

Performance and efficiency analysis of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors

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Abstract

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. The present study is focused primarily upon the performance and efficiency analysis of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors. The steady-state continuity, momentum, energy, and species conservation equations are solved in the fluid phase and the heat equation is solved in the solid phase using a finite volume approach. An adaptive meshing scheme is used for the discretization of the differential equations. Computational fluid dynamics simulations are carried out over a wide range of material conductivities. Continuity in temperature and heat flux is applied at the fluid-solid interfaces. Neither heat-transfer nor mass-transfer correlations are employed. Parallel processing employing a message passing interface is used to speed up the most demanding calculations. The present study aims to explore how to effectively enhance chemical conversion behavior by utilizing catalysts. Particular emphasis is placed upon the effect of wall thermal conductivity on the performance and efficiency of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors. The results indicate that the arrangement leads to improved heat transfer and therefore chemical conversion. The honeycomb structure imparts strength to the overall system permitting the walls to be very thin and thereby being responsible for the low weight and rapid thermal response of the reactor configuration. The heat transfer from the process catalyst to the dividing wall is 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. The process provides more efficient utilization and uniform usage of the heat generated by the exothermic reaction, thus allowing the endothermic reaction to be carried out at a somewhat higher temperature. The temperature control possible with this system is extremely efficient because all the catalytic material in the reactor channels is on the surface of the walls that can transmit heat through the walls directly to the thermal control channels. Adiabatic conditions prevail in the autothermal reactor because the catalytic oxidation reaction is exothermic in nature and the heat generated in the course of such a reaction is usually sufficient to initiate and sustain the endothermic reforming reaction. The thickness of the catalyst coating depends upon the process proceeding within the catalyst matrix. The thin walls and small internal diameters of the channels result in an extremely difficult system for carrying out reactions and transferring heat by giving rise to a high ratio of wall surface area.

Keywords: Chemical processes; Autothermal reactors; Heat transfer; Reaction chambers; Heterogeneous oxidation; Transport phenomena

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1. Introduction

Endothermic catalytic reaction apparatus, for converting hydrocarbon feedstock to hydrogen-rich gases, has attracted increasing attention in recent years [1, 2]. Commercial production of hydrogen is commonly achieved by a process known as steam reforming [3], that involves the endothermic reaction between a mixture of hydrocarbon feedstock and steam passed through a catalyst filled reactor tubing that is heated [4]. In commercial steam reformers for large-scale production of hydrogen from hydrocarbon feeds, endothermic heat is commonly supplied by the combustion of carbonaceous fuel and oxidant in a diffusion or turbulent flame burner that radiates to the refractory walls of a combustion chamber [5], thereby heating them to incandescence, and providing a radiant source for heat transfer to a tubular reaction chamber [6]. Uniform radiation to the surfaces of the tubular reaction chamber is essential since excessive local overheating of the tube surface can result in mechanical failure [6]. In large-scale commercial steam reformers, mal-distribution of heat within the furnace chamber is minimized by providing large spacing between the individual reactor tubes, the furnace walls, and the burner flames [7, 8]. However, for small-scale catalytic reaction apparatus that is uniquely compact, such as for the production of hydrogen for small fuel cell applications, special design features are needed to prevent tube overheating.

A compact reformer comprises an annular reaction chamber concentrically disposed around an internal burner chamber containing a vertically disposed cylindrical radiant burner that uniformly radiates in the radial direction [5, 6]. A uniform radiation pattern to a concentrically disposed annular reaction chamber that surrounds the radiant burner, is provided, thereby avoiding the problems with flame impingement and local overheating of tube surfaces that are associated with the use of diffusion or turbulent flame burners in

compact reformer apparatus [7, 8]. However, there are practical limitations regarding the use of an annular reaction chamber for small-scale reformers having hydrogen production rates of less than about 1500 standard cubic foot per hour. The heat transfer coefficient of gaseous reactants contained within an annular reaction chamber is directly related to the velocity of the gaseous reactants within the annular space [9, 10]. In order to limit the reaction chamber wall temperature, the velocity of gaseous reactants within the annular space must be sufficiently high to absorb the radiant heat flux that impinges on the reaction chamber tube walls [11, 12]. However, for very small-scale reformers, this requires that the width of the annular reaction chamber space be small [13, 14]. It is common practice to limit the maximum diameter of the catalyst particles packed within an annular space to less than 20 percent of the width of the annular space [15, 16] in order to ensure that the catalyst is evenly distributed within the reaction chamber and to prevent gas channeling along the walls of the reaction chamber [17, 18]. However, for an annulus having a small width dimension, this requires use of catalyst particles of particularly small diameters thereby resulting in an undesirably high pressure drop through the catalyst bed.

The benefits of a flameless radiant burner for use in compact catalytic reaction apparatus of annular reaction chamber geometry are known [19, 20]. For small-scale reformer applications, a tubular reaction chamber geometry is preferred over annular reaction chamber geometry in order to simultaneously achieve high heat transfer coefficients and low pressure drops within the reaction chamber [21, 22]. There is need for a compact endothermic catalytic reaction apparatus to achieve the objects of compact design, while avoiding the problems of flame impingement, excessive reaction chamber wall temperatures, and excessive reaction chamber pressure drop by application of a tubular reaction chamber that is heated by the radiant burner [23, 24]. The tubular endothermic reaction chamber may employ a combination of catalyst particle sizes and reactant mass velocities to control the reactor pressure drop and the maximum reaction chamber tube wall temperature within certain needed limits [25, 26]; and the radiant burner is operated at specific ranges of combustion intensity and excess air to control surface temperature of the radiant burner within certain needed limits [27, 28]. The design extends the practical range of tubular endothermic reaction chamber geometry that can be used in combination with radiant burners for converting hydrocarbon feedstock to useful industrial gases.

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. The present study is focused primarily upon the performance and efficiency analysis of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors. The steady-state continuity, momentum, energy, and species conservation equations are solved in the fluid phase and the heat equation is solved in the solid phase using a finite volume approach. An adaptive meshing scheme is used for the discretization of the differential equations. Computational fluid dynamics simulations are carried out over a wide range of material conductivities. Continuity in temperature and heat flux is applied at the fluid-solid interfaces. Neither heat-transfer nor mass-transfer correlations are employed. Parallel processing employing a message passing interface is used to speed up the most demanding calculations. The present study aims to explore how to effectively enhance chemical conversion behavior by utilizing catalysts. Particular emphasis is placed upon the effect of wall thermal conductivity on the performance and efficiency of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors.

2. Numerical methods

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. A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels. The simulated microreactor is a parallel plate reactor with alternating combustion and reforming channels separated by walls. The device is 60 millimeters long. The combustion channel is 700 microns wide, the reforming channel is 700 microns wide, and the wall separating the two channels is 700 microns thick. As a result, a two-dimensional representation of the system may be reasonable because

of the large aspect ratio. The alternating channel configuration allows solving only half of each channel, due to symmetry, plus the wall connecting them. At these length scales, the continuum approximation is still valid. However, in contrast to large scale devices, radical quenching becomes important [29, 30] unless the materials are properly prepared. The commercial computational fluid dynamics software Fluent is used to solve the steady-state continuity, momentum, energy, and species conservation equations in the fluid phase and the heat equation in the solid phase using a finite volume approach.

The reactor body may be constructed from a number of materials using a range of techniques. Suitable materials include ceramics with a low coefficient of thermal expansion which are readily extrudable. These include, but are not limited to, mullite, cordierite, alumina, and silica. Other materials include metals which may be extruded, welded, brazed, or diffusion bonded to make such structures. Using metals, it is sometimes useful to start with metal oxide powders, which are then bonded and reduced to the metallic state. Suitable metals include copper, aluminum, stainless steel, iron, titanium, and mixtures or alloys thereof. The dividing walls of the parallel plate reactor must be of sufficient strength to maintain the integrity of channels. The minimum wall thickness therefore depends upon material of construction. In the present study, 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. Consequently, the two channels will operate with a similar operating temperature. The inlets and outlets are arranged for a co-current flow of the reactants. In an alternative case, the inlets and outlets are arranged for a countercurrent flow of the reactants.

Adaptive meshing is a method of refining the mesh of a simulation based on the solution. An adaptive meshing scheme is used for the discretization of the differential equations. The computational mesh is initialized with 200 axial nodes, 200 radial nodes for the combustion channel and the wall sections, and 200 transverse nodes for the reforming channel. This discretization translates into a total of about 72,000,000 nodes. This initial mesh is adapted and refined during a calculation to increase the accuracy of the solution in regions of high gradients. Specifically, additional nodes are introduced to refine the mesh using the tools built in the computational software so that the normalized gradients in temperature and species between adjacent cells are lower than 10 with a negative exponent of 6. Adaptation is performed if the solution has not converged after about 2,000,000 iterations or when the residuals are around 10 with a negative exponent of 6. This last threshold, while not optimized, is meant to strike a balance between cost and probability for convergence. Specifically, mesh refinement before achieving complete convergence reduces the computational effort, but a too early refinement, namely in a few iterations, may lead to refinement in wrong regions. After mesh refinement, a total of 20,000,000-60,000,000 nodes are used. Such an adaptive meshing strategy, starting with a relatively coarse initial mesh followed by refinement in regions of large gradients, achieves an adequate balance between accuracy and computational effort.

The relationships between the mixture components and the properties are typically complex and unknown. In these cases, it would be advantageous to develop predictive models that are capable of relating the mixture components to the properties so that the properties of new mixtures can be estimated. While there have been various attempts to develop predictive models for chemical mixtures [31, 32], none have gained widespread use. The fluid density is calculated using the ideal gas law. The individual properties of various gaseous species, such as thermal conductivity, are calculated using the kinetic theory of gases, whereas the specific heats are determined as a function of temperature using polynomial fits from the thermodynamic database available in Fluent. Mixture properties, such as specific heat and thermal conductivity, are calculated from pure component values based on the mass-fraction weighted mixing law. Binary species diffusivities are determined using the Chapman-Enskog equation and then are used to calculate the multicomponent mixture diffusivities. For the solid wall, a constant specific heat and an isotropic thermal conductivity are specified. Given that material conductivity varies with temperature and more importantly with the material chosen, computational fluid dynamics simulations are carried out over a wide range of conductivities.

Boundary conditions are chosen and defined in order to represent the behavior of a real physical system that is being simulated. All particular solutions to differential equations rely on enforcing boundary conditions. The

boundary conditions in a problem define how a solution to a differential equation behaves at the boundary of a system. Symmetry boundary condition is applied at the centerline of both channels, implying a zero normal velocity and zero normal gradients of all variables. No-slip boundary condition is applied at each wall-fluid interface. Danckwerts boundary conditions are implemented for the species and temperatures at the inlets to better mimic experimental conditions. Both gases enter the channels at room temperature with a uniform, flat flow velocity. The reactor exits are held at a fixed pressure of 8 atmospheres and the normal gradients of species and temperature, with respect to the direction of the flow, are set to zero. Overall, the device is adiabatic, and hence no heat losses occur through the side walls. Radiation losses play a secondary effect on the operation of the reactor and hence are negligible. Continuity in temperature and heat flux is applied at the fluid-solid interfaces. Neither heat-transfer nor mass-transfer correlations are employed since detailed transport within the solid and fluid phases is explicitly accounted for.

The full problem is solved via a segregated solver using an under-relaxation method. Convergence of the solution is monitored through the residuals of the governing equations and the square root of the sum of the entries of the vector of successive iterations of the solution. The solution is deemed converged when the residuals of the equations as well as the square root of the sum of the entries of the vector of successive iterations are less than around 10 with a negative exponent of 6. The coupling of the heat equation in the wall and the reacting flow equations makes the problem stiff due to the disparity in thermal conductivity between the gases and the wall. Parallel processing employing a message passing interface is used to speed up the most demanding calculations. In most cases, multiple simulations are run simultaneously. Typical simulation times vary from about several hours for high wall thermal conductivity and lower flow rates to about a few days for low wall thermal conductivity and higher flow rates on a single processor depending on the stiffness of the problem. Natural parameter continuation is employed to study the effect of various operating parameters.

