate catalysts. *Studies in Surface Science and Catalysis* , Volume 98, 1995, Pages 178-179.
6. C.J. Bertole, C.A. Mims, and G. Kiss. Support and rhenium effects on the intrinsic site activity and methane selectivity of cobalt Fischer-Tropsch catalysts. *Journal of Catalysis* , Volume 221, Issue 1, 2004, Pages 191-203.
7. A.K. Datye, Y. Jin, L. Mansker, R.T. Motjope, T.H. Dlamini, and N.J. Coville. The nature of the active phase in iron Fischer-Tropsch catalysts. *Studies in Surface Science and Catalysis* , Volume 130, 2000, Pages 1139-1144.
8. D.B. Bukur, L. Nowicki, and X. Lang. Fischer-tropsch synthesis in a stirred tank slurry reactor. *Chemical Engineering Science* , Volume 49, Issue 24, Part A, 1994, Pages 4615-4625.
9. M. Levent, G. Budak, and A. Karabulut. Estimation of concentration and temperature profiles for methane-steam reforming reaction in a porous catalyst. *Fuel Processing Technology* , Volume 55, Issue 3, 1998, Pages 251-263.
10. F. Gallucci, L. Paturzo, and A. Basile. A simulation study of the steam reforming of methane in a dense tubular membrane reactor. *International Journal of Hydrogen Energy* , Volume 29, Issue 6, 2004, Pages 611-617.

11. Y. Matsumura and T. Nakamori. Steam reforming of methane over nickel catalysts at low reaction temperature. *Applied Catalysis A: General* , Volume 258, Issue 1, 2004, Pages 107-114.
12. V.D. Belyaev, T.I. Politova, O.A. Mar'ina, and V.A. Sobyenin. Internal steam reforming of methane over Ni-based electrode in solid oxide fuel cells. *Applied Catalysis A: General* , Volume 133, Issue 1, 1995, Pages 47-57.
13. X. Zhang, C.S.-M. Lee, D.M.P. Mingos, and D.O. Hayward. Oscillatory behaviour during the partial oxidation of methane over cobalt wires and foils. *Applied Catalysis A: General* , Volume 248, Issues 1-2, 2003, Pages 129-142.
14. F. Basile, G. Fornasari, F. Trifirò, and A. Vaccari. Partial oxidation of methane: Effect of reaction parameters and catalyst composition on the thermal profile and heat distribution. *Catalysis Today* , Volume 64, Issues 1-2, 2001, Pages 21-30.
15. U. Pandey, K.R. Putta, K.R. Rout, E.A. Blekkan, E. Rytter, and M. Hillestad. Staging and path optimization of Fischer-Tropsch synthesis. *Chemical Engineering Research and Design* , Volume 187, 2022, Pages 276-289.
16. J.L. Barrera, J.J. Hartvigsen, M. Hollist, J. Pike, A. Yarosh, N.P. Fullilove, and V.A. Beck. Design optimization of integrated cooling inserts in modular Fischer-Tropsch reactors. *Chemical Engineering Science* , Volume 268, 2023, Article Number: 118423.
17. M.A. El-Bousiffi and D.J. Gunn. A dynamic study of steam-methane reforming. *Studies in Surface Science and Catalysis* , Volume 133, 2001, Pages 247-254.
18. I.I. Bobrova, N.N. Bobrov, and A.A. Davydov. Catalytic methane steam reforming: Novel results. *Catalysis Today* , Volume 24, Issue 3, 1995, Pages 257-258.
19. T. Blumberg, Y.D. Lee, T. Morosuk, and G. Tsatsaronis. Exergoenvironmental analysis of methanol production by steam reforming and autothermal reforming of natural gas. *Energy* , Volume 181, 2019, Pages 1273-1284.
20. A.O. Oni, K. Anaya, T. Giwa, G.D. Lullo, and A. Kumar. Comparative assessment of blue hydrogen from steam methane reforming, autothermal reforming, and natural gas decomposition technologies for natural gas-producing regions. *Energy Conversion and Management* , Volume 254, 2022, Article Number: 115245.
21. J.-H. Yang, Y. Yoon, M. Ryu, S.-K. An, J. Shin, and C.-J. Lee. Integrated hydrogen liquefaction process with steam methane reforming by using liquefied natural gas cooling system. *Applied Energy* , Volume 255, 2019, Article Number: 113840.
22. U. Izquierdo, V.L. Barrio, J.F. Cambra, J. Requies, M.B. Güemez, P.L. Arias, G. Kolb, R. Zapf, A.M. Gutiérrez, and J.R. Arraibi. Hydrogen production from methane and natural gas steam reforming in conventional and microreactor reaction systems. *International Journal of Hydrogen Energy* , Volume 37, Issue 8, 2012, Pages 7026-7033.
23. Y. Voloshchuk and A. Richter. Reduced order modeling and large-scale validation for non-catalytic partial oxidation of natural gas. *Chemical Engineering Science* , Volume 255, 2022, Article Number: 117620.
24. A. Al-Musa, S. Shabunya, V. Martynenko, and V. Kalinin. Modeling of natural gas partial oxidation in an in-house developed pilot scale catalytic reactor based on local thermodynamic equilibrium concept. *Applied Thermal Engineering* , Volume 113, 2017, Pages 238-245.
25. B.T. Schädel and O. Deutschmann. Steam reforming of natural gas on noble-metal based catalysts: Predictive modeling. *Studies in Surface Science and Catalysis* , Volume 167, 2007, Pages 207-212.
26. H.C. Lee, Y. Potapova, O.Y. Lim, D. Lee, S. Kim, J.H. Park, and E.D. Park. Hydrogen production by steam reforming of natural gas over highly stable Ru catalyst supported on nanostructured alumina. *Studies in Surface Science and Catalysis* , Volume 167, 2007, Pages 177-182.
27. A. Olivieri and F. Vegliò. Process simulation of natural gas steam reforming: Fuel distribution optimization in the furnace. *Fuel Processing Technology* , Volume 89, Issue 6, 2008, Pages 622-632.
28. E.C. Wanat, K. Venkataraman, and L.D. Schmidt. Steam reforming and water-gas shift of ethanol on Rh and Rh-Ce catalysts in a catalytic wall reactor. *Applied Catalysis A: General* , Volume 276, Issues 1-2, 2004, Pages 155-162.

29. A. Heinzl, B. Vogel, and P. Hübner. Reforming of natural gas-hydrogen generation for small scale stationary fuel cell systems. *Journal of Power Sources* , Volume 105, Issue 2, 2002, Pages 202-207.
30. Q. Ming, T. Healey, L. Allen, and P. Irving. Steam reforming of hydrocarbon fuels. *Catalysis Today* , Volume 77, Issues 1-2, 2002, Pages 51-64.
31. Z.R. Ismagilov, O.Y. Podyacheva, V.V. Pushkarev, N.A. Koryabkina, V.N. Antsiferov, Y.V. Danchenko, O.P. Solonenko, and H. Veringa. Development and study of metal foam heat-exchanging tubular reactor: Catalytic combustion of methane combined with methane steam reforming. *Studies in Surface Science and Catalysis* , Volume 130, 2000, Pages 2759-2764.
32. J.T. Richardson. A gas fired heat-pipe reformer for small-scale hydrogen production. *Studies in Surface Science and Catalysis* , Volume 107, 1997, Pages 567-571.
33. M. Szukiewicz and R. Petrus. Approximate model for diffusion and reaction in a porous pellet and an effectiveness factor. *Chemical Engineering Science* , Volume 59, Issue 2, 2004, Pages 479-483.
34. J. Lee and D.H. Kim. An improved shooting method for computation of effectiveness factors in porous catalysts. *Chemical Engineering Science* , Volume 60, Issue 20, 2005, Pages 5569-5573.
35. D.H. Kim and J. Lee. A robust iterative method of computing effectiveness factors in porous catalysts. *Chemical Engineering Science* , Volume 59, Issue 11, 2004, Pages 2253-2263.
36. R. Baur and R. Krishna. Effectiveness factor for zeolite catalysed isomerization reactions. *Chemical Engineering Journal* , Volume 99, Issue 2, 2004, Pages 105-116.
37. D. Papadias, L. Edsberg, and P. Björnbom. Simplified method for effectiveness factor calculations in irregular geometries of washcoats. *Chemical Engineering Science* , Volume 55, Issue 8, 2000, Pages 1447-1459.
38. S.D. Keegan, N.J. Mariani, S.P. Bressa, G.D. Mazza, and G.F. Barreto. Approximation of the effectiveness factor in catalytic pellets. *Chemical Engineering Journal* , Volume 94, Issue 2, 2003, Pages 107-112.
39. R.E. Hayes, B. Liu, and M. Votsmeier. Calculating effectiveness factors in non-uniform washcoat shapes. *Chemical Engineering Science* , Volume 60, Issue 7, 2005, Pages 2037-2050.
40. X. Zhu and H. Hofmann. Effect of wetting geometry on overall effectiveness factors in trickle beds. *Chemical Engineering Science* , Volume 52, Issue 24, 1997, Pages 4511-4524.
41. T. Boger and A.K. Heibel. Heat transfer in conductive monolith structures. *Chemical Engineering Science* , Volume 60, Issue 7, 2005, Pages 1823-1835.
42. C.O. Vandu, J. Ellenberger, and R. Krishna. Hydrodynamics and mass transfer in an upflow monolith loop reactor: Influence of vibration excitement. *Chemical Engineering Science* , Volume 59, Issues 22-23, 2004, Pages 4999-5008.
43. T. Haakana, E. Kolehmainen, I. Turunen, J.-P. Mikkola, and T. Salmi. The development of monolith reactors: General strategy with a case study. *Chemical Engineering Science* , Volume 59, Issues 22-23, 2004, Pages 5629-5635.
44. T. Valdés-Solis, M.J.G. Linders, F. Kapteijn, G. Marbán, and A.B. Fuertes. Adsorption and breakthrough performance of carbon-coated ceramic monoliths at low concentration of n-butane. *Chemical Engineering Science* , Volume 59, Issue 13, 2004, Pages 2791-2800.
45. M.T. Kreutzer, F. Kapteijn, J.A. Moulijn, and J.J. Heiszwolf. Multiphase monolith reactors: Chemical reaction engineering of segmented flow in microchannels. *Chemical Engineering Science* , Volume 60, Issue 22, 2005, Pages 5895-5916.
46. R.M. Heck, S. Gulati, and R.J. Farrauto. The application of monoliths for gas phase catalytic reactions. *Chemical Engineering Journal* , Volume 82, Issues 1-3, 2001, Pages 149-156.
47. S.-J. Jeong and W.-S. Kim. A study on the optimal monolith combination for improving flow uniformity and warm-up performance of an auto-catalyst. *Chemical Engineering and Processing: Process Intensification* , Volume 42, Issue 11, 2003, Pages 879-895.
48. B. Ozyurt, P. Mogili, B. Mierau, S.G. Sunol, and A.K. Sunol. A hierarchical approach to simultaneous design of products and processes. *Computers & Chemical Engineering* , Volume 20, Supplement 1, 1996, Pages S73-S78.

# Designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming

Junjie Chen

Department of Energy and Power Engineering, School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo, Henan, 454000, P.R. China

\* Corresponding author, E-mail address: jchengn@163.com, <https://orcid.org/0000-0001-6708-071X>

## Abstract

Endothermic reactions performed in microreactors are driven using heat from an external source. However, the temperature of the gas stream providing the heat is limited by constraints imposed by the materials of construction. The present study is focused primarily upon the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. A symmetry boundary condition is used to model half of each system where symmetry exists. Computations are performed using grids with varying nodal densities to determine the optimum node spacing and density that would give the desired accuracy and minimize computation time. The final grid density is determined when the centerline profiles of temperature and species concentration do not show obvious difference. The second-order upwind scheme is used to discretize the mathematical model, and the semi-implicit method for pressure-linked equations algorithm is employed to solve for the pressure and velocity fields. The convergence is judged upon the residuals of all governing equations. The present study aims to provide a fundamental understanding of the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. Particular emphasis is placed upon the effect of various factors on the thermochemical steam reforming processes in heat integrated reactors. The results indicate that steam reforming produces hydrogen and carbon monoxide when heat is added to a catalytic reactor containing steam and hydrocarbons. Alternating channel parallel plate designs can be applied to thermally coupling endothermic steam reforming with combustion in neighboring channels. Balancing the heat requirements of an endothermic reaction with heat generated by an exothermic reaction flowing parallel to and on the opposite side of a separating plate is extraordinarily difficult since the endothermic reaction is likely to have a very different dependence upon concentration and temperature than the endothermic reaction. A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels. The process gas is raised in temperature and this energy can be utilized by the reforming process. The catalyst coating thickness depends upon the process proceeding within the catalyst matrix. The arrangement leads to improved heat transfer and therefore chemical conversion. Heterogeneous combustion aids in spreading the heat generation along the length of the channel and helps prevent hotspot formation.

**Keywords:** Hydrogen production; Endothermic reactions; Discrete channels; Flow arrangements; Chemical conversion; Heterogeneous combustion

## 1. Introduction

Among the various chemical reactions occurring in industrial reactors, the use of catalytic gas-solid reactions is widespread. A packed bed reactor is commonly used for these types of reactions. Conventional packed bed reactors are associated with various difficulties and disadvantages, including pressure drop, intra particle diffusion limitations, flow channeling, and heat transfer limitations [1, 2].

Structured catalyst reactors are frequently used to address these challenges. These structured catalyst reactors are commonly utilized when there is a need for controlled endothermic or exothermic reactions. However, existing structured catalyst reactors, while demonstrating higher performance in comparison to the packed bed reactors, still have a number of drawbacks, including high cost, weight, thermal resistance, and heat management, among others [3, 4]. Important products of the Fischer-Tropsch reaction include gaseous hydrocarbons, such as lower olefins, paraffins, or alcohols, and liquid hydrocarbons, such as higher olefins, paraffins and alcohols [5, 6]. The Fischer-Tropsch reaction is highly exothermic and therefore effective heat transfer and temperature controls are important prerequisites for the successful operation. Furthermore, the reaction operability range, with pressures between 1-30 bar and temperatures ranging from 200 °C to 350 °C, requires an additional control to prevent formation of local hot spots responsible for the deterioration of the catalyst [7, 8]. Thus, there is a need for very efficient heat transfer during the reaction to prevent metallic catalyst deactivation and formation of undesirable products. Accordingly, there remains a need for a reactor that provides an efficient control over endothermic and exothermic chemical reactions, such as those carried out in the presence of a catalyst. For example, there is a need for a reactor for the Fischer-Tropsch catalytic processing of the synthesis gas that ensures very efficient heat transfer during the catalytic reaction.

Natural gas and methane, a major constituent of natural gas, are difficult to economically transport and are not easily converted into liquid fuels or chemicals that are more readily contained and transported. To facilitate transport, methane is typically converted to synthesis gas which is an intermediate in the conversion of methane to liquid fuels, methanol or other chemicals [9, 10]. Synthesis gas is a mixture of hydrogen and carbon monoxide with a hydrogen to carbon monoxide molar ratio of from about 0.6 to about 6. One chemical reaction effective to convert methane to synthesis gas is steam reforming. Methane is reacted with steam and endothermically converted to a mixture of hydrogen and carbon monoxide [11, 12]. The heat energy to sustain the endothermic reaction is generated by the external combustion of fuel. A second chemical reaction effective to convert methane to synthesis gas is partial oxidation. Methane is reacted with oxygen in an exothermic reaction [13, 14]. Synthesis gas can be produced by combined partial oxidation and steam reforming. The synthesis gas is then converted to liquids by the Fischer-Tropsch process or can be converted to methanol by commercial processes [15, 16]. In the primary steam reforming of fluid hydrocarbons, such as natural gas or methane, the feed material and steam are passed through catalyst-containing vertically hanging reformer tubes maintained at an elevated temperature by radiant heat transfer and by contact with combustion gases in the furnace portion of the tubular reactor. The hot reformer tube effluent may be passed to a waste heat recovery zone for the generation of steam that can be used in the steam reforming operations. Conventional primary steam reforming operations are commonly carried out at temperatures of from about 750 °C to about 850 °C or above [17, 18]. The primary steam reforming is a highly endothermic reaction, and the large amounts of required heat are typically provided by combusting external fuel at close to atmospheric pressures in the reforming furnace. Consequently, the reformer tubes are generally made of high alloy, expensive materials having a limited operating life under such extreme conditions [19, 20]. The reaction temperatures existing inside the reformer tubes are generally lower than about 850 °C so that the effluent gas recovered from the primary reformer typically contains 2-6 percent methane [21, 22]. The effluent from primary reforming is sometimes passed to a secondary reforming zone in which unconverted methane present in the reformed gas mixture is catalytically reacted with air, oxygen or other suitable oxygen-containing gas.

Large quantities of hydrogen, or of an ammonia syngas mixture of hydrogen and nitrogen, are produced either by such steam reforming operations or by partial oxidation reactions. Partial oxidation, like secondary reforming, is an exothermic, autothermal, internal combustion process [23, 24]. While secondary reforming is also a catalytic process, however, the various known partial oxidation processes

employ non-catalytic reactions, and thus operate at higher reaction temperatures on the order of about 1300 °C. The significant advantages obtainable by the use of secondary reforming, or by the use of partial oxidation processing, are off-set to some extent by the need to compress the oxygen-containing gas to the desired reaction pressure or higher [25, 26]. Another disadvantage of secondary reforming and of partial oxidation processing is that part of the feed gas is combusted to carbon dioxide and water instead of to desired product. As a result, more natural gas or other feed gas is required to produce a given amount of hydrogen or synthesis gas, although the autothermic processes do not require any fuel. By contrast, the fuel consumption rate for primary reforming is typically between 30 percent and 50 percent of the feed rate [27, 28]. Despite such efforts to improve steam reforming operations, it will be appreciated that there remains a desire to achieve lower steam and fuel requirements and higher thermal efficiencies in such operations [29, 30]. In addition, improved mechanical designs are also desired to reduce the size of the overall reforming systems employed and to achieve other useful purposes, such as a reduction for the thermal stresses to which the primary reformer tubes are subjected [31, 32]. It is also desired to carry out steam reforming operations at higher pressures, as in the range of 20-100 Bar. Such desired improvements also relate to the integration of primary and secondary reforming operations, so as to obtain the benefits of secondary reforming while achieving a more efficient overall reforming operation than has heretofore been possible.

Currently, endothermic reactions performed in microreactors are driven using heat from an external source, such as the effluent from an external combustor. In doing so, the temperature of the gas stream providing the heat is limited by constraints imposed by the materials of construction. Practically, this means that the effluent from an external combustor must be diluted with cool gas to bring the gas temperature down to meet material temperature constraints. This increases the total gas flow rate, raising blower and compressor costs. Moreover, heating the gas stream externally introduces heat losses and expensive high temperature materials to connect the combustor to the microreactor. On the other hand, an integrated combustor can produce heat for the reaction in close proximity to the reaction zone, thus reducing heat losses and increasing efficiency. Because traditional combustion catalysts are not stable at high temperatures due to noble metal sintering, the integrated combustor must transfer heat at a rate sufficient to keep local temperatures at the catalyst surface below this level or risk rapid catalyst deactivation. The present study is focused primarily upon the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. A symmetry boundary condition is used to model half of each system where symmetry exists. Computations are performed using grids with varying nodal densities to determine the optimum node spacing and density that would give the desired accuracy and minimize computation time. The final grid density is determined when the centerline profiles of temperature and species concentration do not show obvious difference. The second-order upwind scheme is used to discretize the mathematical model, and the semi-implicit method for pressure-linked equations algorithm is employed to solve for the pressure and velocity fields. The simulation convergence is judged upon the residuals of all governing equations. The present study aims to provide a fundamental understanding of the designs and operations of heat integrated reactors for thermochemically producing hydrogen from methanol by steam reforming. Particular emphasis is placed upon the effect of various factors on the thermochemical steam reforming processes in heat integrated reactors.

