Thermal chemical reaction characteristics of autothermal fixed bed reactors with structured catalysts and different surface features

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Abstract

Conventional methods of producing a synthesis gas are expensive and complex installations. In order to overcome the complexity and expense of such installations, it is proposed to generate the synthesis gas within autothermal fixed bed reactors that utilize structured catalysts and different surface features to generate the heat necessary to support endothermic heating requirements of the steam reforming reactions. The present study is focused primarily upon the thermal chemical reaction characteristics of autothermal fixed-bed reactors with structured catalysts and different surface features. The heat capacity, thermal conductivity, and viscosity of the mixture are calculated as a mass-weighted average of the values for each constituent. In addition, the material properties of each individual species are functions of the local temperature. When solving the species mass transport equations, binary mass diffusion coefficients are used directly. Only isotropic catalyst structures are considered and the permeability and inertial resistance factor are held constant. The effective thermal conductivity of the catalyst structure system including the porous structure and intervening gas is calculated based upon the porosity of the porous medium, the fluid phase thermal conductivity, and the porous medium effective thermal conductivity as measured in air at ambient conditions. The present study aims to explore how to effectively generate the synthesis gas within autothermal fixed bed reactors that utilize structured catalysts and different surface features. Particular emphasis is placed upon the heat and mass transport phenomena involved in autothermal fixed bed steam reforming reactors. The results indicate that for catalytic thermal chemical reactions, both kinetic impediments are substantially reduced permitting realization of theoretical or near theoretical reaction kinetics. The heat transfer chamber is in thermal contact with the reaction chamber volume, the heat transfer chamber transferring heat at the enhanced heat transfer rate across the wall between the heat transfer chamber and the reaction chamber, thereby obtaining the enhanced production rate per reaction chamber volume for the thermal chemical reaction. Structured catalyst configurations result in high rates of heat transport from the oxidation side to the reforming side. Typically, combustion takes place at low or near-atmospheric pressure, although high pressure combustion is widely practiced. The heat that is generated on the combustion side is quickly transferred on the reforming side. The heat integrated reforming reactor offers several advantages over conventional flame-based reforming reactors. The incorporation of a simultaneous endothermic reaction to provide an improved heat sink may enable a typical heat flux of roughly an order of magnitude above the convective cooling heat flux. The wall can be constructed from any material, but materials that offer low resistance to heat transfer such as metals and metallic alloys are preferred. In this configuration, heat is generated by combustion in the catalytic chamber and is transported very easily and efficiently though the wall to the reforming chamber where the heat demanding reforming reactions take place. The presence of a catalyst and lower temperatures permit significantly higher space velocities to be used compared to flame-based reformers.

Keywords: Hydrocarbons; Reactors; Structures; Properties; Reforming; Combustion

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1. Introduction

Synthesis gas, or syngas, is a mixture of gases prepared as feedstock for a chemical reaction; for example, carbon monoxide and hydrogen to make hydrocarbons or organic chemicals, or hydrogen and nitrogen to make ammonia [1, 2]. Syngas may be produced for use with a Fischer-Tropsch process [3, 4]. The synthetic production of hydrocarbons by the catalytic reaction of carbon monoxide and hydrogen is known and is generally referred to as the Fischer-Tropsch reaction [5, 6]. Numerous catalysts have been used in carrying out the reaction, and at relatively low to medium pressure and temperatures, both saturated and unsaturated hydrocarbons can be produced [7, 8]. The synthesis reaction is very exothermic and temperature sensitive whereby temperature control is required to maintain a desired hydrocarbon product selectivity. Two basic methods have been employed for producing the synthesis gas utilized as feedstock in the Fischer-Tropsch

reaction. The two methods are steam reforming, wherein one or more light hydrocarbons such as methane or ethane are reacted with steam over a catalyst to form carbon monoxide and hydrogen [9, 10], and partial oxidation, wherein one or more light hydrocarbons are combusted or reacted sub-stoichiometrically to produce synthesis gas [11, 12]. The steam reforming reaction is endothermic and a catalyst containing nickel is often utilized [9, 10]. The hydrogen to carbon monoxide ratio of the synthesis gas produced by steam reforming of methane is approximately 3:1. Partial oxidation is the non-catalytic, sub-stoichiometric combustion of light hydrocarbons such as methane or ethane to produce the synthesis gas [11, 12]. The partial oxidation reaction is typically carried out using high purity oxygen. High purity oxygen can be quite expensive. The hydrogen to carbon monoxide ratio of synthesis gas produced by the partial oxidation of methane is approximately 2:1. In some situations, these approaches may be combined.