3. Results and discussion

The steam molar fraction contour plots in the combined parallel plate heat exchanger-reactor are illustrated in Figure 1 for hydrogen production by steam-methanol reforming. As to reliability and cost, conventional industrial catalytic steam reformers have at least two major disadvantages with respect to fuel cell use. First, because conventional industrial steam reformers operate at very high temperatures and pressure differentials, the reformer tubes that contain the catalyst must be constructed of rugged, thick-walled portions of expensive materials [33, 34]. Additionally, conventional industrial steam reformers also tend to be quite large, which again impacts material costs [35, 36]. Smaller steam reformers are designed for use in fuel cell system applications. Such steam reformers employ single-tube and multiple-tube designs. The smaller steam reformer designs have at least two major disadvantages in fuel cell system applications. First, current steam reformer designs tend to lack quick start-up capability. Lack of quick start-up capability can be problematic in some fuel cell applications, particularly where the reformer is expected to have a relatively short duty cycle [37, 38]. Some current steam reformer designs utilize a multi-element burner, but these burners do not adequately provide for quick start-up and lack the flexibility to efficiently operate on multiple fuels, including for example, natural gas, fuel cell anode exhaust or pressure swing absorption off-gas. For example, in a fuel cell power plant a steam reformer may be used to convert natural gas into a hydrogen-rich fuel stream, and it is desirable to have a burner capable of operating on natural gas and air, a reformat stream and air, and the fuel cell anode and cathode exhaust streams. Second, as part of fuel processing systems in fuel cell-related applications or merchant hydrogen production, for example, current steam reformer designs are less than cost-effective [39, 40]. For example, high-pressure burners and reformer vessels increase the parasitic load on the fuel processing system due to associated compressors, thereby decreasing efficiency and increasing cost and complexity. Conversely, in merchant hydrogen production applications, a low-pressure steam reformer vessel increases the fuel processing system parasitic load because of the associated process gas or syngas compressor that is required. In addition, current steam reformer designs tend to be relatively complex, resulting in increased manufacturing costs and reliability concerns. It is desirable for a steam reformer to be able to start up relatively quickly, and to be able to operate efficiently without adding undue complexity or cost. At the same time, it is desirable for a steam reformer to be low-cost, scalable, and compatible

with a variety of fuel processing systems. 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. The fuel and oxidant manifolds and associated distribution tubes may use a shell-and-tube construction, for example, for low-cost manufacturing. The burner may comprise an array of distribution tubes, such as a hexagonal array, for example. The steam reformer of the present combined parallel plate heat exchanger-reactor also employs shell-and-tube construction that is amenable to low-cost, high-volume manufacturing. The reformer tubes may be arranged in an array having a high packing density, such as a hexagonal array, for example, in order to reduce the size and cost of the steam reformer.

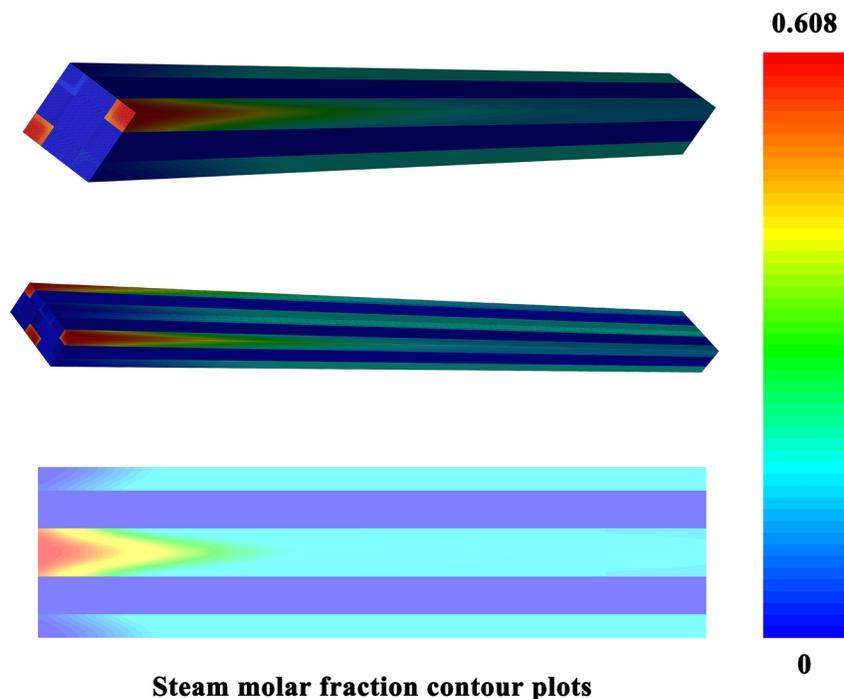


Figure 1. Steam molar fraction contour plots in the combined parallel plate heat exchanger-reactor for hydrogen production by steam-methanol reforming.

The methanol molar fraction contour plots in the combined parallel plate heat exchanger-reactor are illustrated in Figure 2 for hydrogen production by steam-methanol reforming. The combined heat exchanger-reactor consists of sheets of triangularly corrugated material laminated together so as to form a series of roughly parallel passageways. In order for the exchanger to effectively function, the inlet area of the exchanger utilizes a highly complicated design feature characterized by detents and depressed crossflow passageways which effectively causes fluid flow blockage. Consequently, this heat exchanger possesses a high pressure drop. The method of construction recited in the patent and exemplified by the drawings utilize long metal welds or similar materials joining techniques resulting in a structure highly susceptible to internal rupture, leakage and uncontrolled fluid crossover. The combined heat exchanger-reactor consists of a monolithic honeycomb structure wherein the channels of the honeycomb are divided into separate groups, group one channels carrying one fluid with group two channels carrying another fluid which differs from the first either by composition, temperature, pressure, and direction of flow. The main design feature of the combined heat exchanger-reactor is that one group of channels extends outward from the honeycomb parallel to the

direction of fluid flow in the honeycomb, each channel of the group one being in contact through common walls with channels in group two, each channel of group one being separated from other channels of group one by the intervening voids formed by the presence of the channels of group two. One or both of the open ends of the group one channels are manifolded so as to form a separation of entrances of the extended group one channels as compared to the group two channels and the entire system is incorporated into an outer mechanical shell so as to facilitate fluid flow through group one and group two channels, thereby permitting the entry or exit of fluid in group one channels while preventing entry of such same fluid into the group two channels and thereby permitting the independent passage of different fluids through the different channel systems. The common walls which exist between adjacent channels of the different groups facilitate heat transfer from one channel group to another. The honeycomb structure, with its mutually supporting, double cantilevered inner walls, imparts strength to the overall system permitting the walls to be very thin and thereby being responsible for the low weight and rapid thermal response of the combined heat exchanger-reactor configuration. Alternatively, the manifolding of the group one channels may be designed so as to create numerous independent group one channel systems while still being completely surrounded by the group two channel system, thereby permitting numerous independent reactions to proceed simultaneously and permitting more than two independent fluid flows to be conducted under varying conditions within a single chemical reactor and heat exchanger system.

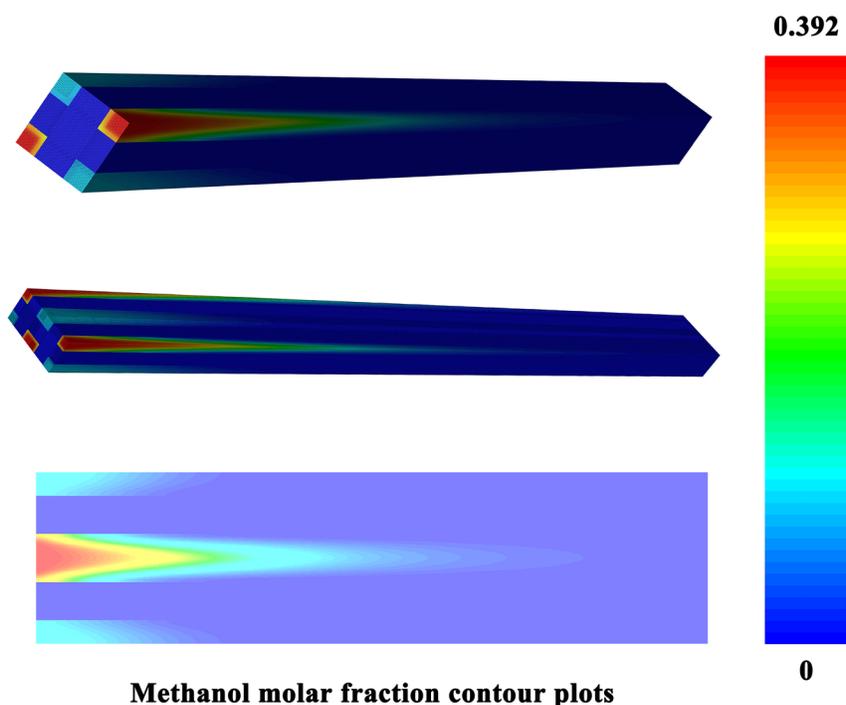


Figure 2. Methanol molar fraction contour plots in the combined parallel plate heat exchanger-reactor for hydrogen production by steam-methanol reforming.

The effect of wall thermal conductivity on the average Nusselt number are illustrated in Figure 3 in the exothermic process of the combined parallel plate heat exchanger-reactor. The channeled, manifolded honeycomb, also referred to as the combined heat exchanger-reactor, may be used without any catalytic material, coated on the walls, purely as a heat exchanger or homogeneous reactor-heat exchanger. By proper choice of materials of construction, the heat exchanger can be designed to transmit both sensible heat by conduction and radiation heat. In this way, many and different reactions can be performed using the manifolded honeycomb system. 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. The energy required or generated through the reaction is removed via a heat transfer fluid in the second channel. The reaction can be a catalytic process and the catalytically active material can be coated onto the monolith passage walls to minimize pressure drop. 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. In this case, the boundary layer will provide a significant resistance to heat transfer and will severely limit the rate of the process. Also, for this arrangement to successfully supply or remove heat and maintain a near isothermal longitudinal profile, considerable heat transfer fluid velocities must be utilized for the combined parallel plate heat exchanger-reactor. 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.

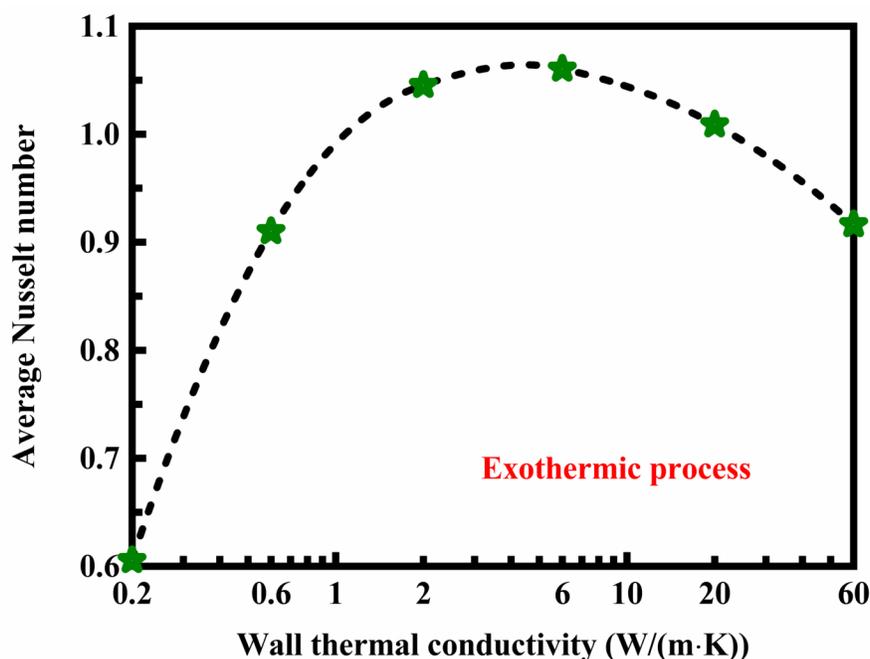


Figure 3. Effect of wall thermal conductivity on the average Nusselt number in the exothermic process of the combined parallel plate heat exchanger-reactor.