## 2. Methods

The highly exothermic reactor is illustrated schematically in Figure 1 with a catalytic heat-recirculating reaction chamber. The catalytic heat-recirculating micro-combustors are modeled as parallel plates of infinite width. This study focuses on the heat-recirculating combustor, for which there are two catalytically active inner walls, two outer walls, and one side wall. Unless otherwise stated, all

walls are 0.2 millimeters thick. The combustion chamber length is 8.0 millimeters, with a gap size of 0.8 millimeters. This gap size is typical to the geometrical confinements of practical honeycomb combustors. Due to the high aspect ratio of the combustion channel, the combustor is modeled as a two-dimensional system. For the heat-recirculating combustor, premixed methane-air mixtures are sent into the central combustion chamber at ambient temperature, and then the hot products formed are split into two streams that flow into two recirculation chambers, each with a gap size of 0.4 millimeters. The 180° turns occur at 8.0 millimeters. The length of each recirculation chamber is 8.4 millimeters, as a result of the additional space from the turns. Based on these, the length of each outer wall is 8.6 millimeters, and the length of side wall is 2.4 millimeters. Unless otherwise stated, the inlet velocity is 0.8 meters per second, and a uniform inlet velocity profile is assumed. These values represent the nominal operating conditions. The parallel plate geometry implies that the third dimension is much larger than these gap sizes in order to ensure two-dimensional validity. To minimize the computational intensity, only half of the system is modeled by taking properly into account the geometrical symmetry.

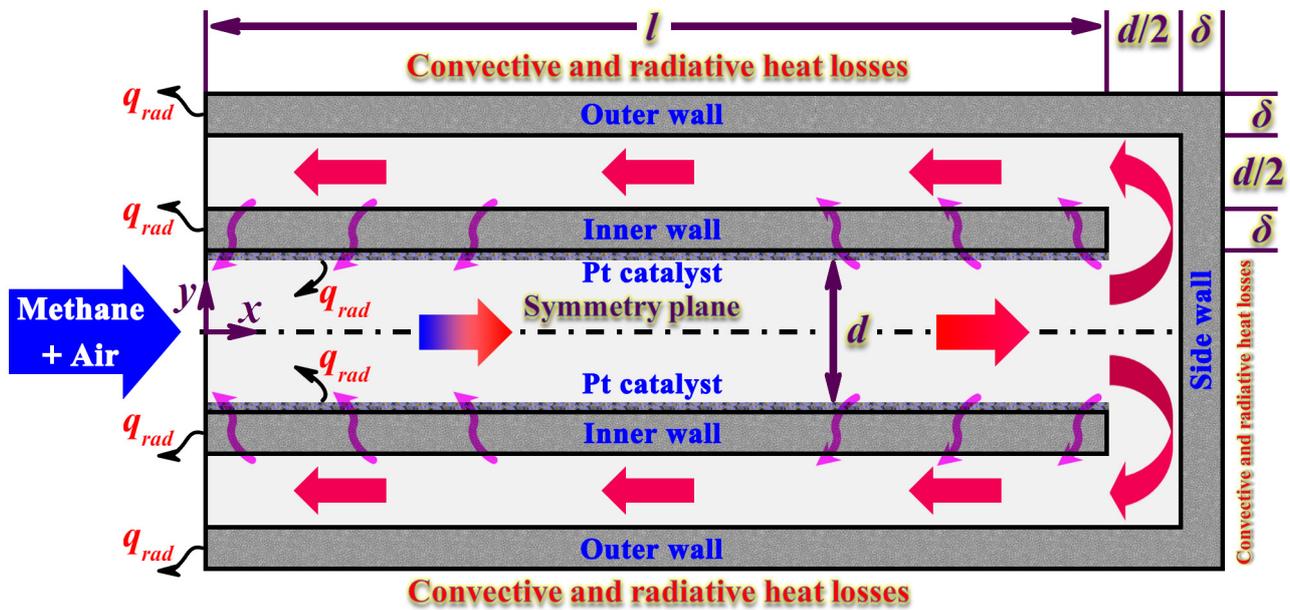


Figure 1. Schematic illustration of the highly exothermic reactor with a catalytic heat-recirculating reaction chamber. The thick arrows indicate the direction of flow, whereas the thin arrows indicate the direction of heat transfer. All external surfaces exposed to the surroundings are subjected to convective and radiative heat losses. Symmetry allows the simulation of only half of each system.

The highly exothermic reactor is illustrated schematically in Figure 2 with a catalytic single-channel reaction chamber. The catalytic single-channel micro-combustors are modeled as parallel plates of infinite width. For the single-channel combustor, this is a simple geometry, consisting of two walls coated with a catalytically active washcoat. This geometry is used here for comparison purposes. The physical properties of the combustor solid structure, such as the density, specific heat, and wall thermal conductivity, are assumed constant, whereas all fluid properties are temperature-dependent. Specifically, the gaseous species-specific heat is computed using a piecewise polynomial fit of temperature, whereas temperature-dependent species transport properties in the gas phase, such as the species thermal conductivity and viscosity, are computed using the kinetic theory of ideal gases. Fluid transport properties, such as the fluid thermal conductivity, specific heat, and viscosity, are computed by a mass-fraction-weighted average of species properties, depending on the local mixture temperature and composition. The fluid density is determined from the ideal gas law for the local mixture temperature, pressure, and composition. Uniform profiles for the species mass fractions, gas temperature, and axial velocity are specified at the inlet. No-slip boundary conditions are

used for both velocity components at the fluid-solid interfaces. A symmetry boundary condition is used to model half of each system where symmetry exists. At the symmetry plane and the outlet, the transverse velocity is set to zero and zero gradient Neumann boundary conditions are used for all other scalars, namely the normal derivatives are set to zero. It is important to note that once the reaction zone shifts approximately past half the length of the combustor, the boundary conditions at the exit may no longer describe the system properly. As a result, the blowout critical conditions are less accurate. To overcome the accuracy problem for a fixed combustor length, one needs to experimentally measure the exit conditions and impose them as boundary conditions.

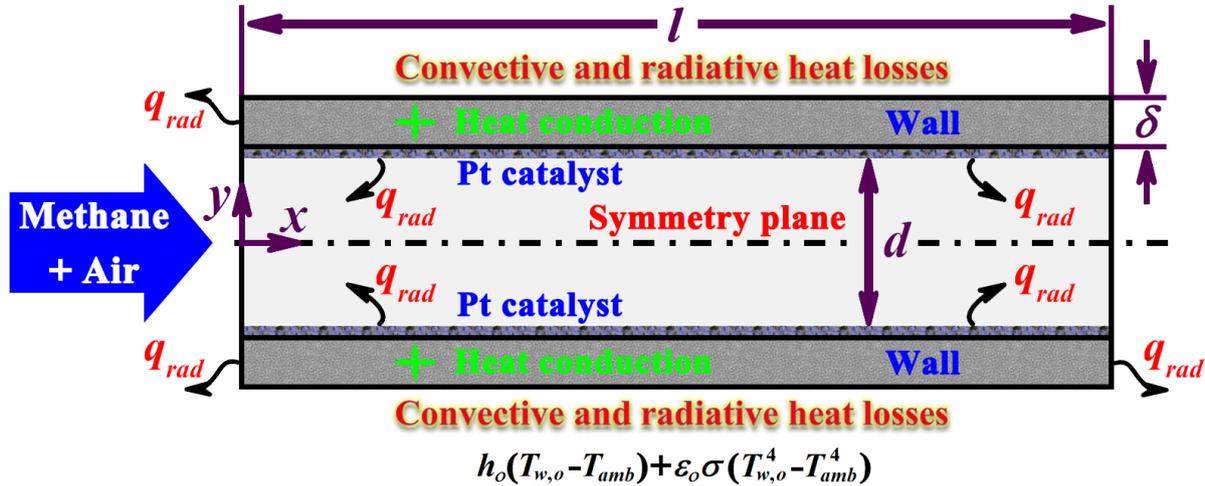


Figure 2. Schematic illustration of the highly exothermic reactor with a catalytic single-channel reaction chamber. The thick arrows indicate the direction of flow, whereas the thin arrows indicate the direction of heat transfer. All external surfaces exposed to the surroundings are subjected to convective and radiative heat losses. Symmetry allows the simulation of only half of each system.

For the single-channel combustor, an orthogonal staggered grid is used to perform these simulations, containing 200 and 80 points in the axial and transverse directions, respectively. The grid is finer where the gradients are steeper, at the entrance and in the vicinity of the active catalytic surface. The solid wall is discretized such that the elements at the fluid-solid interface have the same axial size as the corresponding elements on the fluid sides, resulting in a 200 and 20 grid resolution in the axial and transverse directions, respectively. For the heat-recirculating combustor, a non-uniform grid is used, with elements near the catalytic wall being smaller than those at the symmetry plane, in order to capture more accurately the sharp gradients at the catalytic wall while minimizing the computational intensity. As a result, the grid used contains a 260 and 160 grid resolution in the axial and transverse directions, respectively. Prior to performing these simulations, computations are performed using grids with varying nodal densities to determine the optimum node spacing and density that would give the desired accuracy and minimize computation time. The final grid density is determined when the centerline profiles of temperature and species concentration do not show obvious difference. Solutions obtained with the above grids are reasonably accurate, and larger grid densities yield no obvious advantage. The second-order upwind scheme is used to discretize the mathematical model, and the semi-implicit method for pressure-linked equations algorithm is employed to solve for the pressure and velocity fields. The simulation convergence is judged upon the residuals of all governing equations. Numerical convergence is in general difficult. In order to assist convergence and compute extinction points, natural parameter continuation is implemented.