A combination of partial oxidation and steam reforming, known as autothermal reforming [13, 14], wherein air is used as a source of oxygen for the partial oxidation reaction has also been used for producing synthesis gas heretofore [13, 14]. In low pressure hydrocarbon synthesis processes, autothermal reforming with air is utilized to produce synthesis gas [15, 16]. Autothermal reforming is a combination of partial oxidation and steam reforming where the exothermic heat of the partial oxidation supplies the necessary heat for the endothermic steam reforming reaction [15, 16]. The autothermal reforming process can be carried out in a relatively inexpensive refractory lined carbon steel vessel whereby low cost is typically involved [17, 18]. The autothermal process results in a lower hydrogen to carbon monoxide ratio in the synthesis gas than does steam reforming alone. That is the steam reforming reaction with methane results in a ratio of about 3:1 while the partial oxidation of methane results in a ratio of about 2:1. The optimum ratio for the hydrocarbon synthesis reaction carried out at low or medium pressure over a cobalt catalyst is 2:1. When the feed to the autothermal reforming process is a mixture of light hydrocarbons such as a natural gas stream, some form of additional control is desired to maintain the ratio of hydrogen to carbon monoxide in the synthesis gas at the optimum ratio of about 2:1. In producing a product from the synthesis unit, a residue gas is frequently produced [19, 20]. For some processes, the use of this gas to create energy has been suggested [19, 20]. Systems that have utilized the residue gas have required numerous additional components and steps to do so [21, 22]. In producing a synthesis gas for a chemical process, it is desirable to produce the synthesis gas as efficiently as possible [21, 22]. The ability to develop a process with low capital expense may be an imperative to development of large-scale systems.

Synthesis gas containing hydrogen and carbon monoxide is produced for a variety of industrial applications, for example, the production of hydrogen, chemicals and synthetic fuel production. Conventionally, the synthesis gas is produced in a fired reformer in which natural gas and steam is reformed to the synthesis gas in catalyst filled reformer tubes [23, 24]. The endothermic heating requirements for steam methane reforming reactions occurring within the reformer tubes are provided by burners firing into the furnace that are fueled by part of the natural gas. In order to increase the hydrogen content of the synthesis gas, the synthesis gas can be subjected to water-gas shift reactions to react residual steam in the synthesis gas with the carbon monoxide [23, 24]. Such steam methane reformers are optimized for hydrogen production and typically are fed with a reactant stream containing hydrocarbons and steam at a steam-to-carbon ratio of 1.5 to 3.5, depending on the quantity of carbon dioxide in the reactant stream, to thereby produce the synthesis gas at a hydrogen to carbon monoxide ratio of 3 or higher [25, 26]. This is not optimum for the production of synthesis gas for synthetic fuel production where a hydrogen to carbon monoxide ratio of 1.8 to 2.0 within the synthesis gas is more desirable [27, 28]. Consequently, where synthetic fuel production is a desired use of the synthesis gas, an autothermal reformer is typically used in which the steam-to-carbon ratio of the reactant is typically between 0.5 and 0.6. In such a reactor, oxygen is used to combust part of the feed to create additional steam and heat to reform the hydrocarbons contained in the feed to the synthesis gas. For a large-scale installation, an air separation plant may be required to supply the oxygen.

Conventional methods of producing a synthesis gas are expensive and complex installations. In order to overcome the complexity and expense of such installations, it has been proposed to generate the synthesis gas within reactors that utilize an oxygen transport membrane to supply oxygen and thereby generate the heat necessary to support endothermic heating requirements of the steam methane reforming reactions [29,