The effect of wall thermal conductivity on the average Nusselt number are illustrated in Figure 4 in the endothermic process of the combined parallel plate heat exchanger-reactor. The process may be carried out in a single autothermal reactor without the need to provide multiple sequential catalyst zones in the reactor. The catalytic partial oxidation reaction is exothermic in nature and the heat generated thereby is used to carry out the steam reforming reaction which is endothermic in nature. By having the catalytic partial oxidation layers in intimate contact with the steam reforming catalyst layers, the process heat can be more effectively managed in an adiabatic reactor, namely an autothermal reactor. By having the two catalyst layers in contact with one another, heat loss which otherwise occurs from the use of multiple autothermal reactors or an autothermal reactor containing multiple catalyst zones is significantly minimized. The process results in savings in reactor volume and monolith substrate costs as well as less pressure drop throughout the catalytic partial oxidation and steam reforming reactions. The process thereby provides more efficient utilization and uniform usage of the heat generated by the exothermic catalytic partial oxidation reaction,

thus allowing the endothermic steam reforming reaction to be carried out at a somewhat higher temperature due to lower heat loss and concomitant higher reaction rate and under adiabatic conditions. The result is that the catalytic partial oxidation reaction temperature is somewhat lowered, estimated to be by about 60 degrees and concomitantly, the steam reforming reaction temperature is estimated to be raised by about 60 degrees, thereby improving catalyst life and resulting in higher steam reforming reaction rates. Moreover, by utilizing the catalytic partial oxidation and steam reforming catalysts as layers in contact with one another, adverse reactions such as the reaction of oxygen with rhodium and the reaction of oxygen with platinum, may be avoided. The overall process consists of first preheating the reactants to the required temperature. It ensures good thermal management for the products leaving the reactor to be used to preheat the incoming reactants to a temperature close to the reaction temperature. The methanol, oxygen, and associated nitrogen flow through the inlets of the inlet manifold and into the reaction channels of the flow path. Heterogeneous oxidation occurs in the catalyst attached to the wall. As the stream flows down through the flow path, the conversion increases until the stream passes through the outlets. In the adjacent flow paths, preheated methanol and steam enter the second discrete set of channels through inlets, contact the catalyst coated onto the wall, and reaction occurs. 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.

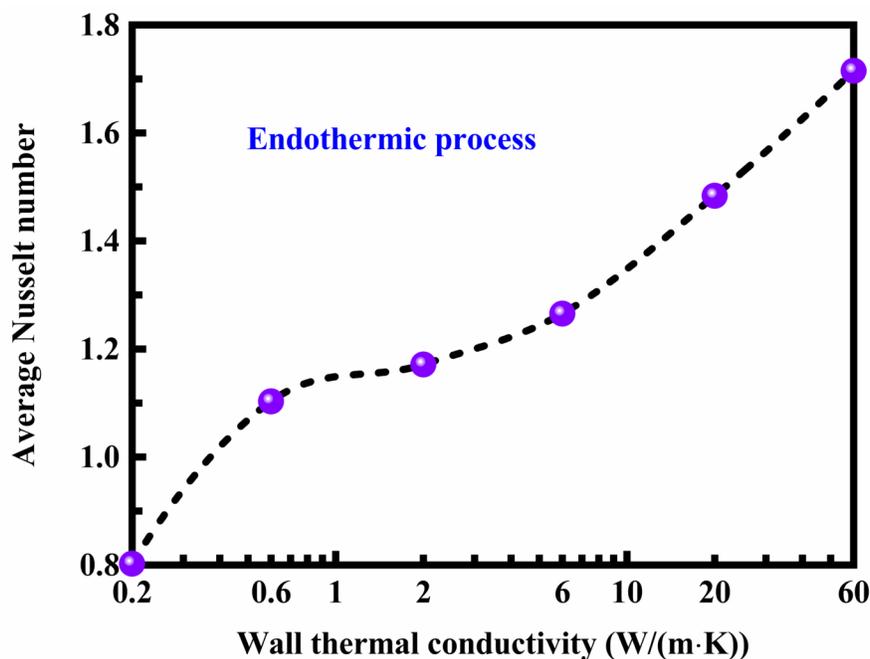


Figure 4. Effect of wall thermal conductivity on the average Nusselt number in the endothermic process of the combined parallel plate heat exchanger-reactor.

The temperature contour plots in the combined parallel plate heat exchanger-reactor are illustrated in Figure 5 for hydrogen production by steam-methanol reforming. 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. Utilizing high gas velocities typically results in reactors with large length to width ratios which again results in systems with high pressure drops. The smaller the characteristic dimension of the catalyst particle the higher is the utilization of the catalyst. This is sometimes expressed as a higher effectiveness factor. However, beds formed from small particles exhibit higher pressure drops than similar beds formed from larger particle. Consequently, 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 interior walls of the channels of either or both groups of channels may be coated with a catalytic material converting that group of channels into a catalytic reactor. Consequently, this reactor group is in intimate contact with the separately manifolded channels of the other group because of the common wall design and as a result, highly exothermic or endothermic reactions may be carried out under much greater temperature control than was possible in fixed bed or fluidized bed or countercurrent flow reactors. This greater temperature control can result in much greater product selectivity and yield for a wide variety of chemical reactions. Now heat can be removed or added to the reactor as required the temperature being regulated merely by careful control of the flow of reactants through the reactor channels and control of coolant or heat source flow through the coolant channels. The temperature control possible with this system is extremely efficient because all the catalytic material in the reactor channels, where heat is either absorbed or liberated due to chemical reactions taking place, is on the surface of the walls that can transmit heat through the walls directly to the thermal control channels. Most of the heat liberated or absorbed in the chemical reaction is conducted through the walls which support the catalyst and thereby eliminating the necessity for heat conduction through the gas phase which is a much less efficient way to cool a catalytic particle. In addition, this configuration allows not only most of the heat to be conducted through solid walls but also allows all the walls on which the catalysts reside to have all common walls with the coolant channels. Consequently, one has an extremely uniform and precise method of controlling the catalyst temperature because no two catalytic surfaces share a common wall, Also, it is possible to fabricate a structure with very thin walls and this too contributes to greater efficiency and ease of temperature control. In traditional systems, the catalyst is on particles randomly packed into a reactor tube. Exothermic reactions occurring generate heat at the catalytic particles even in the center of the tube. This heat must migrate through the gas phase and through the particles in the reaction tube to the wall of the tube and only then pass through the wall to be dissipated in a coolant. This passage of heat through the reactor tube gas and particle phase before finally contacting the wall is responsible for the difficulty encountered in controlling the temperature in the reactors traditionally used.

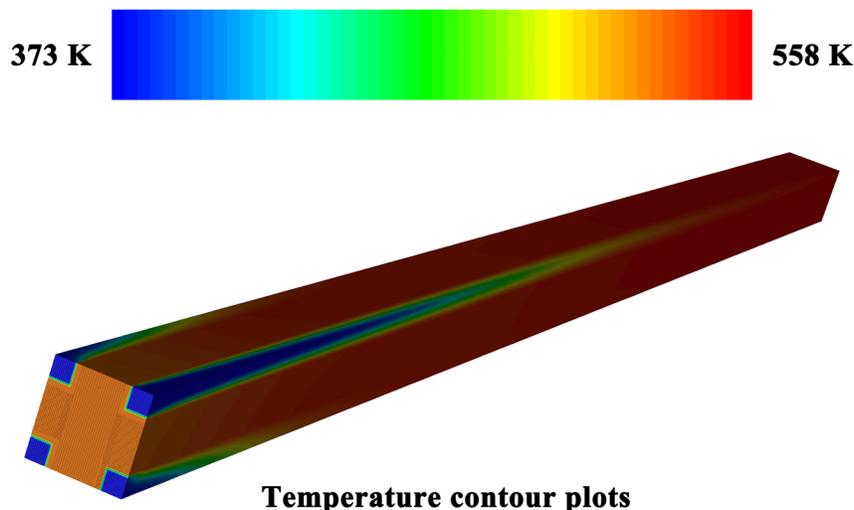


Figure 5. Temperature contour plots in the combined parallel plate heat exchanger-reactor for hydrogen production by steam-methanol reforming.

The hydrogen molar fraction contour plots in the combined parallel plate heat exchanger-reactor are illustrated in Figure 6 for hydrogen production by steam-methanol reforming. The autothermal parallel plate heat exchanger-reactor contains the layered catalyst member. The stream is contacted with the layered catalyst member at a temperature sufficient to initiate and sustain both catalytic partial oxidation and steam reforming. The amounts of the hydrocarbon feed, water and air in the inlet stream introduced into the autothermal reactor are typically controlled to maintain a water to carbon ratio of at least about 0.3:1.0 and an oxygen to carbon ratio of from about 0.2 to 0.7:1.0. In general, adiabatic conditions will prevail in the autothermal reactor due to the fact that the partial oxidation reaction is exothermic in nature and the heat generated in the course of such a reaction is usually sufficient to initiate and sustain the steam reforming reaction which is endothermic in nature. Accordingly, by proper selection of the preheat temperature, reactor design, and volumetric hourly rate, both reactions may be carried out within the reactor while the reactor temperature is kept within the range of about 200 to about 280 °C without the need to supply external heat or cooling to the reactor. However, it is necessary to supply heat or cooling to the reactor as desired in order to continuously maintain both reactions at high reaction rates. In the second step of the process, the hydrocarbon feed is catalytically partially oxidized by contact with the catalytic partial oxidation catalyst layers. The resultant effluent will comprise hydrogen and carbon oxides. In the third step of the process, hydrocarbons remaining in the feed which are not catalytically partially oxidized are steam reformed by contact with the steam reforming catalyst layers, thereby producing a hydrogen-rich effluent. Preferably, the hydrogen-rich gas effluent from the third step of the process is subjected to a further water-gas shift reaction. In the course of the steam reforming reaction, the hydrocarbon reacts with water to yield a product gas containing primarily hydrogen and carbon monoxide, plus any unreacted hydrocarbons. In order to reduce the carbon monoxide level and increase the hydrogen gas level, the effluent may be passed into a converter in which the effluent is contacted with a catalyst such that the carbon monoxide will at with water to yield carbon dioxide and firer amounts of hydrogen.

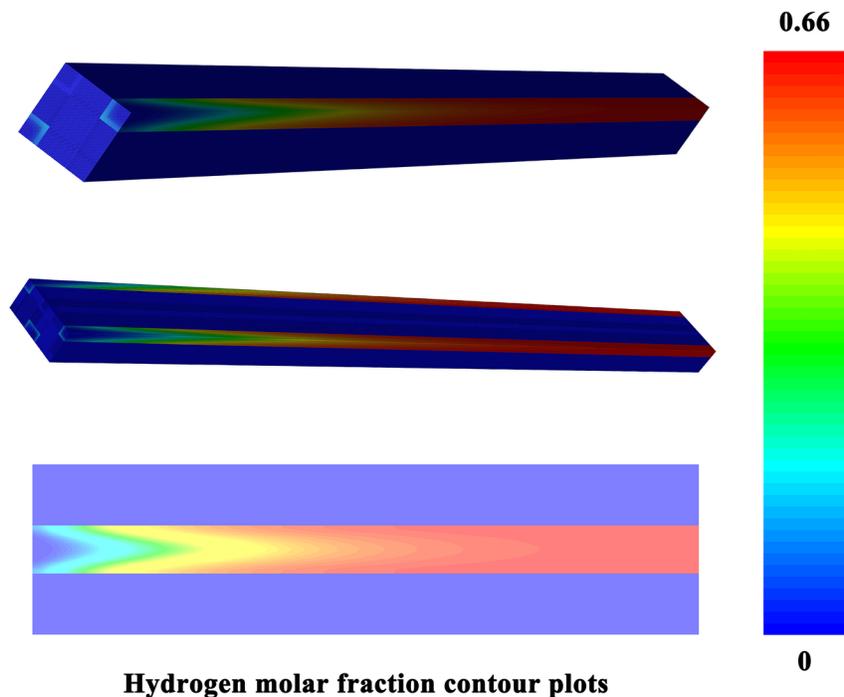


Figure 6. Hydrogen molar fraction contour plots in the combined parallel plate heat exchanger-reactor for hydrogen production by steam-methanol reforming.