The heat integrated reactor with multiple parallel channels is illustrated schematically in Figure 3 for thermochemically producing hydrogen from methanol by steam reforming. The heat integrated reactor can be used to produce hydrogen for fuel cells for the production of electricity. The reactor consists of two sets of flow channels: one where the steam reforming reaction takes place and one

where combustion of the same fuel provides the heat necessary to carry out the reaction. Heat is transferred across the channel walls, and the system results in a compact configuration. The two sets of uniform parallel reaction channels are separated by the walls that separate the combustion region from the reforming region, and are in close thermal contact as to facilitate the efficient transfer of heat from the combustion region to the reforming region. In this manner, greater heat integration and utilization is accomplished inside the reactor. The reactor operates in the so-called co-current mode, namely combustion and reforming mixtures flow in the same direction, and the combustion and reforming channels are arranged alternately. Combustion takes place over a structured catalyst comprising copper-oxide and zinc-oxide. Steam reforming is a catalytic reaction and takes place over a structured catalyst comprising copper and zinc-oxide. The washcoat for applying the combustion and reforming catalysts is high surface area aluminum oxide, and it must be in close contact with the channel walls to facilitate efficient heat transfer. On account of the symmetry of the system, only two half combustion and reforming channels associated with the surrounding walls are modeled.

**For clarity, walls are not displayed.**

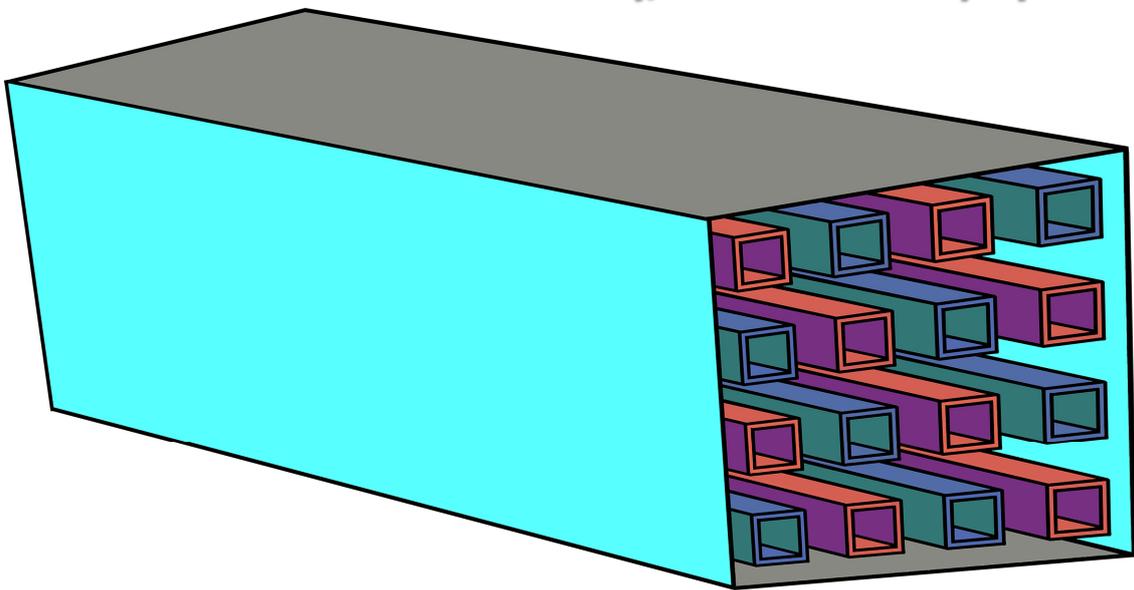


Figure 3. Schematic illustration of the heat integrated reactor with multiple parallel channels for thermochemically producing hydrogen from methanol by steam reforming.

The computational domain of the heat integrated reactor is illustrated schematically in Figure 4 for thermochemically producing hydrogen from methanol by steam reforming. A methanol-steam mixture is supplied to the reforming channels to be reformed, and a methanol-air mixture is supplied to the combustion channels to be combusted. The temperatures and pressures of the two streams entering the combustion channels and the reforming channels, respectively, are the same. The temperature of the two streams is 373 K at the flow inlets. The system operates at a pressure of up to 1.5 MPa. Typically, high pressure combustion is widely practiced, although combustion can take place at low or near-atmospheric pressure. Steam reforming can take place at pressures somewhat above atmospheric to moderately high, up to 5.0 MPa. The channel walls should be of sufficient strength to allow for the pressure differential between the two streams entering the reactor. The composition of the mixture entering the combustion channels should be such as to ensure complete combustion of the fuel. Although a stoichiometric ratio of fuel to air is sufficient, an equivalence ratio of 0.8 is employed with the present study. The composition of the mixture entering the reforming channels is determined by the stoichiometries of the reforming reaction for the given fuel. It is typical practice to provide a higher than stoichiometric steam-to-fuel ratio to minimize possible side reactions that can cause carbon

formation to the detriment of the catalyst and the reactor. A steam-to-carbon molar ratio of 1.4 is employed with the present study. The fluids flow essentially parallel to the axes of the channels. The velocity of the fluid flowing into the reforming channels is 2.0 meters per second at the flow inlets. In contrast, the velocity of the fluid flowing into the combustion channels varies depending on the desired design requirements. Theoretically, the washcoats can be of any shape. The washcoats can be shaped into any of various configurations, but they must be designed to increase the area available for heat exchange, thereby minimizing the length of the channels and the associated pressure drop. The mass transfer coefficient can be estimated from the relation between the pore Reynolds and Schmidt numbers and the asymptotic Sherwood number. The local mass transport coefficient is dependent upon the local velocity of the fluid, reaction rate, and local pore structure. The term bulk flow region refers to open areas or open channels within the reaction chamber. A contiguous bulk flow region allows rapid gas flow through the reaction chamber without large pressure drops. Equilibrium conversion is defined in the classical manner, where the maximum attainable conversion is a function of the reactor temperature, pressure, and feed composition. For the case of hydrocarbon steam reforming reactions, the equilibrium conversion increases with increasing temperature and decreases with increasing pressure.

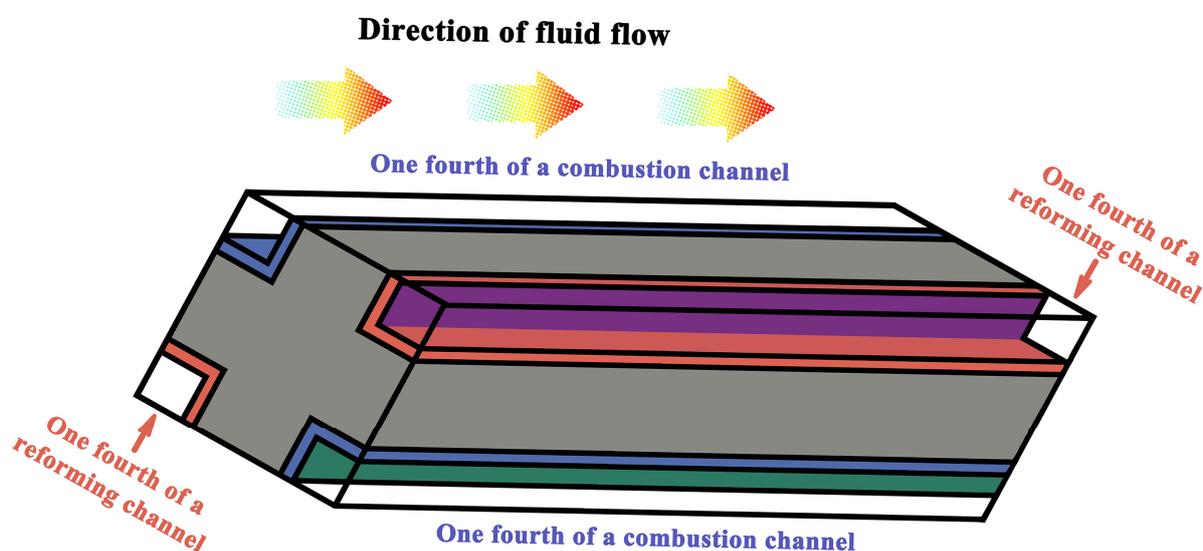


Figure 4. Schematic illustration of the computational domain of the heat integrated reactor for thermochemically producing hydrogen from methanol by steam reforming.

### 3. Results and discussion

The contour plots of temperature, methanol mole fraction, and hydrogen mole fraction under nominal operating conditions are presented in Figure 5 for the heat integrated reactor. Chemical reactions that produce heat and those that take up heat form two very important classes of reactions. Some highly exothermic reactions, reactions with a large but negative heat of reaction, require heat to be removed from a system to prevent overheating. One example is the partial oxidation of ethylene to produce ethylene oxide, an important intermediate in the production of ethylene glycol. This reaction oxidizes ethylene over a catalyst to produce ethylene oxide and heat. If the reaction temperature is too high, ethylene oxide will decompose to carbon dioxide and water. In order to reduce degradation into undesired products, the reaction temperature must be held under control by removing heat produced by the partial oxidation. Conversely, endothermic reactions, those with a positive heat of reaction, do not produce heat but require heat for the reaction to proceed. Steam reforming of hydrocarbons is an endothermic reaction of considerable interest for hydrogen production as a fuel for fuel cells. Steam reforming produces hydrogen and carbon monoxide when heat is added to a catalytic reactor containing steam and hydrocarbons. Although exothermic and endothermic reactions are easy to implement, to do

so with a compact and simple reactor design is challenging due to the limitations of heat transfer between the reaction and the outside of the reactor. One aspect in building compact reactors with adequate thermal exchange requires a provision for high interfacial area between the reaction stream and the reactor body. Microchannel technology is capable of high heat and mass transfer coefficients between a bulk reaction fluid and the catalytic heat exchange surface. Alternating channel parallel plate designs can be applied to thermally coupling endothermic steam reforming with combustion in neighboring channels. Such designs enable orders of magnitude size reduction over conventional shell-and-tube steam reformers. Enclosed parallel flow channels are typically formed by stacking plates separated by spacers, and fitting the stack with appropriate headers so that alternating channels contain the reforming reaction with exothermic combustion in the intermediate channels. Microchannel reactors exchange heat between chemically reacting fluid streams where flow is parallel to and on opposite sides of a thermally conductive separating plate. In this design, enclosed channels are formed by stacking plates separated by spacers, and the stack is fitted with appropriate headers so that alternating channels contain the reaction fluid with heat exchange fluid in the intermediate channels. The reaction channels can be filled with catalyst, and the heat exchange channels can have a structured packing to increase the heat exchange area. Another approach to increasing the surface area for reaction on each side of the separating plate is to add fins or other surface features. Indeed, this approach is adopted in plate-type reactor designs. Although somewhat successful, the design still adds complexity and the alternating coupled reaction chambers continue to restrict the overall size of each chamber. All of these examples share the same general flow geometry where thermal energy transfers between chemically reacting fluid streams that flow parallel to and on opposite sides of a separating plate.