30]. A typical oxygen transport membrane has a dense layer that, while being impervious to air or other oxygen containing gas, will transport oxygen ions when subjected to an elevated operational temperature and a difference in oxygen partial pressure across the membrane. This difference in oxygen partial pressure can be produced by compressing the supplied air or from combustion of hydrocarbons fed to a permeate side of the membrane and supported by permeated oxygen or a combination of the two methods [31, 32]. For example, a reactant gas feed is combined with steam. The reactant gas feed can be natural gas or other hydrocarbon containing gas. This combined feed stream is then heated and introduced into an adiabatic pre-reformer to produce an intermediate stream that contains carbon monoxide, carbon dioxide, steam, hydrogen, and methane. The intermediate stream can be combined with carbon dioxide and steam. The resulting reactant stream is then introduced with air into reactant and oxidant sides, respectively, of an oxygen transport membrane reformer [33, 34]. The oxygen transport membrane reformer has an oxygen transport membrane separating the reactant and oxidant sides of the reformer. The reactant gas reacts with oxygen that has permeated through the oxygen transport membrane to produce a synthesis gas. Preferably a reforming catalyst is applied to at least a portion of the reactant side surface of oxygen transport membrane or packed into the reactant side to promote the reforming reactions [35, 36]. In an integrated system, an oxygen transport membrane reformer is connected to a downstream reactor such as a Fischer-Tropsch reactor to produce a liquid product. The presence of the pre-reforming stage will prevent the breakdown of higher order hydrocarbons present in the reactant feed stream and the resulting carbon deposition that would otherwise occur had the higher order hydrocarbons been fed directly to the reactor [37, 38]. Such carbon deposition will degrade reforming catalyst used in connection with the oxygen transport membrane reactor.

Heat is supplied to an endothermic reforming reaction inside a reaction passage separated from an air passage by an oxygen transport membrane [39, 40]. A reactant gas, for example, methane flows through the reaction passage is combusted with permeated oxygen to provide the heat to support the reforming reaction [39, 40]. Further heat is supplied to the reforming reaction by either combusting a fuel with retentate or a fuel with a second permeate produced by another oxygen transport membrane or within a combustion passage. Alternatively, an oxygen transport membrane can be situated between an air passage and a combustion passage and a barrier is located between the combustion passage and the reaction passage [41, 42]. In such case, the oxygen transport membrane supplies oxygen permeated to support combustion of a fuel in the combustion passage and thereby generate heat that is transferred to the reaction passage [41, 42]. A staged reactor system has a sequential arrangement of reactor stages to produce a synthesis gas product. Each of the reactor stages has an oxidant side separated from a reactant side by an oxygen transport membrane [43, 44]. The reactant sides are linked together so that a reactant stream containing methane and steam is introduced into the system and sequentially reacted with oxygen permeating through the membrane to produce a synthesis gas product for use in a downstream reactor [45, 46]. Catalyst beds can be located within the reactant side of the reactor stages or can be positioned between the reactor stages.

Both steam and a reactant gas from a downstream process utilizing the synthesis gas can be introduced into the feed between stages [47, 48]. The presence of the multiple stages allows the temperature within each of the reaction stages to be controlled to prevent the oxygen transport membrane from being degraded and to control the deposition of soot throughout the membrane system [47, 48]. Staged reactor systems can employ oxygen transport membranes in which the air or other oxygen containing stream fed to each of the stages can be controlled to control the temperatures and conversation that can be obtained in producing a synthesis gas. The problem with all of these reactor systems is that an oxygen transport membrane will operate at high temperatures of about 900 °C to about 1100 °C. Where hydrocarbons such as methane and also higher order hydrocarbons are subjected to such temperatures, carbon formation will occur [49, 50]. Additionally, where oxygen is supplied by an oxygen transport membrane, the area of the membrane is distributed throughout the reactor [51, 52]. As such, the oxygen is not generally available at the entrance to the reactor [53, 54]. This also results in an aggravated carbon formation problem at the entrance that is especially the case at low steam-to-carbon ratios. In any case, a reactant containing methane and steam will produce a relatively low oxygen flux across the membrane resulting in the membrane area required for such a reactor to be larger and it will add to the expense and complexity in such a reactor [55, 56]. Additionally, a steam methane reforming catalyst must be periodically replaced. In these reactor designs where the catalyst is employed adjacent to the oxygen transport membrane, catalyst replacement becomes an expensive if not impractical exercise [57, 58]. It is therefore necessary to provide a method and apparatus in which the oxygen transport membrane is not directly used to react the steam and methane components of the reactant feed, but rather, to generate the heat required to support endothermic heating requirements of steam methane reforming reactions within a separate reactor.