The Sherwood number profiles in the exothermic process are presented in Figure 7 along the length of the combined parallel plate heat exchanger-reactor. The combined parallel plate heat exchanger-reactor system can be used for a number of reactions as a wide range of process conditions are possible. It is inevitable that the catalyst coating will eventually deactivate to the point where economics drive for its replacement. It is sometimes possible to extend a catalyst life and reclaim some activity by techniques such as hydrogen treatment or methods to remove carbon buildup. These techniques can be readily applied to the combined parallel plate heat exchanger-reactor. The combined parallel plate heat exchanger-reactor also allows the body to be removed and monolith replacement performed. This is simply achieved by removing the relevant inlet manifold and outlet manifold and removing any monolith supports or containment structure. A new monolith can be inserted and reverse procedure applied. If the endothermic catalyst requires high temperature hydrogen activation, the heat can be supplied via the exothermic channels. The spent monolith can be recycled after recovery of any of the precious metal components of the catalyst. 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 to 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 methanol. 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. 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. An advantage of the reactor system 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, and the stream remaining after hydrogen removal from a membrane gas shift reactor. 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. When using large channels, it is possible that the reaction will become diffusion limited, such that the rate of reaction is dictated by the rate at which unreacted molecules can diffuse from the center of the channel into the catalyst matrix. In this case, it is possible to add flow disturbance elements in the channel or emanating from the wall. These elements will produce a degree of convective mixing by forming local flow disturbances in an otherwise laminar environment. If a heat transfer fluid is used to remove the heat of reaction from a reaction occurring in any adjacent channel, then these flow disturbance elements would provide a useful and low pressure drop method of enhancing thermal performance.

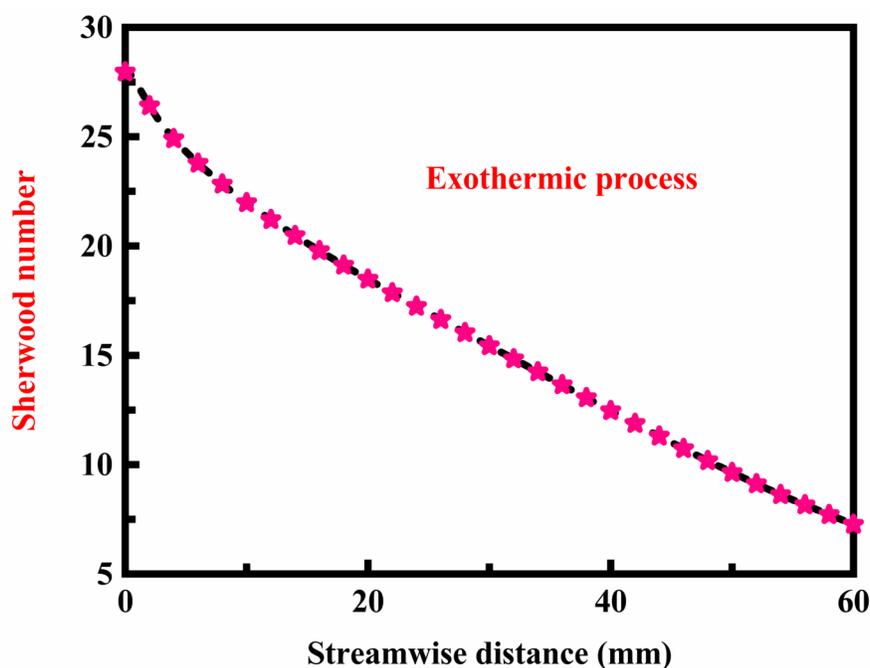


Figure 7. Sherwood number profiles in the exothermic process along the length of the combined parallel plate heat exchanger-reactor.

The Sherwood number profiles in the endothermic process are presented in Figure 8 along the length of the combined parallel plate heat exchanger-reactor. The channels of the group one channel system which have common walls with group two systems but not with other group one channels can be prepared so as to have permeable walls, these group one walls being coated with catalytic material on the inner surfaces for their entire length, part of their length or any combination of lengths desired. Different reactants each composed

of one or more components are fed into different channels of the group one channels and there are converted, either catalytically or thermally, into products, then these products permeate through the walls into the channel system wherein they react further with each other resulting in the finally desired product. In this way, short-lived unstable intermediates can be efficiently introduced to each other without the need for going through difficult intermediate isolation steps. In addition, such a system with permeable walls can be used to introduce different reactants in different group one channels to each other in the group two channels in a highly controlled manner such that the different reactant in the different group one channels are not comingled in high concentrations before the desired reaction is allowed to take place between the different reactants. The honeycomb design because of its use of mutually supporting wall design, permits the preparation of very thin walls which would crack due to normally occurring stresses if not mutually supported, namely if exposed or structurally independent. The thin walls and small internal diameters of the channels result in an extremely difficult system for carrying out reactions and transferring heat by giving rise to a high ratio of wall surface area, also referred to a geometric surface area, to reactor volume. The channel walls may be of from 0.5 to 5.0 millimeters in thickness. The channels may be of any length from 10 millimeters up to several meters, for example, 10 meters; however, length intermediate between these extremes is preferred for reasons of handling and also to insure sufficient length for any contemplated reaction or use. Lengths ranging from 2-20 centimeters, preferably 4-8 centimeters, most preferably 6 centimeters are contemplated [41, 42]. The channels should have an internal diameter, calculated by using the hydraulic diameter as a measure [43, 44]. This is to ensure a channel diameter of sufficient dimensions so that heat will have the shortest path possible to migrate to the walls, thereupon to diffuse through the walls into neighboring channels for dissipation and to ensure wall surface area to support sufficient catalyst [45, 46]. The channels of the different systems can be arranged in any pattern desired so long as every channel wall of the group one channel system, also referred to as the reacting channels, is in contact with at least one channel wall of the other channel system, also referred to as the coolant channels [47, 48]. This can be accomplished for example, by surrounding each channel of group one channels with channels of system two. The honeycomb may have any overall diameter so long as this overall diameter is at least 6 times the internal channel diameter as measured by the hydraulic diameter, namely ensuring that every wall of the group one channels is contacted by channels of group two. The channels of the honeycomb may be coated with catalytic material, such as those materials selected from the group consisting of Group VIII, Group VB, Group VIB, Group VIIB, Group IB, metals and oxides from the previously mentioned groups and mixtures thereof.

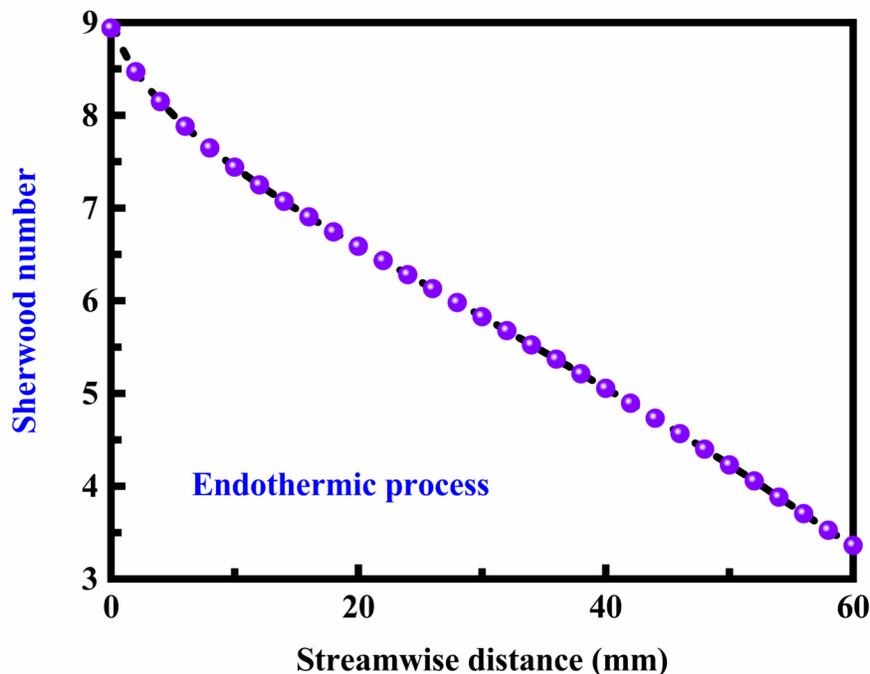


Figure 8. Sherwood number profiles in the endothermic process along the length of the combined parallel plate heat exchanger-reactor.

4. Conclusions

The steady-state continuity, momentum, energy, and species conservation equations are solved in the fluid phase and the heat equation is solved in the solid phase using a finite volume approach. An adaptive meshing scheme is used for the discretization of the differential equations. Computational fluid dynamics simulations are carried out over a wide range of material conductivities. Continuity in temperature and heat flux is applied at the fluid-solid interfaces. Neither heat-transfer nor mass-transfer correlations are employed. Parallel processing employing a message passing interface is used to speed up the most demanding calculations. The major conclusions are summarized as follows:

- The arrangement leads to improved heat transfer and therefore chemical conversion.
- The honeycomb structure imparts strength to the overall system permitting the walls to be very thin and thereby being responsible for the low weight and rapid thermal response of the combined parallel plate heat exchanger-reactor configuration.
- The heat transfer from the process catalyst to the dividing wall is 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.
- The process provides more efficient utilization and uniform usage of the heat generated by the exothermic oxidation reaction, thus allowing the endothermic steam reforming reaction to be carried out at a somewhat higher temperature.
- The temperature control possible with this system is extremely efficient because all the catalytic material in the reactor channels is on the surface of the walls that can transmit heat through the walls directly to the thermal control channels.
- Adiabatic conditions prevail in the autothermal reactor due to the fact that the oxidation reaction is exothermic in nature and the heat generated in the course of such a reaction is usually sufficient to initiate and sustain the steam reforming reaction which is endothermic in nature.
- The thickness of the catalyst coating depends upon the process proceeding within the catalyst matrix,

and the process products are highly dependent upon the catalyst thickness.

- The thin walls and small internal diameters of the channels result in an extremely difficult system for carrying out reactions and transferring heat by giving rise to a high ratio of wall surface area.

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Performance and efficiency analysis of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors

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Abstract

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. The present study is focused primarily upon the performance and efficiency analysis of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors. The steady-state continuity, momentum, energy, and species conservation equations are solved in the fluid phase and the heat equation is solved in the solid phase using a finite volume approach. An adaptive meshing scheme is used for the discretization of the differential equations. Computational fluid dynamics simulations are carried out over a wide range of material conductivities. Continuity in temperature and heat flux is applied at the fluid-solid interfaces. Neither heat-transfer nor mass-transfer correlations are employed. Parallel processing employing a message passing interface is used to speed up the most demanding calculations. The present study aims to explore how to effectively enhance chemical conversion behavior by utilizing catalysts. Particular emphasis is placed upon the effect of wall thermal conductivity on the performance and efficiency of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors. The results indicate that the arrangement leads to improved heat transfer and therefore chemical conversion. The honeycomb structure imparts strength to the overall system permitting the walls to be very thin and thereby being responsible for the low weight and rapid thermal response of the reactor configuration. The heat transfer from the process catalyst to the dividing wall is 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. The process provides more efficient utilization and uniform usage of the heat generated by the exothermic reaction, thus allowing the endothermic reaction to be carried out at a somewhat higher temperature. The temperature control possible with this system is extremely efficient because all the catalytic material in the reactor channels is on the surface of the walls that can transmit heat through the walls directly to the thermal control channels. Adiabatic conditions prevail in the autothermal reactor because the catalytic oxidation reaction is exothermic in nature and the heat generated in the course of such a reaction is usually sufficient to initiate and sustain the endothermic reforming reaction. The thickness of the catalyst coating depends upon the process proceeding within the catalyst matrix. The thin walls and small internal diameters of the channels result in an extremely difficult system for carrying out reactions and transferring heat by giving rise to a high ratio of wall surface area.