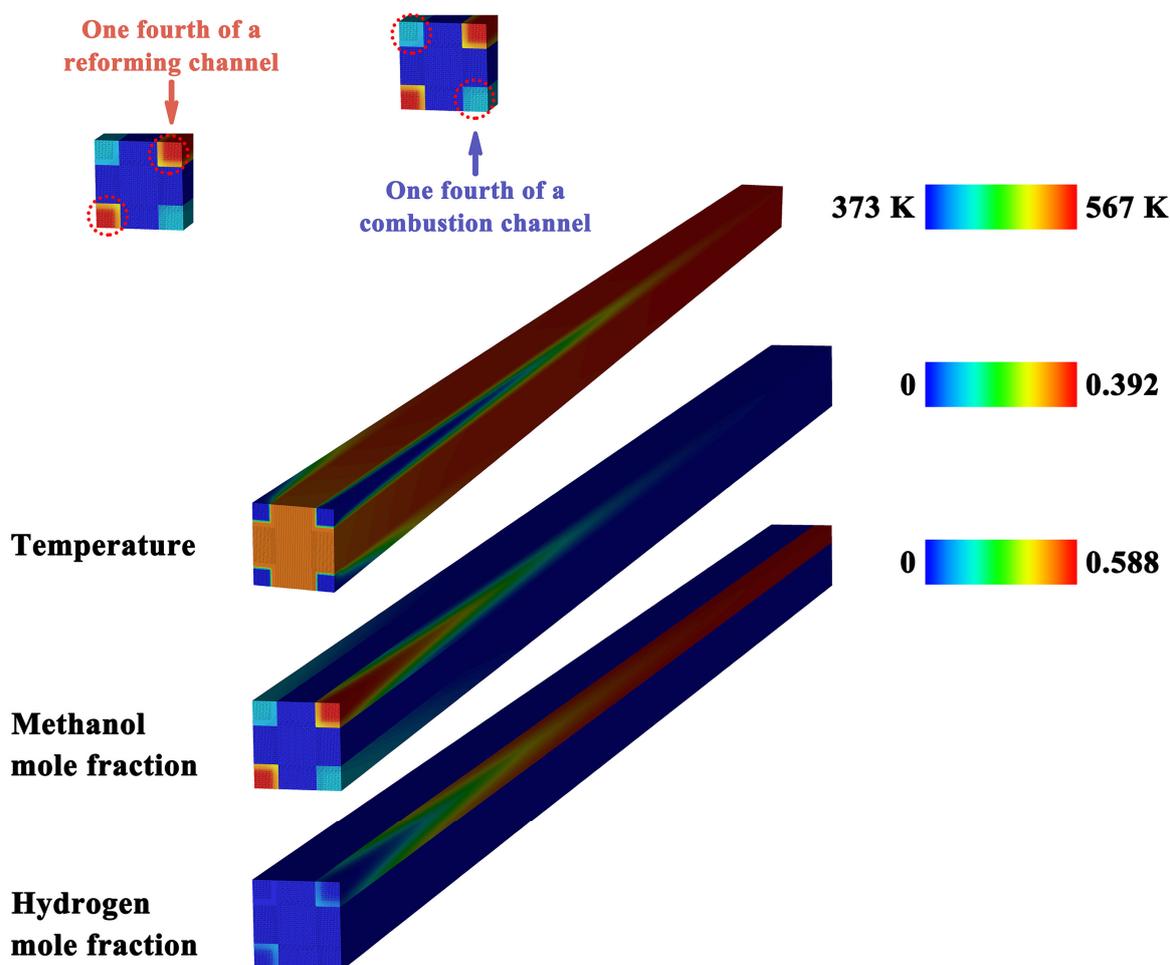


Figure 5. Contour plots of temperature, methanol mole fraction, and hydrogen mole fraction under nominal operating conditions for the heat integrated reactor.

The contour plots of water mole fraction, oxygen mole fraction, and carbon dioxide mole fraction under nominal operating conditions are presented in Figure 6 for the heat integrated reactor. A reaction chamber has dimensions of height, width and length. The length of the reaction chamber is typically longer. Typically, the sides of the reaction chamber are defined by reaction chamber walls. These walls are preferably made of a hard material such as a ceramic, an iron-based alloy, or high temperature nickel-based superalloys. More preferably, the reaction chamber walls are comprised of stainless steel which is durable and has good thermal conductivity. In addition to thermal transfer between adjacent reaction chambers, in some cases, a reaction chamber can be in thermal contact with a microchannel heat exchanger. This combination of reaction chambers and heat exchangers can result in high rates of thermal transfer. The catalyst could also be applied by other methods such as wash coating. On metal surfaces, it is preferred to first apply a buffer layer by chemical vapor deposition or thermal oxidation, which improves adhesion of subsequent wash coats. Preferred reactors and methods of conducting reactions in integrated reactors can be characterized by their properties. The devices may be made of materials such as plastic, metal, ceramic and composites, depending on the desired characteristics. Walls separating the device from the environment may be thermally insulating. However, the walls separating adjacent exothermic and endothermic reaction chambers should be thermally conductive.

Introduction of laterally distributed combustion fuel and air in co-flow with endothermic reactant flow concentrates the heat transfer at the endothermic reactor inlet, where the concentration gradient is highest, thus obtaining superior results over systems that distribute the combustion fuel evenly over the entire surface of the combustion catalyst. Although the examples with distributed combustion still exhibit excellent heat flux in comparison to conventional steam reformers. The present design could use alternate exothermic reactions, such as oxidation reactions, including partial oxidation reaction, to drive an endothermic reaction. During operation, a reactant enters a combustion or reaction chamber in a bulk flow path flowing past and in contact with a porous material or porous catalyst. A portion of the reactant molecularly transversely diffuses into the porous catalyst and reacts to form a product or products, and then the products diffuse transversely into the bulk flow path and out of the reactor. A short heat transport distance is desired for good performance. These short heat transport distances, combined with preferred reactor configurations, can provide surprisingly high volumetric productivity and low pressure drop. The reactor designs suffer from a fundamental limitation resulting from the flow configuration in which a reacting stream flows parallel to a heat transfer surface through which the majority of heat is transferred perpendicular to the direction of fluid flow. Regardless of the reaction taking place in the reaction channels, its reaction rate will vary along the flow length of that channel due to changes in concentration and temperature. Balancing the heat requirements of an endothermic reaction with heat generated by an exothermic reaction flowing parallel to and on the opposite side of a separating plate is extraordinarily difficult since the endothermic reaction is likely to have a very different dependence upon concentration and temperature than the endothermic reaction. Along the flow length of the plate that divides these reactions, the heat flux through the plate that is perpendicular to fluid flow will vary due to temperature and reaction rate differences along the flow length of the plate. Since the thermally coupled reactions are so closely coupled, neither reaction can run at a significantly different reaction rate at any point along the channel length. Thus, each reaction will exhibit a peak in reaction rate at nearly the same position within the reactor with slower reaction rates before and after this peak, which leads to the need for a long reactor channel to ensure complete conversion. A specific example of this reaction rate problem encountered in the parallel flow arrangement is demonstrated by attempts to drive endothermic steam reforming with exothermic combustion in microchannel and alternating parallel plate reactors. A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels. Thus, the stacked reactor becomes an alternating series of endothermic and exothermic

reactors separated by thin heat exchange walls. Unfortunately, the combustion reaction is difficult to control with convenient combustion catalysts and fuels, and most of the combustion occurs near the fuel inlet. This uneven combustion results in uneven heat transfer to the endothermic reaction and poor overall reactor performance. The geometry allows intimate thermal contact whilst keeping the streams from becoming mixed. The reactor body is constructed by modification of a substantially rigid and essentially nonporous monolith honeycomb. Prior to modification the monolith consists of a honeycombed body having a matrix of thin walls defining a multiplicity of discrete channels which pass through the body of the structure from one face to the opposing face. The monolith is modified in such a way as to produce a rigid body containing at least two discrete process flow paths which have a number of dividing walls in common. A channel is defined as any individual passageway through the monolith body and a flow path is the group of channels used for a single reaction. The inlets to the first reaction flow paths and the inlets to the second reaction flow paths are in the inlet manifold such that the reactants run in a co-current configuration. The reactants also leave the reactor in the same outlet manifold via the first reaction outlets and the second reaction outlets. The fuel processor is described using the steam reformation of methane and oxidation of methane reactions to illustrate the concept. The inlets and outlets may be arranged for a countercurrent flow of the reactants.