Conventional methods of producing a synthesis gas are expensive and complex installations. In order to overcome the complexity and expense of such installations, it is proposed to generate the synthesis gas within autothermal fixed bed reactors that utilize structured catalysts and different surface features to generate the heat necessary to support endothermic heating requirements of the steam reforming reactions. The present study is focused primarily upon the thermal chemical reaction characteristics of autothermal fixed bed reactors with structured catalysts and different surface features. The heat capacity, thermal conductivity, and viscosity of the mixture are calculated as a mass-weighted average of the values for each constituent. In addition, the material properties of each individual species are functions of the local temperature. When solving the species mass transport equations, binary mass diffusion coefficients are used directly. Only isotropic catalyst structures are considered and the permeability and inertial resistance factor are held constant. The effective thermal conductivity of the catalyst structure system including the porous structure and intervening gas is calculated based upon the porosity of the porous medium, the fluid phase thermal conductivity, and the porous medium effective thermal conductivity as measured in air at ambient conditions. The present study aims to explore how to effectively generate the synthesis gas within autothermal fixed bed reactors that utilize structured catalysts and different surface features. Particular emphasis is placed upon the heat and mass transport phenomena involved in autothermal fixed bed steam reforming reactors.

2. Methods

The methanol steam reforming reaction in a microchannel reactor is the focus of this study. The water gas shift reaction also is included as it occurs on the steam reforming catalyst. In the endothermic microchannel steam reforming reactor, heat is provided by combustion in adjacent microchannels. In the present study, the performance of the steam reforming channel is evaluated and a constant temperature thermal boundary condition is imposed on the wall to simulate the adjacent combustion. These simulations do not consider the effect of external heat transfer resistance outside of the reforming channel. This assumption will become more significant as the reaction is further intensified. Pressure is set at 8 bar at the outlet, unless specified otherwise. Constant temperature is imposed on the channel walls. For all the cases considered, the wall temperature is the same as the feed temperature. The catalyst structure is modeled as porous media where chemical reactions take place. The complex interaction between mass and heat transfer, as well as chemical reactions within the catalyst structure, lead to internal catalyst temperature and species concentration distributions. An entrance length equal to 20 times the open channel gap is imposed upstream of the catalyst to avoid an entrance region effect in comparing reactor performance under different variables. For commercial microchannel reactors of interest, a heat exchanger is upstream of the reactor section for preheat and thus the flow field is fully developed and laminar. The higher grid line density within the catalyst structure reflects the understanding that temperature and species concentrations gradients inside the catalyst structure will be greater than those in the flow-by gap. Six meshes of the same structure are built with varying level of refinement to verify the mesh independency of the computational fluid dynamics solution.

The mixture of interest is composed of methanol, steam, hydrogen, carbon monoxide, and carbon dioxide. Ideal gas is assumed in calculating the density of the mixture. The heat capacity, thermal conductivity, and viscosity of the mixture are calculated as a mass-weighted average of the values for each constituent. In addition, the material properties of each individual species are assumed to be, in general, functions of the local temperature. The exception to this is the mass diffusivity of each individual species. For part of the modeling cases, when the reactor wall temperature and the feed inlet temperature are specified at 260 °C, the mass diffusivity of each species is assumed to be independent of the temperature. When solving the species mass transport equations, binary mass diffusion coefficients are used directly. In other words, a dilute system is assumed and considered reasonable as excess steam is present. For flow simulation in the catalyst structure, Darcy's law is used. The following parameters are provided to the computational fluid dynamics code: permeability and inertial resistance factor. These parameters may be defined differently based upon different coordinate directions. In the present study, only isotropic catalyst structures are considered and the permeability and inertial resistance factor are held constant. The effective thermal conductivity of the catalyst structure system including the porous structure and intervening gas is calculated based upon the porosity of the porous medium, the fluid phase thermal conductivity, and the porous medium effective thermal conductivity as measured in air at ambient conditions.