Keywords: Chemical processes; Autothermal reactors; Heat transfer; Reaction chambers; Heterogeneous oxidation; Transport phenomena

1. Introduction

Endothermic catalytic reaction apparatus, for converting hydrocarbon feedstock to hydrogen-rich gases, has attracted increasing attention in recent years [1, 2]. Commercial production of hydrogen is

commonly achieved by a process known as steam reforming [3], that involves the endothermic reaction between a mixture of hydrocarbon feedstock and steam passed through a catalyst filled reactor tubing that is heated [4]. In commercial steam reformers for large-scale production of hydrogen from hydrocarbon feeds, endothermic heat is commonly supplied by the combustion of carbonaceous fuel and oxidant in a diffusion or turbulent flame burner that radiates to the refractory walls of a combustion chamber [5], thereby heating them to incandescence, and providing a radiant source for heat transfer to a tubular reaction chamber [6]. Uniform radiation to the surfaces of the tubular reaction chamber is essential since excessive local overheating of the tube surface can result in mechanical failure [6]. In large-scale commercial steam reformers, mal-distribution of heat within the furnace chamber is minimized by providing large spacing between the individual reactor tubes, the furnace walls, and the burner flames [7, 8]. However, for small-scale catalytic reaction apparatus that is uniquely compact, such as for the production of hydrogen for small fuel cell applications, special design features are needed to prevent tube overheating.

A compact reformer comprises an annular reaction chamber concentrically disposed around an internal burner chamber containing a vertically disposed cylindrical radiant burner that uniformly radiates in the radial direction [5, 6]. A uniform radiation pattern to a concentrically disposed annular reaction chamber that surrounds the radiant burner, is provided, thereby avoiding the problems with flame impingement and local overheating of tube surfaces that are associated with the use of diffusion or turbulent flame burners in compact reformer apparatus [7, 8]. However, there are practical limitations regarding the use of an annular reaction chamber for small-scale reformers having hydrogen production rates of less than about 1500 standard cubic foot per hour. The heat transfer coefficient of gaseous reactants contained within an annular reaction chamber is directly related to the velocity of the gaseous reactants within the annular space [9, 10]. In order to limit the reaction chamber wall temperature, the velocity of gaseous reactants within the annular space must be sufficiently high to absorb the radiant heat flux that impinges on the reaction chamber tube walls [11, 12]. However, for very small-scale reformers, this requires that the width of the annular reaction chamber space be small [13, 14]. It is common practice to limit the maximum diameter of the catalyst particles packed within an annular space to less than 20 percent of the width of the annular space [15, 16] in order to ensure that the catalyst is evenly distributed within the reaction chamber and to prevent gas channeling along the walls of the reaction chamber [17, 18]. However, for an annulus having a small width dimension, this requires use of catalyst particles of particularly small diameters thereby resulting in an undesirably high pressure drop through the catalyst bed.

The benefits of a flameless radiant burner for use in compact catalytic reaction apparatus of annular reaction chamber geometry are known [19, 20]. For small-scale reformer applications, a tubular reaction chamber geometry is preferred over annular reaction chamber geometry in order to simultaneously achieve high heat transfer coefficients and low pressure drops within the reaction chamber [21, 22]. There is need for a compact endothermic catalytic reaction apparatus to achieve the objects of compact design, while avoiding the problems of flame impingement, excessive reaction chamber wall temperatures, and excessive reaction chamber pressure drop by application of a tubular reaction chamber that is heated by the radiant burner [23, 24]. The tubular endothermic reaction chamber may employ a combination of catalyst particle sizes and reactant mass velocities to control the reactor pressure drop and the maximum reaction chamber tube wall temperature within certain needed limits [25, 26]; and the radiant burner is operated at specific ranges of combustion intensity and excess air to control surface temperature of the radiant burner within certain needed limits [27, 28]. The design extends the practical range of tubular endothermic reaction chamber geometry that can be used in combination with radiant burners for converting hydrocarbon feedstock to useful industrial gases.

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. The present study is focused primarily upon the performance and efficiency analysis of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors. The steady-state continuity, momentum, energy, and species conservation equations are solved in the fluid phase and the heat equation is solved in the solid phase using a finite volume approach. An adaptive meshing scheme is used for the discretization of the differential equations. Computational fluid dynamics simulations are carried out over a wide range of material conductivities. Continuity in temperature and heat flux is applied at the fluid-solid interfaces. Neither heat-transfer nor mass-transfer correlations are employed. Parallel processing employing a message passing interface is used to speed up the most demanding calculations. The present study aims to explore how to effectively enhance chemical conversion behavior by utilizing catalysts. Particular emphasis is placed upon the effect of wall thermal conductivity on the performance and efficiency of steam-methanol reforming processes in combined parallel plate heat exchanger-reactors.

2. Numerical methods

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. A convenient way to supply heat is to couple the endothermic reaction with an exothermic combustion reaction in the heat exchange channels. The simulated microreactor is a parallel plate reactor with alternating combustion and reforming channels separated by walls. The device is 60 millimeters long. The combustion channel is 700 microns wide, the reforming channel is 700 microns wide, and the wall separating the two channels is 700 microns thick. As a result, a two-dimensional representation of the system may be reasonable because of the large aspect ratio. The alternating channel configuration allows solving only half of each channel, due to symmetry, plus the wall connecting them. At these length scales, the continuum approximation is still valid. However, in contrast to large scale devices, radical quenching becomes important [29, 30] unless the materials are properly prepared. The commercial computational fluid dynamics software Fluent is used to solve the steady-state continuity, momentum, energy, and species conservation equations in the fluid phase and the heat equation in the solid phase using a finite volume approach.

The reactor body may be constructed from a number of materials using a range of techniques. Suitable materials include ceramics with a low coefficient of thermal expansion which are readily extrudable. These include, but are not limited to, mullite, cordierite, alumina, and silica. Other materials include metals which may be extruded, welded, brazed, or diffusion bonded to make such structures. Using metals, it is sometimes useful to start with metal oxide powders, which are then bonded and reduced to the metallic state. Suitable metals include copper, aluminum, stainless steel, iron, titanium, and mixtures or alloys thereof. The dividing walls of the parallel plate reactor must be of sufficient strength to maintain the integrity of channels. The minimum wall thickness therefore depends upon material of construction. In the present study, 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. Consequently, the two channels will operate with a similar operating temperature. The inlets and outlets are arranged for a co-current flow of the reactants. In an alternative case, the inlets and outlets are arranged for a countercurrent flow of the reactants.

Adaptive meshing is a method of refining the mesh of a simulation based on the solution. An adaptive meshing scheme is used for the discretization of the differential equations. The computational mesh is initialized with 200 axial nodes, 200 radial nodes for the combustion channel and the wall

sections, and 200 transverse nodes for the reforming channel. This discretization translates into a total of about 72,000,000 nodes. This initial mesh is adapted and refined during a calculation to increase the accuracy of the solution in regions of high gradients. Specifically, additional nodes are introduced to refine the mesh using the tools built in the computational software so that the normalized gradients in temperature and species between adjacent cells are lower than 10 with a negative exponent of 6. Adaptation is performed if the solution has not converged after about 2,000,000 iterations or when the residuals are around 10 with a negative exponent of 6. This last threshold, while not optimized, is meant to strike a balance between cost and probability for convergence. Specifically, mesh refinement before achieving complete convergence reduces the computational effort, but a too early refinement, namely in a few iterations, may lead to refinement in wrong regions. After mesh refinement, a total of 20,000,000-60,000,000 nodes are used. Such an adaptive meshing strategy, starting with a relatively coarse initial mesh followed by refinement in regions of large gradients, achieves an adequate balance between accuracy and computational effort.

The relationships between the mixture components and the properties are typically complex and unknown. In these cases, it would be advantageous to develop predictive models that are capable of relating the mixture components to the properties so that the properties of new mixtures can be estimated. While there have been various attempts to develop predictive models for chemical mixtures [31, 32], none have gained widespread use. The fluid density is calculated using the ideal gas law. The individual properties of various gaseous species, such as thermal conductivity, are calculated using the kinetic theory of gases, whereas the specific heats are determined as a function of temperature using polynomial fits from the thermodynamic database available in Fluent. Mixture properties, such as specific heat and thermal conductivity, are calculated from pure component values based on the mass-fraction weighted mixing law. Binary species diffusivities are determined using the Chapman-Enskog equation and then are used to calculate the multicomponent mixture diffusivities. For the solid wall, a constant specific heat and an isotropic thermal conductivity are specified. Given that material conductivity varies with temperature and more importantly with the material chosen, computational fluid dynamics simulations are carried out over a wide range of conductivities.

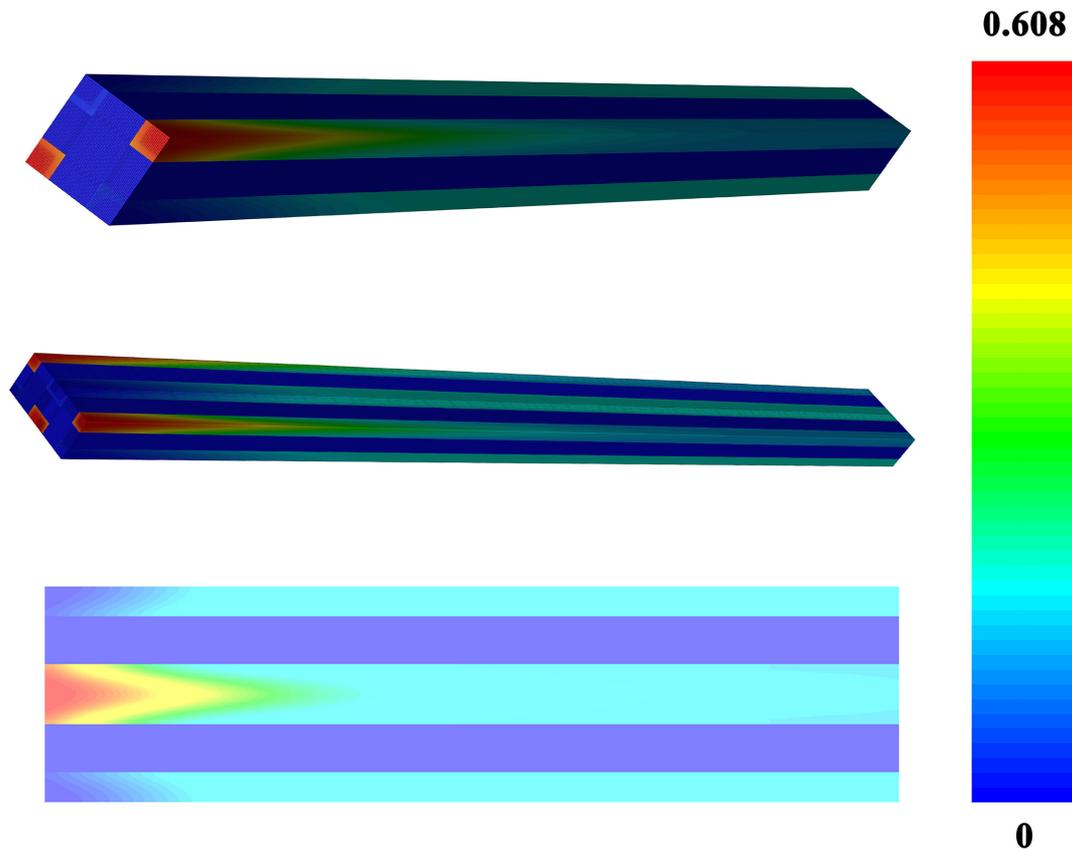
Boundary conditions are chosen and defined in order to represent the behavior of a real physical system that is being simulated. All particular solutions to differential equations rely on enforcing boundary conditions. The boundary conditions in a problem define how a solution to a differential equation behaves at the boundary of a system. Symmetry boundary condition is applied at the centerline of both channels, implying a zero normal velocity and zero normal gradients of all variables. No-slip boundary condition is applied at each wall-fluid interface. Danckwerts boundary conditions are implemented for the species and temperatures at the inlets to better mimic experimental conditions. Both gases enter the channels at room temperature with a uniform, flat flow velocity. The reactor exits are held at a fixed pressure of 8 atmospheres and the normal gradients of species and temperature, with respect to the direction of the flow, are set to zero. Overall, the device is adiabatic, and hence no heat losses occur through the side walls. Radiation losses play a secondary effect on the operation of the reactor and hence are negligible. Continuity in temperature and heat flux is applied at the fluid-solid interfaces. Neither heat-transfer nor mass-transfer correlations are employed since detailed transport within the solid and fluid phases is explicitly accounted for.