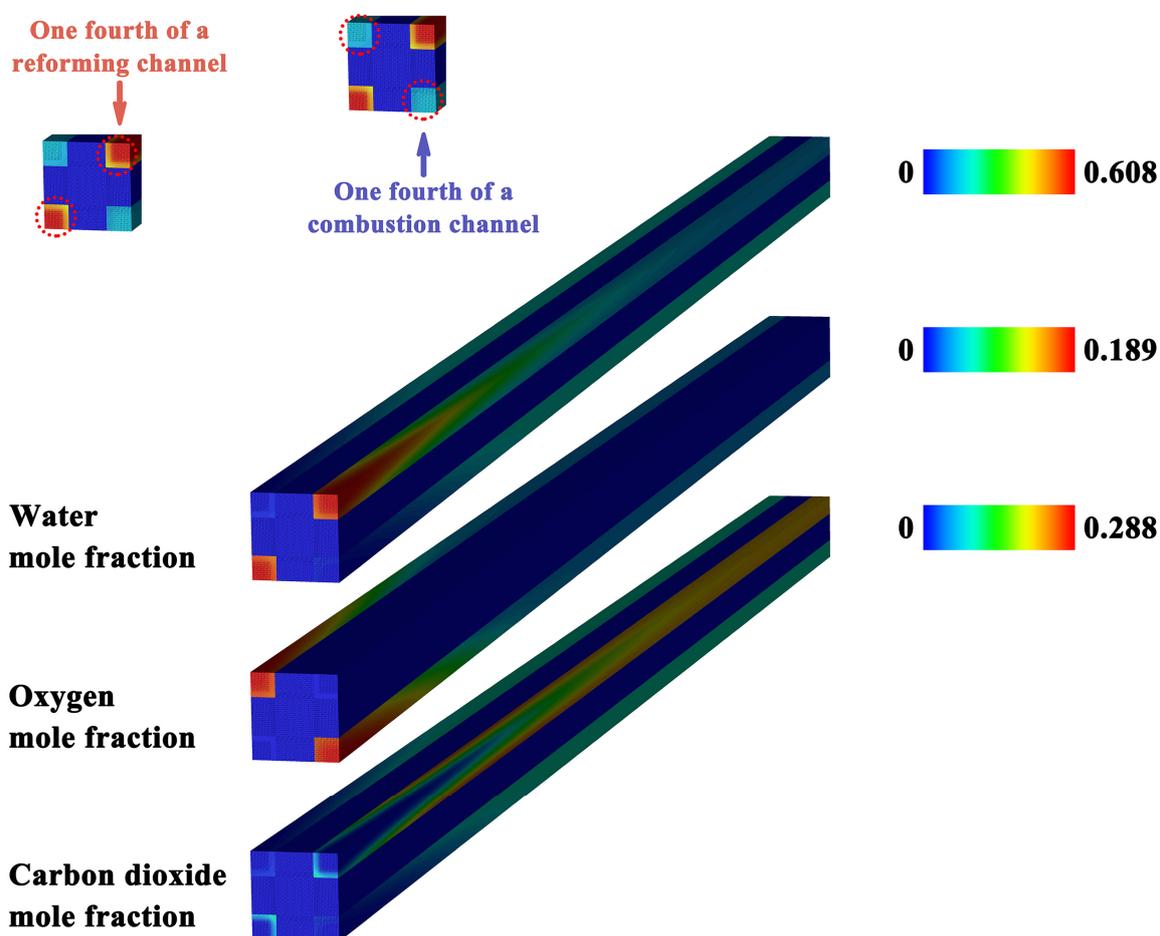


Figure 6. Contour plots of water mole fraction, oxygen mole fraction, and carbon dioxide mole fraction under nominal operating conditions for the heat integrated reactor.

The Nusselt number profiles along the length of the heat integrated reactor are presented in Figure 7 under nominal operating conditions for thermochemically producing hydrogen from methanol by steam reforming. Many chemical processes utilize catalysts to enhance chemical conversion behavior. A catalyst promotes the rate of chemical conversion but does not affect the energy transformations which occur during the reaction. Often catalytic processes are conducted within tubes which are packed

with a suitable catalytic substance. The process gas flows within the tube and contacts the catalytic packing where reaction proceeds. The tube is placed within a hot environment such as a furnace such that the energy for the process can be supplied through the tube wall via conduction. The mechanism for heat transfer with this arrangement is rather tortuous as heat must first be transferred through the outer boundary layer of the tube, conducted through the often-heavy gauge wall of the tube and then pass through the inner boundary layer into the process gas. The process gas is raised in temperature and this energy can be utilized by the process for chemical reaction. The process engineer is often caused to compromise between the pressure drop within the tube reactor with the overall heat transfer and catalytic effectiveness. The inner heat transfer coefficient can be effectively increased by raising the superficial velocity of the process gas. The higher gas velocity therefore improves the thermal effectiveness of the system. However, higher gas velocities increase the system's pressure drop and results in increased compressor sizes and associated operating costs. A reactor must be of sufficient length to allow a reaction to proceed to the required conversion [33, 34]. Utilizing high gas velocities typically results in reactors with large length to width ratios which again results in systems with high pressure drops [35, 36]. The smaller the characteristic dimension of the catalyst particle the higher is the utilization of the catalyst [37, 38]. This is sometimes expressed as a higher effectiveness factor [39, 40]. However, beds formed from small particles exhibit higher pressure drops than similar beds formed from larger particle. So, an engineer designs a system with expectable compromises between heat transfer, catalyst utilization, system conversion, and pressure drop. Therefore, a reactor for conducting catalytic processes which can promote overall heat transfer and levels of conversion whilst minimizing pressure drop is desired. The dividing walls must be of sufficient strength to maintain the integrity of channels. The minimum wall thickness therefore depends upon material of construction. The wall thickness is in the range of about 0.5 millimeter to 5 millimeters and more particularly in the range of about 0.5 millimeter to 2 millimeters. The wall will act as a thermal barrier to heat transfer, however, as the wall is very thin its resistance is small. The heat for the reaction is supplied directly through the wall from the oxidation channels occurring on the opposing side of the dividing wall. As the heat transfer characteristics are highly independent of the bulk reactants velocity, a velocity can be chosen to ensure that the reactants exiting the reactor has attained the desired level of conversion or indeed reached any equilibrium. It is interesting to note that in such an arrangement it is desirable to operate the reactants in a co-current flow arrangement. This ensures that the area with the greatest heat generation is adjacent to the area with the greatest heat requirement. However, cases may exist where a countercurrent flow arrangement is desirable. The system can be used to for a number of reactions as a wide range of process conditions are possible. A number of techniques are available in which to deposit an active catalyst onto the wall of the monolith. One such technique is that of the washcoat as is used in catalytic converters. Others include the sol-gel technique, metal sputtering, or the grinding of commercial catalyst pellets followed by attachment through the use of a cement or sol-gel. Many of the coating techniques allow different thicknesses of coating to be applied. It may also be possible to increase or decrease the thickness of the coating along the channel length. This technique can be used enhance the kinetics in the downstream sections of the channel. The thickness of the catalyst coating depends upon the process proceeding within the catalyst matrix. The products of some processes are highly dependent upon the catalyst thickness. In this case, the thickness should be no larger than the characteristic length beyond which the product spectrum degrades. For some processes the catalyst thickness has no effect on the product spectrum, an example of which is the steam reforming of methane. In this case the catalyst thicknesses can be of any dimension. However, excessively thick coatings are avoided as the catalyst interior performs little reaction due to diffusion limitations and acts as a thermal barrier. Many catalysts are prone to deactivation due to diffusion of an impurity into the catalyst. In cases where the catalyst is supported on a metallic surface, the source of the impurity is

often the metal surface itself. Metals have low diffusion coefficients, however, as the catalyst is in intimate contact with the support over extended periods and at elevated temperature, small amounts of the metallic substrate will diffuse into the catalyst structure. A common example of this effect is the poisoning of nickel-based steam reforming catalysts with iron. It is possible to minimize this effect by using a dense and nonporous barrier coating located between the metal surfaces and the active catalyst. However, this problem can be circumnavigated through the use of ceramic structures.

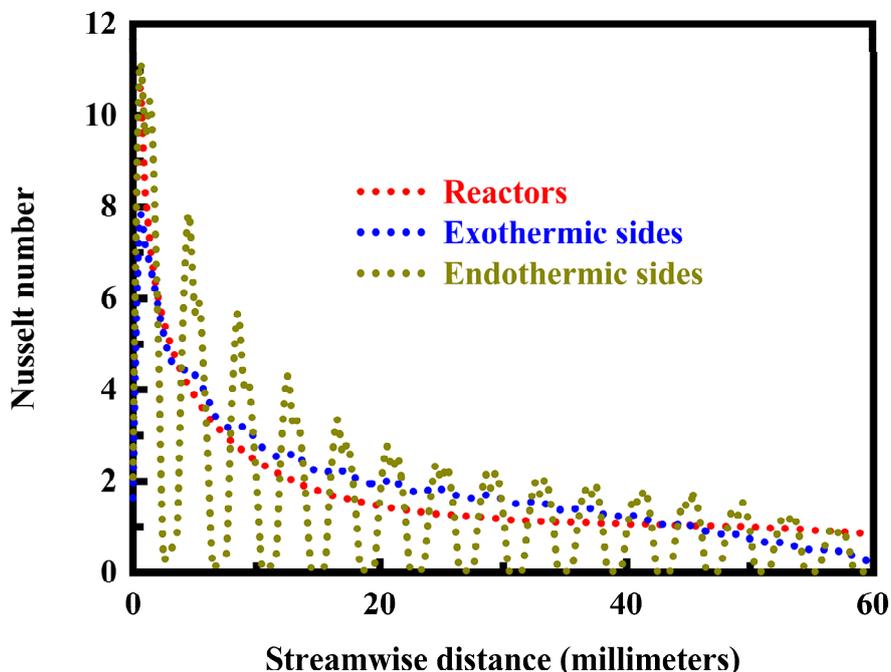


Figure 7. Nusselt number profiles along the length of the heat integrated reactor under nominal operating conditions for thermochemically producing hydrogen from methanol by steam reforming.