When molecules diffuse through a porous material, their effective diffusivity through the porous network is reduced relative to their diffusivity when they diffuse in an open volume. A high porosity factor value favors diffusion. However, it is not desirable to greatly increase the porosity, since this porosity does not participate in the adsorption capacity. In general, both the bulk and Knudsen diffusion are assumed to contribute to the mass transport rate within the pore volume. For equimolar binary counter-diffusion, the effective diffusivity is calculated based upon the effective diffusivity within the porous medium, the bulk diffusivity in the pore, and the Knudsen diffusivity. The bulk diffusivity of each species in the pores of the porous medium is affected by the connection of the pores of different sizes. A simple parallel pore model yields for the effective bulk diffusivity based upon the molecular mass diffusivity of species and the tortuosity factor of the porous medium. The tortuosity factor is a property of the adsorbent and does not depend on the diffusing molecule. This factor takes into account the diffusion length when the molecules diffuse through a three-dimensional porous space constituted of pores that are interconnected via restrictions, relative to rectilinear cylindrical pores with the same mean pore diameter. The catalyst support structure of interest in this study possesses larger than average pore size compared to a catalyst pellet. The contribution from the Knudsen diffusion is calculated to be relatively small. The tortuosity factor is not known for the felt-like porous catalyst support structure, and as such this parameter is allowed to vary in the simulation matrix.

Limited production rates may result from longer residence time which is typically seconds to minutes in conventional thermal chemical reaction vessels [59, 60]. As it is conventionally defined, residence time is equal to the volume of the reaction zone divided by the inlet volumetric flow rate of reactants at the reaction system's temperature and pressure. The reaction zone is the total volume of the catalyst and surrounding area through which reactants and products flow [61, 62]. In the water gas shift reaction, carbon monoxide and water are converted to carbon dioxide and hydrogen. Conventionally, this reaction suffers from multiplesecond residence times when carried out in fixed bed reactors [63, 64]. Theoretical kinetics suggests that residence times on the order of milliseconds could, theoretically, be obtained [65, 66]. There are two kinetic retarding aspects to conventional reactors. The first is a diffusion limitation as reactants diffuse into and out of a catalyst-bearing porous pellet and the second is a heat transfer limitation which is a combination of heat transfer parameters of catalyst supports and overall reactor geometry. Because the water gas shift reaction is critical to a multi-reactor fuel processing system that supports distributed energy production through the use of a fuel cell, there is a need for a smaller, faster water gas shift reactor [67, 68]. The term microchannel reactor may refer to an apparatus comprising a plurality of process microchannels wherein a process may be conducted. The process may be a steam reforming reaction process. The process microchannels may be operated in parallel. The microchannel reactor may include a header or manifold assembly for providing for the flow of fluid into the process microchannels, and a footer or manifold assembly providing for the flow of fluid out of the process microchannels. The microchannel reactor may comprise one or more heat exchange channels adjacent to and in thermal contact with the process microchannels. The heat exchange channels provide heating and cooling for the fluids in the process microchannels. The heat exchange channels may be combustion channels. The heat exchange channels and combustion channels may be microchannels. The term volume with respect to volume within a process microchannel may include all volume in the process microchannel a process fluid may flow through or flow by. This volume may include volume within surface features that may be positioned in the process microchannel and adapted for the flow of fluid in a flowthrough manner or in a flow-by manner. The term thermal contact may refer to two bodies, for example, two channels, that may or may not be in physical contact with each other or adjacent to each other but still exchange heat with each other. One body in thermal contact with another body may heat or cool the other body.

3. Results and discussion

The hydrogen mole fraction contour plots in the autothermal fixed bed reactor are illustrated in Figure 1 with structured catalysts and square surface features. The term surface feature may refer to a depression in a channel wall and a projection from a channel wall that disrupts flow within the channel. The surface features may have a depth, a width, and for non-circular surface features a length. The surface features may be used to disrupt flow and create advective flow at an angle to the bulk flow direction. Each of the microchannels may have a cross-section having any shape, for example, a square, rectangle, circle, and semi-circle. These features cooperate with the reaction kinetics in terms of transferring heat at a rate sufficient to avoid substantial impediment of the kinetics. For a heat transfer chamber in thermal contact with the reaction chamber volume, the heat transfer chamber transfers heat at an enhanced heat transfer rate across a wall between the heat transfer chamber and the reaction chamber, thereby obtaining the enhanced production rate per reaction chamber volume for the thermal chemical reaction wherein a ratio of the enhanced production rate per reaction chamber volume to a conventional production rate per conventional reaction chamber volume for the thermal chemical reaction is at least 2. These features are effective for both catalytic and non-catalytic thermal chemical reactions. For catalytic chemical reactions, addition of a catalyst upon the porous insert permits flow of reactants past catalyst sites rather than limiting reactant motion to diffusion as in conventional systems. Thus, for catalytic thermal chemical reactions, both kinetic impediments are substantially reduced permitting realization of theoretical or near theoretical reaction kinetics. In a thermal chemical reaction, the rate of production, namely reaction kinetics, is limited by the rate of heat transfer either to or from the reaction site. In order to obtain an enhanced heat transfer rate and thereby an enhanced production rate, the reaction chamber of the autothermal fixed bed reactor has a porous insert within the reaction chamber volume wherein the reaction chamber volume with the porous insert has a mean porosity less than 0.8 and a transport distance no greater than 0.8 mm, thereby transferring reaction heat at an enhanced heat transfer rate through the porous insert.