The full problem is solved via a segregated solver using an under-relaxation method. Convergence of the solution is monitored through the residuals of the governing equations and the square root of the sum of the entries of the vector of successive iterations of the solution. The solution is deemed converged when the residuals of the equations as well as the square root of the sum of the entries of the vector of successive iterations are less than around 10 with a negative exponent of 6. The coupling of the heat equation in the wall and the reacting flow equations makes the problem stiff due to the

disparity in thermal conductivity between the gases and the wall. Parallel processing employing a message passing interface is used to speed up the most demanding calculations. In most cases, multiple simulations are run simultaneously. Typical simulation times vary from about several hours for high wall thermal conductivity and lower flow rates to about a few days for low wall thermal conductivity and higher flow rates on a single processor depending on the stiffness of the problem. Natural parameter continuation is employed to study the effect of various operating parameters.

3. Results and discussion

The steam molar fraction contour plots in the combined parallel plate heat exchanger-reactor are illustrated in Figure 1 for hydrogen production by steam-methanol reforming. As to reliability and cost, conventional industrial catalytic steam reformers have at least two major disadvantages with respect to fuel cell use. First, because conventional industrial steam reformers operate at very high temperatures and pressure differentials, the reformer tubes that contain the catalyst must be constructed of rugged, thick-walled portions of expensive materials [33, 34]. Additionally, conventional industrial steam reformers also tend to be quite large, which again impacts material costs [35, 36]. Smaller steam reformers are designed for use in fuel cell system applications. Such steam reformers employ single-tube and multiple-tube designs. The smaller steam reformer designs have at least two major disadvantages in fuel cell system applications. First, current steam reformer designs tend to lack quick start-up capability. Lack of quick start-up capability can be problematic in some fuel cell applications, particularly where the reformer is expected to have a relatively short duty cycle [37, 38]. Some current steam reformer designs utilize a multi-element burner, but these burners do not adequately provide for quick start-up and lack the flexibility to efficiently operate on multiple fuels, including for example, natural gas, fuel cell anode exhaust or pressure swing absorption off-gas. For example, in a fuel cell power plant a steam reformer may be used to convert natural gas into a hydrogen-rich fuel stream, and it is desirable to have a burner capable of operating on natural gas and air, a reformat stream and air, and the fuel cell anode and cathode exhaust streams. Second, as part of fuel processing systems in fuel cell-related applications or merchant hydrogen production, for example, current steam reformer designs are less than cost-effective [39, 40]. For example, high-pressure burners and reformer vessels increase the parasitic load on the fuel processing system due to associated compressors, thereby decreasing efficiency and increasing cost and complexity. Conversely, in merchant hydrogen production applications, a low-pressure steam reformer vessel increases the fuel processing system parasitic load because of the associated process gas or syngas compressor that is required. In addition, current steam reformer designs tend to be relatively complex, resulting in increased manufacturing costs and reliability concerns. It is desirable for a steam reformer to be able to start up relatively quickly, and to be able to operate efficiently without adding undue complexity or cost. At the same time, it is desirable for a steam reformer to be low-cost, scalable, and compatible with a variety of fuel processing systems. 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. The fuel and oxidant manifolds and associated distribution tubes may use a shell-and-tube construction, for example, for low-cost manufacturing. The burner may comprise an array of distribution tubes, such as a hexagonal array, for example. The steam reformer of the present combined parallel plate heat exchanger-reactor also employs shell-and-tube construction that is amenable to low-cost, high-volume manufacturing. The reformer tubes may be arranged in an array having a high packing density, such as a hexagonal array, for example, in order to reduce the size and cost of the steam reformer.

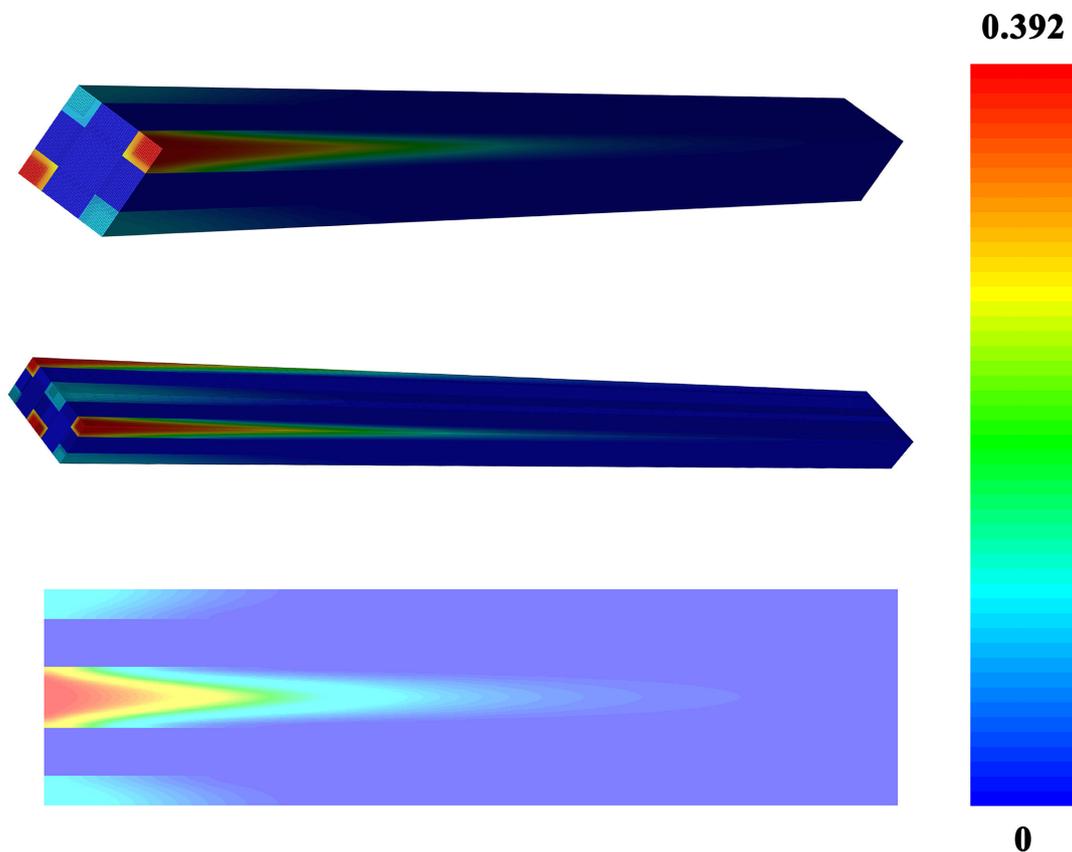


Steam molar fraction contour plots

Figure 1. Steam molar fraction contour plots in the combined parallel plate heat exchanger-reactor for hydrogen production by steam-methanol reforming.

The methanol molar fraction contour plots in the combined parallel plate heat exchanger-reactor are illustrated in Figure 2 for hydrogen production by steam-methanol reforming. The combined heat exchanger-reactor consists of sheets of triangularly corrugated material laminated together so as to form a series of roughly parallel passageways. In order for the exchanger to effectively function, the inlet area of the exchanger utilizes a highly complicated design feature characterized by detents and depressed crossflow passageways which effectively causes fluid flow blockage. Consequently, this heat exchanger possesses a high pressure drop. The method of construction recited in the patent and exemplified by the drawings utilize long metal welds or similar materials joining techniques resulting in a structure highly susceptible to internal rupture, leakage and uncontrolled fluid crossover. The combined heat exchanger-reactor consists of a monolithic honeycomb structure wherein the channels of the honeycomb are divided into separate groups, group one channels carrying one fluid with group two channels carrying another fluid which differs from the first either by composition, temperature, pressure, and direction of flow. The main design feature of the combined heat exchanger-reactor is that one group of channels extends outward from the honeycomb parallel to the direction of fluid flow in the honeycomb, each channel of the group one being in contact through common walls with channels in group two, each channel of group one being separated from other channels of group one by the intervening voids formed by the presence of the channels of group two. One or both of the open ends of the group one channels are manifolded so as to form a separation of entrances of the extended group one channels as compared to the group two channels and the entire system is incorporated into an outer mechanical shell so as to facilitate fluid flow through group one and group two channels, thereby permitting the entry or exit of fluid in group one channels while preventing entry of such same fluid into the group two channels and thereby permitting the independent passage of different fluids through the different channel systems. The common walls which exist between adjacent channels of the

different groups facilitate heat transfer from one channel group to another. The honeycomb structure, with its mutually supporting, double cantilevered inner walls, imparts strength to the overall system permitting the walls to be very thin and thereby being responsible for the low weight and rapid thermal response of the combined heat exchanger-reactor configuration. Alternatively, the manifolding of the group one channels may be designed so as to create numerous independent group one channel systems while still being completely surrounded by the group two channel system, thereby permitting numerous independent reactions to proceed simultaneously and permitting more than two independent fluid flows to be conducted under varying conditions within a single chemical reactor and heat exchanger system.



Methanol molar fraction contour plots

Figure 2. Methanol molar fraction contour plots in the combined parallel plate heat exchanger-reactor for hydrogen production by steam-methanol reforming.

The effect of wall thermal conductivity on the average Nusselt number are illustrated in Figure 3 in the exothermic process of the combined parallel plate heat exchanger-reactor. The channeled, manifolded honeycomb, also referred to as the combined heat exchanger-reactor, may be used without any catalytic material, coated on the walls, purely as a heat exchanger or homogeneous reactor-heat exchanger. By proper choice of materials of construction, the heat exchanger can be designed to transmit both sensible heat by conduction and radiation heat. In this way, many and different reactions can be performed using the manifolded honeycomb system. 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. The energy required or generated through the reaction is removed via a heat transfer fluid in the second channel. The reaction can be a catalytic process and the catalytically active material can be coated onto the monolith passage walls to minimize pressure drop. 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. In this case, the boundary layer will provide a significant resistance to heat transfer and will

severely limit the rate of the process. Also, for this arrangement to successfully supply or remove heat and maintain a near isothermal longitudinal profile, considerable heat transfer fluid velocities must be utilized for the combined parallel plate heat exchanger-reactor. 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.

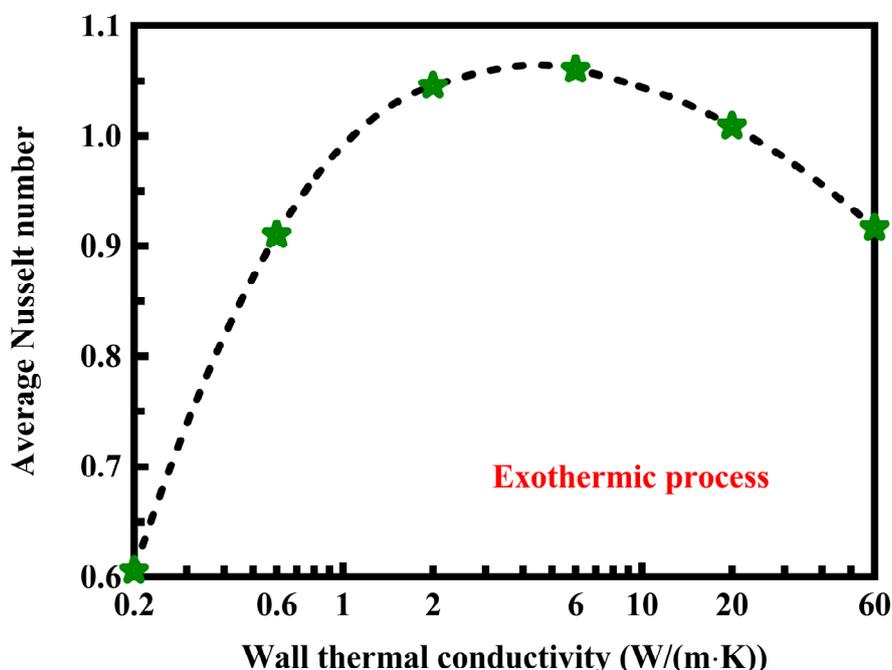


Figure 3. Effect of wall thermal conductivity on the average Nusselt number in the exothermic process of the combined parallel plate heat exchanger-reactor.