The Sherwood number profiles along the length of the heat integrated reactor are presented in Figure 8 under nominal operating conditions for thermochemically producing hydrogen from methanol by steam reforming. An advantage of the arrangement is the low thermal inertia of the system. This allows the reactor to operate with inherently fast thermal response and is particularly advantageous during startup. The low thermal inertia will minimize startup time to the order of minutes from the order of hours, which is typical for large packed tube technology. With suitable ancillary equipment, the system can be operated with a level of control and operating flexibility not encountered in traditional steam reformers. Another deficiency of traditional heat transfer equipment is start-up time and thermal response to transients. As reactors are traditionally large and heavy, they have significant thermal inertia. Therefore, the system takes significant time to re-equilibrate from any change in load or process operating conditions. Therefore, a reactor with enhanced response characteristics particularly for rapid start up is desired. The design consists of multiple packed tubes, of small diameter, being placed in intimate contact with a heat generating flame. The arrangement leads to improved heat transfer and therefore chemical conversion. However, the packed tube results in a significant pressure drop and the author states the process is still heat transfer limited. Therefore, a reactor design which minimizes the process side pressure drop and does not suffer from heat transfer limitation is required. It is proposed that the arrangement can either be used as a heat exchanger, where energy is transferred from one stream to another via conduction through the wall or it is suitable as a chemical reactor where the second set of channels allow the introduction of a heat transfer fluid [41, 42]. It is noted that the reaction can be a catalytic process and the catalytically active material can be coated onto the monolith passage walls to minimize pressure drop [43, 44]. In this arrangement the heat transfer from the process catalyst to the dividing wall will be highly efficient, however, the uptake of the energy by the heat

transfer fluid will suffer from all of the limitations of traditional heat transfer operations [45, 46]. In this case the boundary layer will provide a significant resistance to heat transfer and will severely limit the rate of the process [47, 48]. The high velocities will reduce the characteristic thickness of the boundary layer and ensure that a sufficient mass of heat transfer fluid is available to absorb the heat of reaction without significantly changing temperature. These requirements will lead to excessive pressure drop through the coolant channels. Therefore, a reactor design which minimizes the heat transfer fluid side pressure drop is required. Combining endothermic and exothermic reactions on opposing sides of dividing walls of adjacent channels can serve as an efficient method of heat transfer. It is proposed that steam reforming of a hydrocarbon be performed by one layer and the energy for this process be supplied by a hydrocarbon oxidative process being promoted in the subsequent layer. Various hybrids of this theme are proposed. However, as the heat is supplied by an autothermal reaction, oxygen must be supplied along with the fuel stream. As well as the oxygen, associated nitrogen is present. This nitrogen acts to absorb process energy which lowers the thermal efficiency of the process as well as diluting the desired product, hydrogen. The presence of the nitrogen increases the load on downstream partial oxidation units which act to oxidize carbon monoxide to carbon dioxide. The nitrogen also reduces the streams suitability for use in fuel cells. Therefore, a reactor which can supply sufficient energy to an endothermic reaction without mixing the streams is needed. It should be noted that an advantage is the ability to use low calorific fuel for the exothermic reaction. Such fuel is not ideally suited to homogeneous combustion and results in a highly unstable flame. Heterogeneous combustion aids in spreading the heat generation along the length of the channel and helps prevent hotspot formation. The use of low caloric value gas allows the use of certain waste streams as the fuel to supply the heat. Examples of such streams include the off-gas stream from a fuel cell, the gaseous components from a Fischer-Tropsch synthesis. It should be further noted that the heat generation rate per unit area is approximately matched to the heat requirement in the adjacent channel. This can be achieved by controlling the catalyst thickness in each channel. A trial-and-error process may be required to obtain the optimum catalyst thicknesses for some processes. If the processes are not thermally matched, the overall efficiency of the reactor will be reduced. Suitable metals include copper, aluminum, stainless steel, iron, titanium, and mixtures or alloys thereof.

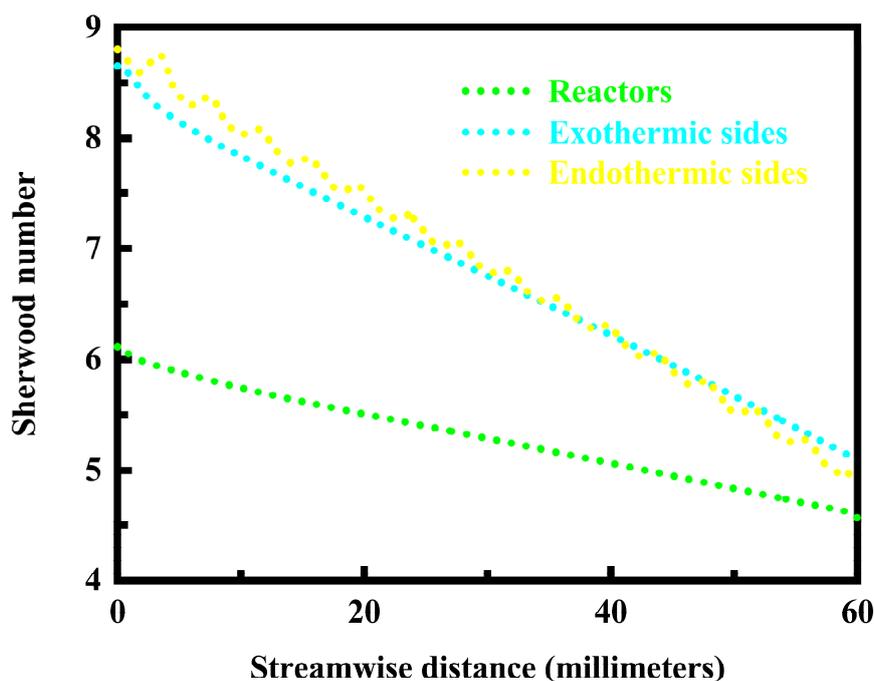


Figure 8. Sherwood number profiles along the length of the heat integrated reactor under nominal operating conditions for thermochemically producing hydrogen from methanol by steam reforming.

## 4. Conclusions

Computations are performed using grids with varying nodal densities to determine the optimum node spacing and density that would give the desired accuracy and minimize computation time. The final grid density is determined when the centerline profiles of temperature and species concentration do not show obvious difference. The second-order upwind scheme is used to discretize the mathematical model, and the semi-implicit method for pressure-linked equations algorithm is employed to solve for the pressure and velocity fields. The simulation convergence is judged upon the residuals of all governing equations. Particular emphasis is placed upon the effect of various factors on the thermochemical steam reforming processes in heat integrated reactors. The major conclusions are summarized as follows:

- Steam reforming produces hydrogen and carbon monoxide when heat is added to a catalytic reactor containing steam and hydrocarbons.
- Alternating channel parallel plate designs can be applied to thermally coupling endothermic steam reforming with combustion in neighboring channels.
- Balancing the heat requirements of an endothermic reaction with heat generated by an exothermic reaction flowing parallel to and on the opposite side of a separating plate is extraordinarily difficult since the endothermic reaction is likely to have a very different dependence upon concentration and temperature than the endothermic reaction.
- A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels.
- The process gas is raised in temperature and this energy can be utilized by the reforming process.
- The catalyst coating thickness depends upon the process proceeding within the catalyst matrix.
- The arrangement leads to improved heat transfer and therefore chemical conversion.
- Heterogeneous combustion aids in spreading the heat generation along the length of the channel and helps prevent hotspot formation.

## References

- [1] M. Menzinger, V. Yakhnin, A. Jaree, P.L. Silveston, and R.R. Hudgins. Dynamic responses of packed bed reactors. *Chemical Engineering Science*, Volume 59, Issue 19, 2004, Pages 4011-4022.
- [2] G. Langhendries, G.V. Baron, and P.A. Jacobs. Selective and efficient hydrocarbon oxidation in a packed bed membrane reactor. *Chemical Engineering Science*, Volume 54, Issue 10, 1999, Pages 1467-1472.
- [3] V. Höller, I. Yuranov, L. Kiwi-Minsker, and A. Renken. Structured multiphase reactors based on fibrous catalysts: Nitrite hydrogenation as a case study. *Catalysis Today*, Volume 69, Issues 1-4, 2001, Pages 175-181.
- [4] P. Aguiar, N. Lapeña-Rey, D. Chadwick, and L. Kershenbaum. Improving catalyst structures and reactor configurations for autothermal reaction systems: Application to solid oxide fuel cells. *Chemical Engineering Science*, Volume 56, Issue 2, 2001, Pages 651-658.
- [5] R. Carli, C.L. Bianchi, R. Bernasconi, G. Frontini, and V. Ragaini. Fisher-Tropsch synthesis on ruthenium supported titanium silicate catalysts. *Studies in Surface Science and Catalysis*, Volume 98, 1995, Pages 178-179.
- [6] C.J. Bertole, C.A. Mims, and G. Kiss. Support and rhenium effects on the intrinsic site activity and methane selectivity of cobalt Fischer-Tropsch catalysts. *Journal of Catalysis*, Volume 221, Issue 1, 2004, Pages 191-203.
- [7] A.K. Datye, Y. Jin, L. Mansker, R.T. Motjope, T.H. Dlamini, and N.J. Coville. The nature of the