Figure 1. Hydrogen mole fraction contour plots in the autothermal fixed bed reactor with structured catalysts and square surface features.

The hydrogen mole fraction contour plots in the autothermal fixed bed reactor are illustrated in Figure 2 with structured catalysts and circular surface features. The surface features may have two or more layers stacked on top of each other or intertwined in a three-dimensional pattern. The pattern in each discrete layer may be the same or different. Flow may rotate in each layer or only in one layer. Sub-layers, which may not be adjacent to the bulk flow path of the channel, may be used to create additional surface area. The flow may rotate in the first level of surface features and diffuse molecularly into the second or more sublayers to promote reaction. Three-dimensional surface features may be made via metal casting, laser cutting, etching, ablation, or other processes where varying patterns may be broken into discrete planes as if stacked on top of one another. The porous insert may be a powder, a porous monolith, metal or ceramic foam, honeycomb, tube bank, stacked microchannel assembly, fibers, or combinations thereof. In view of the cost of replacing spent catalyst, for catalytic reactors, it is preferred that the porous insert be removable from the reaction chamber. The porous insert may be arranged to provide single or multiple flow passages for reactants through the reaction chamber volume. The porous insert may rest on or contact raised features formed on the interior surfaces of the reaction chamber. For catalytic thermal chemical reactions, a preferred porous insert is a porous support with a catalyst material thereon. More preferred is a porous insert with a solution deposited interfacial layer between the porous support and the catalyst material. A more preferred porous insert has a buffer layer between the porous support and the interfacial layer. The heat transfer chamber is in thermal contact with the reaction chamber volume, the heat transfer chamber transferring heat at the enhanced heat transfer rate across the wall between the heat transfer chamber and the reaction chamber, thereby obtaining the enhanced production rate per reaction chamber volume for the thermal chemical reaction. The method of making the preferred catalyst has the steps of selecting a porous support, vapor depositing a buffer layer on the porous support, solution depositing an interfacial layer thereon, and depositing a catalyst metal onto the interfacial layer. When a metal foam is used as the porous support, the metal foam is etched prior to vapor depositing the buffer layer. Etching is preferably with an acid. Optionally a catalyst layer may be deposited onto the interfacial layer.



Figure 2. Hydrogen mole fraction contour plots in the autothermal fixed bed reactor with structured catalysts and circular surface features.

The bulk reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor are presented in Figure 3 with structured catalysts and square surface features. The length and width of a surface feature may be defined in the same way as the length and width of a channel. The depth of the surface features may correspond to the direction of stacking a stacked and bonded microchannel device with surface features formed on or in the sheet surfaces. The dimensions for the surface features may refer the maximum dimension of a surface feature. All of the reforming reactions are endothermic, requiring substantial amounts of heat input which must be covered by an external heat supply. The heat deficit becomes even larger since the reactions take place at temperatures in the range of 200-280 °C, which means that the reactants must be heated-up to such temperatures. The required heat is typically supplied by placing the catalyst containing tubes of the reactor in rows inside a fired furnace. The high temperature of the flame necessitates that the combustion burners must be placed at a sufficient distance from the reforming tubes to prevent the tubes from high temperature exposure which could destroy the tubes. This is a rather inefficient arrangement since the hydrogen producing reforming reaction forms a small part of overall reactor. Materials limitations also dictate the avoidance of extremely high temperatures for the reforming reactor tubes, further limiting the ability to place the combustion burners in close proximity to the reforming tubes. All these mean that traditional steam methane reforming reactor configurations are very large and new configurations must be developed to decrease the size and the cost of such systems. In a reformer, tubes are coated with a combustion catalyst on the outer surface and a reforming catalyst on the inner surface. Structured catalyst configurations result in high rates of heat transport from the oxidation side to the reforming side. However, in such a configuration catalyst replacement is a problem. A reactor consists of a bundle of small diameter ceramic or metallic tubes enclosed in a thermally insulated vessel. Catalysts are deposited on the internal and external surfaces of the tubes and heat is transferred across the tube walls. Part of the tubes of the autothermal fixed bed reactor may not be covered by catalyst and may act as heat exchange zones. Although this system resulted in a compact configuration the replacement of the catalyst is problematic and as a result the whole reactor must be replaced when the catalyst effectiveness for either the combustion or the reforming reaction declines.