The effect of wall thermal conductivity on the average Nusselt number are illustrated in Figure 4 in the endothermic process of the combined parallel plate heat exchanger-reactor. The process may be carried out in a single autothermal reactor without the need to provide multiple sequential catalyst zones in the reactor. The catalytic partial oxidation reaction is exothermic in nature and the heat generated thereby is used to carry out the steam reforming reaction which is endothermic in nature. By having the catalytic partial oxidation layers in intimate contact with the steam reforming catalyst layers, the process heat can be more effectively managed in an adiabatic reactor, namely an autothermal reactor. By having the two catalyst layers in contact with one another, heat loss which otherwise occurs from the use of multiple autothermal reactors or an autothermal reactor containing multiple catalyst zones is significantly minimized. The process results in savings in reactor volume and monolith substrate costs as well as less pressure drop throughout the catalytic partial oxidation and steam reforming reactions. The process thereby provides more efficient utilization and uniform usage of the heat generated by the exothermic catalytic partial oxidation reaction, thus allowing the endothermic steam reforming reaction to be carried out at a somewhat higher temperature due to lower heat loss and concomitant higher reaction rate and under adiabatic conditions. The result is that the catalytic partial oxidation reaction temperature is somewhat lowered, estimated to be by about 60 degrees and concomitantly, the steam reforming reaction temperature is estimated to be raised by about 60 degrees, thereby improving catalyst life and resulting in higher steam reforming reaction rates. Moreover, by utilizing the catalytic partial oxidation and steam reforming catalysts as layers in contact with one another, adverse reactions such as the reaction of oxygen with rhodium and the reaction of oxygen with platinum, may be avoided. The overall process consists of first preheating the reactants to the required

temperature. It ensures good thermal management for the products leaving the reactor to be used to preheat the incoming reactants to a temperature close to the reaction temperature. The methanol, oxygen, and associated nitrogen flow through the inlets of the inlet manifold and into the reaction channels of the flow path. Heterogeneous oxidation occurs in the catalyst attached to the wall. As the stream flows down through the flow path, the conversion increases until the stream passes through the outlets. In the adjacent flow paths, preheated methanol and steam enter the second discrete set of channels through inlets, contact the catalyst coated onto the wall, and reaction occurs. 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.

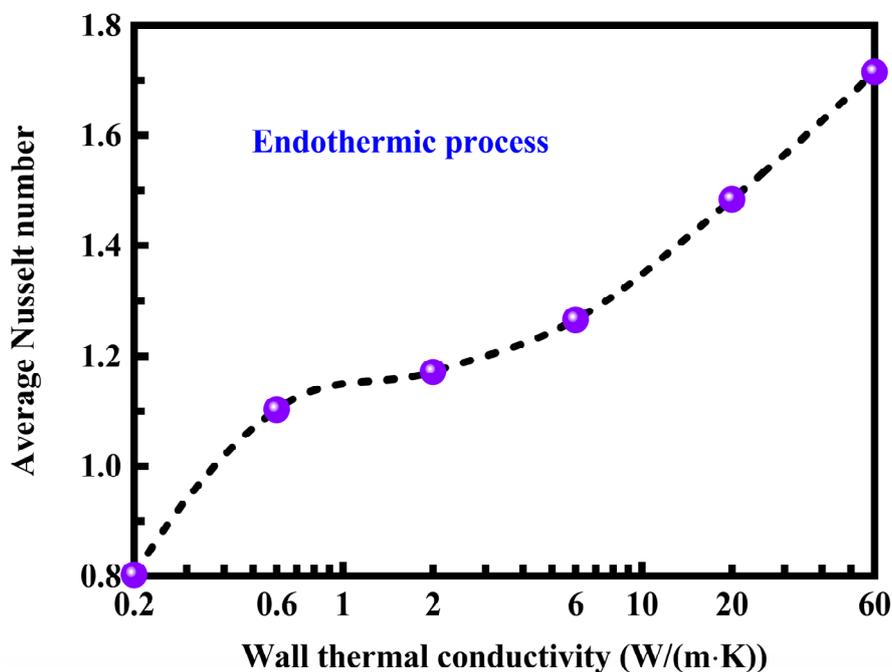


Figure 4. Effect of wall thermal conductivity on the average Nusselt number in the endothermic process of the combined parallel plate heat exchanger-reactor.

The temperature contour plots in the combined parallel plate heat exchanger-reactor are illustrated in Figure 5 for hydrogen production by steam-methanol reforming. 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. Utilizing high gas velocities typically results in reactors with large length to width ratios which again results in systems with high pressure drops. The smaller the characteristic dimension of the catalyst particle the higher is the utilization of the catalyst. This is sometimes expressed as a higher effectiveness factor. However, beds formed from small particles exhibit higher pressure drops than similar beds formed from larger particle. Consequently, 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 interior walls of the channels of either or both groups of channels may be coated with a catalytic material converting that group of channels into a catalytic reactor. Consequently, this reactor group is in intimate contact with the separately manifolded channels of the other group because of the common wall design and as a result, highly exothermic or endothermic reactions may be carried out under much greater temperature control than was possible in fixed bed or fluidized bed or countercurrent flow reactors. This greater temperature control can result in much greater product selectivity and yield for a wide variety of chemical reactions. Now heat can be removed or added to the reactor as required the temperature being regulated merely by careful control of the flow of reactants through the reactor channels and control of coolant or heat source flow through the coolant channels. The temperature control possible with this system is extremely efficient because all the catalytic material in the reactor channels, where heat is either absorbed or liberated due to chemical reactions taking place, is on the surface of the walls that can transmit heat through the walls directly to the thermal control channels. Most of the heat liberated or absorbed in the chemical reaction is conducted through the walls which support the catalyst and thereby eliminating the necessity for heat conduction through the gas phase which is a much less efficient way to cool a catalytic particle. In addition, this configuration allows not only most of the heat to be conducted through solid walls but also allows all the walls on which the catalysts reside to have all common walls with the coolant channels. Consequently, one has an extremely uniform and precise method of controlling the catalyst temperature because no two catalytic surfaces share a common wall, Also, it is possible to fabricate a structure with very thin walls and this too contributes to greater efficiency and ease of temperature control. In traditional systems, the catalyst is on particles randomly packed into a reactor tube. Exothermic reactions occurring generate heat at the catalytic particles even in the center of the tube. This heat must migrate through the gas phase and through the particles in the reaction tube to the wall of the tube and only then pass through the wall to be dissipated in a coolant. This passage of heat through the reactor tube gas and particle phase before finally contacting the wall is responsible for the difficulty encountered in controlling the temperature in the reactors traditionally used.

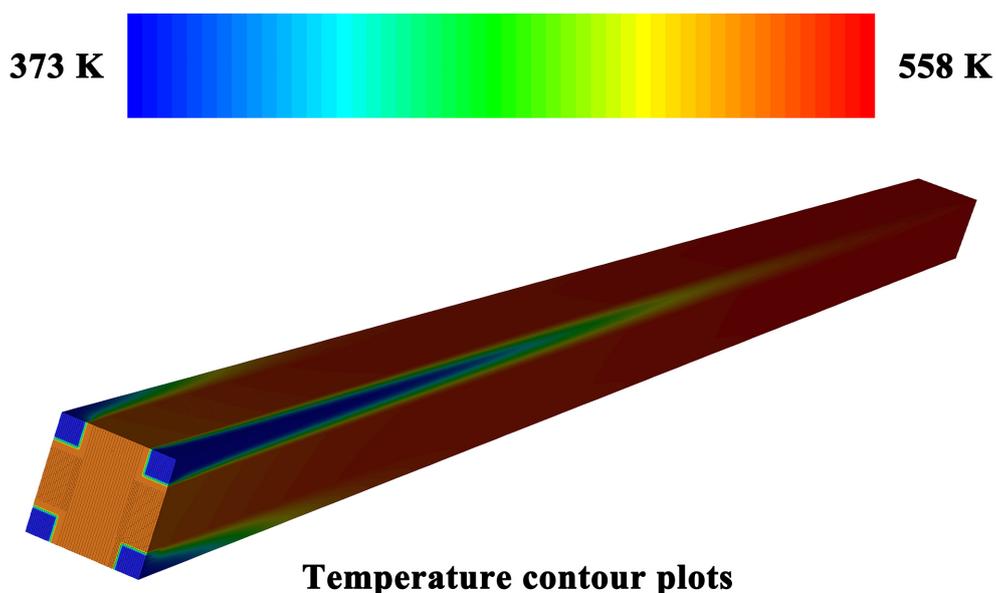


Figure 5. Temperature contour plots in the combined parallel plate heat exchanger-reactor for hydrogen production by steam-methanol reforming.

The hydrogen molar fraction contour plots in the combined parallel plate heat exchanger-reactor are illustrated in Figure 6 for hydrogen production by steam-methanol reforming. The autothermal

parallel plate heat exchanger-reactor contains the layered catalyst member. The stream is contacted with the layered catalyst member at a temperature sufficient to initiate and sustain both catalytic partial oxidation and steam reforming. The amounts of the hydrocarbon feed, water and air in the inlet stream introduced into the autothermal reactor are typically controlled to maintain a water to carbon ratio of at least about 0.3:1.0 and an oxygen to carbon ratio of from about 0.2 to 0.7:1.0. In general, adiabatic conditions will prevail in the autothermal reactor due to the fact that the partial oxidation reaction is exothermic in nature and the heat generated in the course of such a reaction is usually sufficient to initiate and sustain the steam reforming reaction which is endothermic in nature. Accordingly, by proper selection of the preheat temperature, reactor design, and volumetric hourly rate, both reactions may be carried out within the reactor while the reactor temperature is kept within the range of about 200 to about 280 °C without the need to supply external heat or cooling to the reactor. However, it is necessary to supply heat or cooling to the reactor as desired in order to continuously maintain both reactions at high reaction rates. In the second step of the process, the hydrocarbon feed is catalytically partially oxidized by contact with the catalytic partial oxidation catalyst layers. The resultant effluent will comprise hydrogen and carbon oxides. In the third step of the process, hydrocarbons remaining in the feed which are not catalytically partially oxidized are steam reformed by contact with the steam reforming catalyst layers, thereby producing a hydrogen-rich effluent. Preferably, the hydrogen-rich gas effluent from the third step of the process is subjected to a further water-gas shift reaction. In the course of the steam reforming reaction, the hydrocarbon reacts with water to yield a product gas containing primarily hydrogen and carbon monoxide, plus any unreacted hydrocarbons. In order to reduce the carbon monoxide level and increase the hydrogen gas level, the effluent may be passed into a converter in which the effluent is contacted with a catalyst such that the carbon monoxide will at with water to yield carbon dioxide and firer amounts of hydrogen.