- active phase in iron Fischer-Tropsch catalysts. *Studies in Surface Science and Catalysis*, Volume 130, 2000, Pages 1139-1144.
- [8] D.B. Bukur, L. Nowicki, and X. Lang. Fischer-tropsch synthesis in a stirred tank slurry reactor. *Chemical Engineering Science*, Volume 49, Issue 24, Part A, 1994, Pages 4615-4625.
- [9] M. Levent, G. Budak, and A. Karabulut. Estimation of concentration and temperature profiles for methane-steam reforming reaction in a porous catalyst. *Fuel Processing Technology*, Volume 55, Issue 3, 1998, Pages 251-263.
- [10] F. Gallucci, L. Paturzo, and A. Basile. A simulation study of the steam reforming of methane in a dense tubular membrane reactor. *International Journal of Hydrogen Energy*, Volume 29, Issue 6, 2004, Pages 611-617.
- [11] Y. Matsumura and T. Nakamori. Steam reforming of methane over nickel catalysts at low reaction temperature. *Applied Catalysis A: General*, Volume 258, Issue 1, 2004, Pages 107-114.
- [12] V.D. Belyaev, T.I. Politova, O.A. Mar'ina, and V.A. Sobyenin. Internal steam reforming of methane over Ni-based electrode in solid oxide fuel cells. *Applied Catalysis A: General*, Volume 133, Issue 1, 1995, Pages 47-57.
- [13] X. Zhang, C.S.-M. Lee, D.M.P. Mingos, and D.O. Hayward. Oscillatory behaviour during the partial oxidation of methane over cobalt wires and foils. *Applied Catalysis A: General*, Volume 248, Issues 1-2, 2003, Pages 129-142.
- [14] F. Basile, G. Fornasari, F. Trifirò, and A. Vaccari. Partial oxidation of methane: Effect of reaction parameters and catalyst composition on the thermal profile and heat distribution. *Catalysis Today*, Volume 64, Issues 1-2, 2001, Pages 21-30.
- [15] U. Pandey, K.R. Putta, K.R. Rout, E.A. Blekkan, E. Rytter, and M. Hillestad. Staging and path optimization of Fischer-Tropsch synthesis. *Chemical Engineering Research and Design*, Volume 187, 2022, Pages 276-289.
- [16] J.L. Barrera, J.J. Hartvigsen, M. Hollist, J. Pike, A. Yarosh, N.P. Fullilove, and V.A. Beck. Design optimization of integrated cooling inserts in modular Fischer-Tropsch reactors. *Chemical Engineering Science*, Volume 268, 2023, Article Number: 118423.
- [17] M.A. El-Bousiffi and D.J. Gunn. A dynamic study of steam-methane reforming. *Studies in Surface Science and Catalysis*, Volume 133, 2001, Pages 247-254.
- [18] I.I. Bobrova, N.N. Bobrov, and A.A. Davydov. Catalytic methane steam reforming: Novel results. *Catalysis Today*, Volume 24, Issue 3, 1995, Pages 257-258.
- [19] T. Blumberg, Y.D. Lee, T. Morosuk, and G. Tsatsaronis. Exergoenvironmental analysis of methanol production by steam reforming and autothermal reforming of natural gas. *Energy*, Volume 181, 2019, Pages 1273-1284.
- [20] A.O. Oni, K. Anaya, T. Giwa, G.D. Lullo, and A. Kumar. Comparative assessment of blue hydrogen from steam methane reforming, autothermal reforming, and natural gas decomposition technologies for natural gas-producing regions. *Energy Conversion and Management*, Volume 254, 2022, Article Number: 115245.
- [21] J.-H. Yang, Y. Yoon, M. Ryu, S.-K. An, J. Shin, and C.-J. Lee. Integrated hydrogen liquefaction process with steam methane reforming by using liquefied natural gas cooling system. *Applied Energy*, Volume 255, 2019, Article Number: 113840.
- [22] U. Izquierdo, V.L. Barrio, J.F. Cambra, J. Requies, M.B. Güemez, P.L. Arias, G. Kolb, R. Zapf, A.M. Gutiérrez, and J.R. Arraibi. Hydrogen production from methane and natural gas steam reforming in conventional and microreactor reaction systems. *International Journal of Hydrogen Energy*, Volume 37, Issue 8, 2012, Pages 7026-7033.
- [23] Y. Voloshchuk and A. Richter. Reduced order modeling and large-scale validation for non-catalytic partial oxidation of natural gas. *Chemical Engineering Science*, Volume 255, 2022, Article Number:

117620.

- [24] A. Al-Musa, S. Shabunya, V. Martynenko, and V. Kalinin. Modeling of natural gas partial oxidation in an in-house developed pilot scale catalytic reactor based on local thermodynamic equilibrium concept. *Applied Thermal Engineering*, Volume 113, 2017, Pages 238-245.
- [25] B.T. Schädel and O. Deutschmann. Steam reforming of natural gas on noble-metal based catalysts: Predictive modeling. *Studies in Surface Science and Catalysis*, Volume 167, 2007, Pages 207-212.
- [26] H.C. Lee, Y. Potapova, O.Y. Lim, D. Lee, S. Kim, J.H. Park, and E.D. Park. Hydrogen production by steam reforming of natural gas over highly stable Ru catalyst supported on nanostructured alumina. *Studies in Surface Science and Catalysis*, Volume 167, 2007, Pages 177-182.
- [27] A. Olivieri and F. Vegliò. Process simulation of natural gas steam reforming: Fuel distribution optimisation in the furnace. *Fuel Processing Technology*, Volume 89, Issue 6, 2008, Pages 622-632.
- [28] E.C. Wanat, K. Venkataraman, and L.D. Schmidt. Steam reforming and water-gas shift of ethanol on Rh and Rh-Ce catalysts in a catalytic wall reactor. *Applied Catalysis A: General*, Volume 276, Issues 1-2, 2004, Pages 155-162.
- [29] A. Heinzl, B. Vogel, and P. Hübner. Reforming of natural gas-hydrogen generation for small scale stationary fuel cell systems. *Journal of Power Sources*, Volume 105, Issue 2, 2002, Pages 202-207.
- [30] Q. Ming, T. Healey, L. Allen, and P. Irving. Steam reforming of hydrocarbon fuels. *Catalysis Today*, Volume 77, Issues 1-2, 2002, Pages 51-64.
- [31] Z.R. Ismagilov, O.Y. Podyacheva, V.V. Pushkarev, N.A. Koryabkina, V.N. Antsiferov, Y.V. Danchenko, O.P. Solonenko, and H. Veringa. Development and study of metal foam heat-exchanging tubular reactor: Catalytic combustion of methane combined with methane steam reforming. *Studies in Surface Science and Catalysis*, Volume 130, 2000, Pages 2759-2764.
- [32] J.T. Richardson. A gas fired heat-pipe reformer for small-scale hydrogen production. *Studies in Surface Science and Catalysis*, Volume 107, 1997, Pages 567-571.
- [33] M. Szukiewicz and R. Petrus. Approximate model for diffusion and reaction in a porous pellet and an effectiveness factor. *Chemical Engineering Science*, Volume 59, Issue 2, 2004, Pages 479-483.
- [34] J. Lee and D.H. Kim. An improved shooting method for computation of effectiveness factors in porous catalysts. *Chemical Engineering Science*, Volume 60, Issue 20, 2005, Pages 5569-5573.
- [35] D.H. Kim and J. Lee. A robust iterative method of computing effectiveness factors in porous catalysts. *Chemical Engineering Science*, Volume 59, Issue 11, 2004, Pages 2253-2263.
- [36] R. Baur and R. Krishna. Effectiveness factor for zeolite catalysed isomerization reactions. *Chemical Engineering Journal*, Volume 99, Issue 2, 2004, Pages 105-116.
- [37] D. Papadias, L. Edsberg, and P. Björnbom. Simplified method for effectiveness factor calculations in irregular geometries of washcoats. *Chemical Engineering Science*, Volume 55, Issue 8, 2000, Pages 1447-1459.
- [38] S.D. Keegan, N.J. Mariani, S.P. Bressa, G.D. Mazza, and G.F. Barreto. Approximation of the effectiveness factor in catalytic pellets. *Chemical Engineering Journal*, Volume 94, Issue 2, 2003, Pages 107-112.
- [39] R.E. Hayes, B. Liu, and M. Votsmeier. Calculating effectiveness factors in non-uniform washcoat shapes. *Chemical Engineering Science*, Volume 60, Issue 7, 2005, Pages 2037-2050.
- [40] X. Zhu and H. Hofmann. Effect of wetting geometry on overall effectiveness factors in trickle beds. *Chemical Engineering Science*, Volume 52, Issue 24, 1997, Pages 4511-4524.
- [41] T. Boger and A.K. Heibel. Heat transfer in conductive monolith structures. *Chemical Engineering Science*, Volume 60, Issue 7, 2005, Pages 1823-1835.
- [42] C.O. Vandu, J. Ellenberger, and R. Krishna. Hydrodynamics and mass transfer in an upflow monolith loop reactor: Influence of vibration excitement. *Chemical Engineering Science*, Volume

59, Issues 22-23, 2004, Pages 4999-5008.

- [43] T. Haakana, E. Kolehmainen, I. Turunen, J.-P. Mikkola, and T. Salmi. The development of monolith reactors: General strategy with a case study. *Chemical Engineering Science*, Volume 59, Issues 22-23, 2004, Pages 5629-5635.
- [44] T. Valdés-Solís, M.J.G. Linders, F. Kapteijn, G. Marbán, and A.B. Fuertes. Adsorption and breakthrough performance of carbon-coated ceramic monoliths at low concentration of n-butane. *Chemical Engineering Science*, Volume 59, Issue 13, 2004, Pages 2791-2800.
- [45] M.T. Kreutzer, F. Kapteijn, J.A. Moulijn, and J.J. Heiszwolf. Multiphase monolith reactors: Chemical reaction engineering of segmented flow in microchannels. *Chemical Engineering Science*, Volume 60, Issue 22, 2005, Pages 5895-5916.
- [46] R.M. Heck, S. Gulati, and R.J. Farrauto. The application of monoliths for gas phase catalytic reactions. *Chemical Engineering Journal*, Volume 82, Issues 1-3, 2001, Pages 149-156.
- [47] S.-J. Jeong and W.-S. Kim. A study on the optimal monolith combination for improving flow uniformity and warm-up performance of an auto-catalyst. *Chemical Engineering and Processing: Process Intensification*, Volume 42, Issue 11, 2003, Pages 879-895.
- [48] B. Ozyurt, P. Mogili, B. Mierau, S.G. Sunol, and A.K. Sunol. A hierarchical approach to simultaneous design of products and processes. *Computers & Chemical Engineering*, Volume 20, Supplement 1, 1996, Pages S73-S78.