Figure 3. Bulk reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor with structured catalysts and square surface features.

The bulk reactant mole fraction profiles at different temperatures along the length of the autothermal fixed

bed reactor are presented in Figure 4 with structured catalysts and circular surface features. A surface feature may comprise a recess or a protrusion based on the projected area at the base of the surface feature or the top of the surface feature. If the area at the top of the surface feature is the same or exceeds the area at the base of the surface feature, then the surface feature may be considered to be recessed. If the area at the base of the surface feature exceeds the area at the top of the surface feature, then it may be considered to be protruded. For this description, the surface features may be described as recessed although it is to be understood that by changing the aspect ratio of the surface feature it may be alternatively defined as a protrusion. The temperatures and pressures of the two streams entering the combustor and the reformer, respectively, need not be the same. Typically, combustion takes place at low or near-atmospheric pressure, although high pressure combustion is widely practiced. For a process microchannel defined by walls that intersect only the tops of the surface features, especially for a flat channel, all surface features may be defined as recessed and it is to be understood that a similar channel could be created by protruding surface features from the base of a channel with a cross section that includes the base of the surface features. As a feature, the integrated combustor-steam reformer assembly includes a tubular section defined by a cylindrical wall and a housing defining an axially extending concentric annular passage in heat transfer relation to each other. A fuel-air mixture is supplied to the tubular section. The inside wall of the tubular section is in contact with a ferroalloy sheet coated with a catalyst that induces the combustion reaction in the feed. A fuel-steam mixture is supplied to the annular passage. The annular passage is either filled with a suitable catalyst in pellet form which promotes the reformation reaction, or it contains, in close contact with the tube, ferroalloy sheets coated with the reforming catalyst. Reforming can take place at pressures somewhat above atmospheric to moderately high. The cylindrical wall of the tubular section should be of sufficient strength to allow for the pressure differential between the two streams. It is also apparent that different geometries can be used instead of cylindrical shapes should they offer advantages in particular applications. The composition of the mixture entering the combustor should be such as to ensure complete combustion of the fuel. Although a stoichiometric ratio of air to fuel is sufficient, higher ratios can be employed. It is typical practice to provide a higher than stoichiometric steam-to-fuel ratio to minimize possible side reactions that can cause carbon formation to the detriment of the catalyst and the reactor. The structured combustion catalyst can preferably be in the form of a corrugated metal foil made of a high temperature resistant metal or metal alloy. A metal alloy such as an alloy with the formula ferroalloy, can be used for high temperature combustion catalyst support. The corrugated foil is supported on a rod or tube placed inside tube. The corrugated foil is wrapped on the tube or rod so that the corrugated channels run parallel to the axis of the tube. Reforming takes place on the catalyst placed in reforming zone enclosed between tube and reactor wall.



Figure 4. Bulk reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor with structured catalysts and circular surface features.