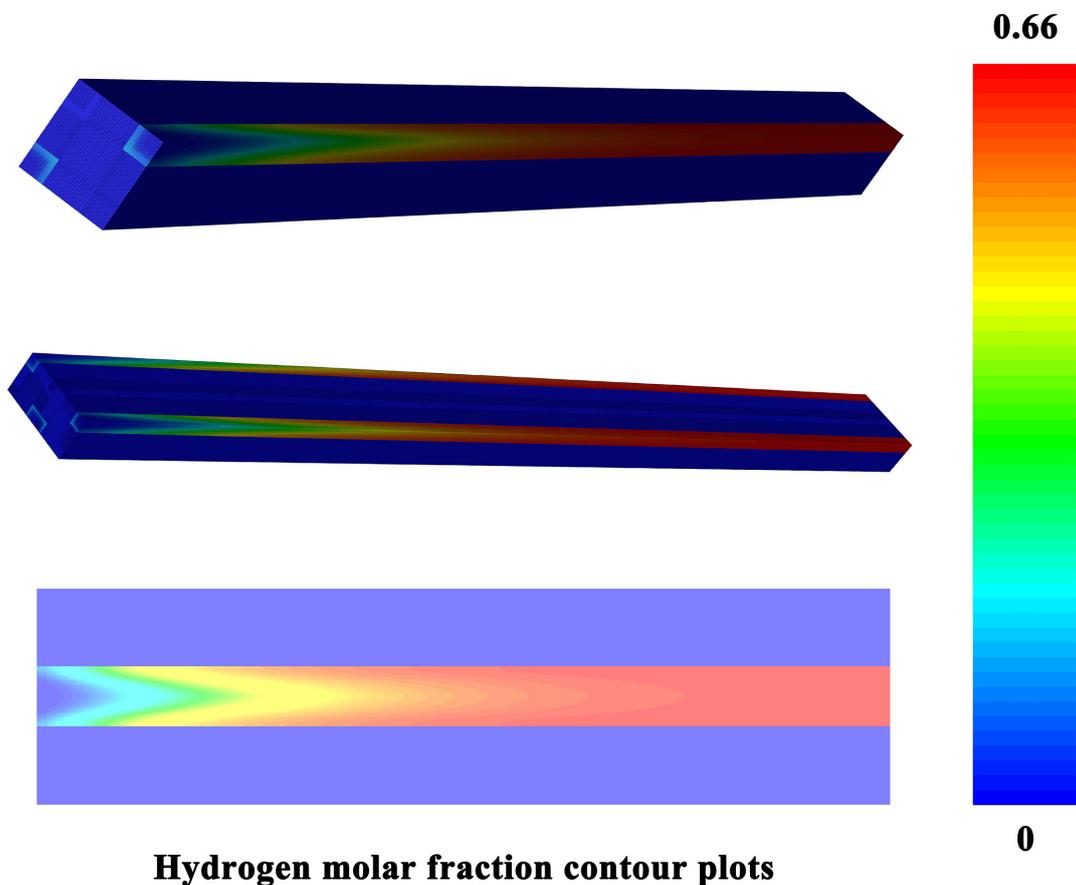


Figure 6. Hydrogen molar fraction contour plots in the combined parallel plate heat exchanger-reactor for hydrogen production by steam-methanol reforming.

The Sherwood number profiles in the exothermic process are presented in Figure 7 along the length of the combined parallel plate heat exchanger-reactor. The combined parallel plate heat exchanger-reactor system can be used for a number of reactions as a wide range of process conditions are possible. It is inevitable that the catalyst coating will eventually deactivate to the point where economics drive for its replacement. It is sometimes possible to extend a catalyst life and reclaim some activity by techniques such as hydrogen treatment or methods to remove carbon buildup. These techniques can be readily applied to the combined parallel plate heat exchanger-reactor. The combined parallel plate heat exchanger-reactor also allows the body to be removed and monolith replacement performed. This is simply achieved by removing the relevant inlet manifold and outlet manifold and removing any monolith supports or containment structure. A new monolith can be inserted and reverse procedure applied. If the endothermic catalyst requires high temperature hydrogen activation, the heat can be supplied via the exothermic channels. The spent monolith can be recycled after recovery of any of the precious metal components of the catalyst. 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 to 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 methanol. 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. 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. An advantage of the reactor system 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, and the stream remaining after hydrogen removal from a membrane gas shift reactor. 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. When using large channels, it is possible that the reaction will become diffusion limited, such that the rate of reaction is dictated by the rate at which unreacted molecules can diffuse from the center of the channel into the catalyst matrix. In this case, it is possible to add flow disturbance elements in the channel or emanating from the wall. These elements will produce a degree of convective mixing by forming local flow disturbances in an otherwise laminar environment. If a heat transfer fluid is used to remove the heat of reaction from a reaction occurring in any adjacent channel, then these flow disturbance elements would provide a useful and low pressure drop method of enhancing thermal performance.

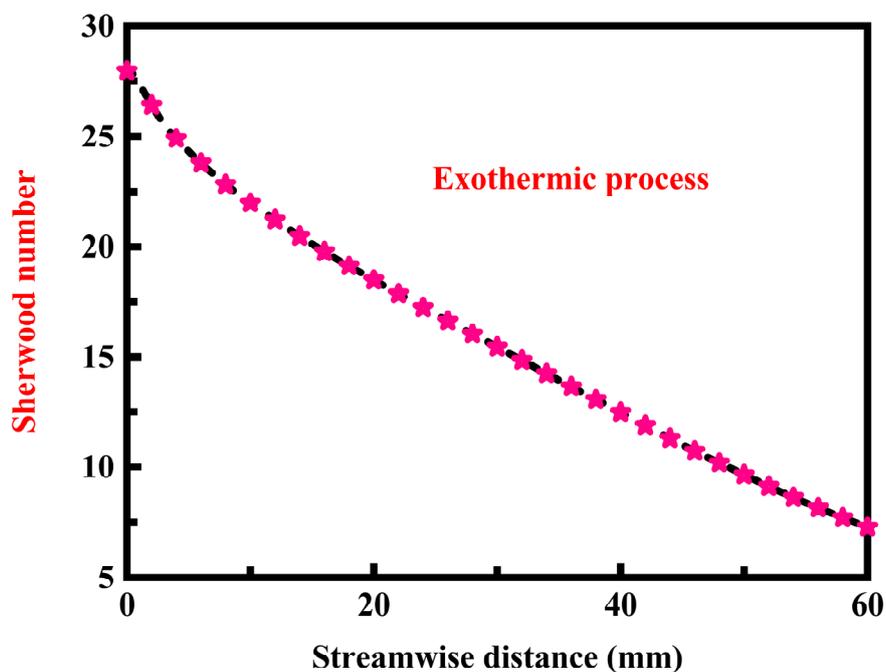


Figure 7. Sherwood number profiles in the exothermic process along the length of the combined parallel plate heat exchanger-reactor.

The Sherwood number profiles in the endothermic process are presented in Figure 8 along the length of the combined parallel plate heat exchanger-reactor. The channels of the group one channel system which have common walls with group two systems but not with other group one channels can be prepared so as to have permeable walls, these group one walls being coated with catalytic material on the inner surfaces for their entire length, part of their length or any combination of lengths desired. Different reactants each composed of one or more components are fed into different channels of the group one channels and there are converted, either catalytically or thermally, into products, then these products permeate through the walls into the channel system wherein they react further with each other resulting in the finally desired product. In this way, short-lived unstable intermediates can be efficiently introduced to each other without the need for going through difficult intermediate isolation steps. In addition, such a system with permeable walls can be used to introduce different reactants in different group one channels to each other in the group two channels in a highly controlled manner such that the different reactant in the different group one channels are not comingled in high concentrations before the desired reaction is allowed to take place between the different reactants. The honeycomb design because of its use of mutually supporting wall design, permits the preparation of very thin walls which would crack due to normally occurring stresses if not mutually supported, namely if exposed or structurally independent. The thin walls and small internal diameters of the channels result in an extremely difficult system for carrying out reactions and transferring heat by giving rise to a high ratio of wall surface area, also referred to a geometric surface area, to reactor volume. The channel walls may be of from 0.5 to 5.0 millimeters in thickness. The channels may be of any length from 10 millimeters up to several meters, for example, 10 meters; however, length intermediate between these extremes is preferred for reasons of handling and also to insure sufficient length for any contemplated reaction or use. Lengths ranging from 2-20 centimeters, preferably 4-8 centimeters, most preferably 6 centimeters are contemplated [41, 42]. The channels should have an internal diameter, calculated by using the hydraulic diameter as a measure [43, 44]. This is to ensure a channel diameter of sufficient dimensions so that heat will have the shortest path possible to migrate to the walls, thereupon to diffuse through the walls into neighboring channels for dissipation and to ensure wall surface area to support sufficient catalyst [45, 46]. The channels of the different systems can be arranged in any pattern desired

so long as every channel wall of the group one channel system, also referred to as the reacting channels, is in contact with at least one channel wall of the other channel system, also referred to as the coolant channels [47, 48]. This can be accomplished for example, by surrounding each channel of group one channels with channels of system two. The honeycomb may have any overall diameter so long as this overall diameter is at least 6 times the internal channel diameter as measured by the hydraulic diameter, namely ensuring that every wall of the group one channels is contacted by channels of group two. The channels of the honeycomb may be coated with catalytic material, such as those materials selected from the group consisting of Group VIII, Group VB, Group VIB, Group VIIB, Group IB, metals and oxides from the previously mentioned groups and mixtures thereof.

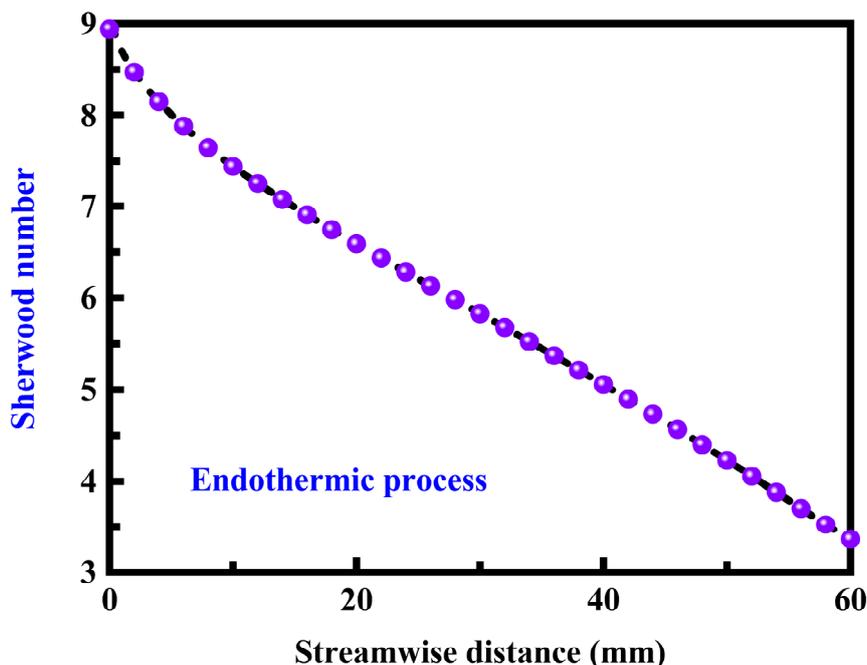


Figure 8. Sherwood number profiles in the endothermic process along the length of the combined parallel plate heat exchanger-reactor.

4. Conclusions

The steady-state continuity, momentum, energy, and species conservation equations are solved in the fluid phase and the heat equation is solved in the solid phase using a finite volume approach. An adaptive meshing scheme is used for the discretization of the differential equations. Computational fluid dynamics simulations are carried out over a wide range of material conductivities. Continuity in temperature and heat flux is applied at the fluid-solid interfaces. Neither heat-transfer nor mass-transfer correlations are employed. Parallel processing employing a message passing interface is used to speed up the most demanding calculations. The major conclusions are summarized as follows:

- The arrangement leads to improved heat transfer and therefore chemical conversion.
- The honeycomb structure imparts strength to the overall system permitting the walls to be very thin and thereby being responsible for the low weight and rapid thermal response of the combined parallel plate heat exchanger-reactor configuration.
- The heat transfer from the process catalyst to the dividing wall is 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.
- The process provides more efficient utilization and uniform usage of the heat generated by the exothermic oxidation reaction, thus allowing the endothermic steam reforming reaction to be carried out at a somewhat higher temperature.

- The temperature control possible with this system is extremely efficient because all the catalytic material in the reactor channels is on the surface of the walls that can transmit heat through the walls directly to the thermal control channels.
- Adiabatic conditions prevail in the autothermal reactor due to the fact that the oxidation reaction is exothermic in nature and the heat generated in the course of such a reaction is usually sufficient to initiate and sustain the steam reforming reaction which is endothermic in nature.
- The thickness of the catalyst coating depends upon the process proceeding within the catalyst matrix, and the process products are highly dependent upon the catalyst thickness.
- The thin walls and small internal diameters of the channels result in an extremely difficult system for carrying out reactions and transferring heat by giving rise to a high ratio of wall surface area.

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