The methanol mole fraction contour plots in the autothermal fixed bed reactor are illustrated in Figure 5 with structured catalysts and square surface features. For some reactions, for example certain single reactions that are chemically irreversible or endothermic, maximizing the reaction temperature is often desired because both kinetics and conversion increase with increasing temperature. However, for many reactions, trade-offs exist between kinetics, equilibrium, and reaction selectivity. For example, reversible exothermic chemical reactions generally exhibit improved reaction kinetics but lower equilibrium conversion with increasing temperature. Lowering the reaction temperature favors higher conversion but typically requires more catalyst and a larger reactor. Accordingly, more efficient utilization of catalyst and reactor resources for a desired conversion likely requires a non-uniform temperature trajectory for the reactants as they progress through the reaction process. For a single reversible exothermic reaction, a theoretical optimum temperature trajectory would start at a high temperature to take advantage of fast kinetics and proceed in monotonically decreasing fashion to lower temperatures to improve conversion. There are also reasons related to energy efficiency to control the temperature trajectory of chemical reactions. For both endothermic and exothermic chemical reactions, greater thermodynamic reversibility, and therefore greater system efficiently can theoretically be achieved with reaction temperature control. Thermal chemical reactions are those chemical reactions that produce or consume heat. Examples of thermal chemical reactions include hydrocarbon conversion reactions such as steam reforming, water-gas shift reactions and combustion. The methanol steam reforming reaction is usually carried out in the presence of a catalyst at temperatures up to about 280 °C. Because the intrinsic kinetics of a thermal chemical reaction can be much faster than the heat transfer rate between the reaction vessel and the thermal sink, source or environment, the actual rate of product production is slower than the intrinsic rate. Intrinsic kinetics means the rate at which products could theoretically be formed at the catalyst surface. The major advantage is the heat integration between the combustion and the reforming zones. Combustion takes place on the catalytic film which is coated on the structured catalyst placed on one side of the wall separating the two zones. The heat that is generated on the combustion side is quickly transferred and used on the reforming side. This rapid heat transfer is critical in maintaining the combustion side catalyst at temperatures below 300 °C and, more preferably, below 280 °C. These temperatures ensure acceptable catalyst life and permit the use of a very compact combustion zone which allows the reactor assembly to be dramatically smaller compared with a flame-based reformer which needs to maintain a significant distance between the flame generation and the reforming sections. The lower temperatures also allow the use of less expensive alloys for the construction of the reactor. The lower temperatures also mean no nitrogen oxide emissions as their formation requires much higher temperatures. When employing a quench type reformer, preheated process gas of methanol and steam is introduced in a first bed with the reforming catalyst and partially converted to a gas containing hydrogen. A part of the hydrogen is then oxidized with oxygen containing atmosphere being introduced into the partial reformed process gas from the top catalyst bed and oxidized in a bed of oxidation catalyst arranged between the top catalyst bed and a subsequent fixed bed of reforming catalyst. Heat evolving from the exothermic oxidation reaction proceeding in the oxidation catalyst bed is, thereby, transferred to the reacting process gas in an amount sufficient to maintain the endothermic reforming reactions in subsequent reforming catalyst bed. The oxygen containing atmosphere may be added to the process gas in several steps, whereby each step is performed. The oxygen containing atmosphere for use in the process, may be any atmosphere containing oxygen in an amount sufficient to the oxidation of the required amount of hydrogen in order to provide the necessary heat for the endothermic reforming reactions at a reasonable reaction rate. The oxygen containing atmosphere may be pure oxygen, oxygen-enriched air, or oxygen depleted air. An advantage by using air or oxygen depleted air in the above process will be that valuable ammonia synthesis gas is produced in the process.



Figure 5. Methanol mole fraction contour plots in the autothermal fixed bed reactor with structured catalysts and square surface features.

The methanol mole fraction contour plots in the autothermal fixed bed reactor are illustrated in Figure 6 with structured catalysts and circular surface features. The heat exchange channels comprise process channels wherein an endothermic reaction is conducted. These heat exchange process channels may be microchannels. Examples of endothermic reactions that may be conducted in the heat exchange channels include steam reforming and dehydrogenation reactions. The heat integrated reforming reactor offers several advantages over conventional flame-based reforming reactors. The incorporation of a simultaneous endothermic reaction to provide an improved heat sink may enable a typical heat flux of roughly an order of magnitude above the convective cooling heat flux. The catalytic combustion takes place at lower temperatures that permit close coupling of the combustion and reforming zones. In a flame-based reformer the flame must be at a significant

distance from the tube containing the reforming catalyst to prevent the tube from melting [69, 70]. As a result, the integrated reforming reactor is several times smaller than a flame based reforming reactor and consequently has a much lower capital and installation cost [71, 72]. The flame-based reformers can consist of hundreds of tubes and burners and a sophisticated feed flow distribution system is required to distribute the combustion feed and reforming feed to all burners and tubes evenly [73, 74]. The heat integrated reformer has a single inlet for the reforming and single inlet for the combustion feed gases which results in simple and inexpensive feed flow system [75, 76]. The flame reformers even with the use of low nitrogen oxides burners still produce significant emissions of nitrogen oxides in the combustion gases that have to be controlled with a separate selective catalytic reduction catalyst and ammonia injection [77, 78]. The heat integrated reformer operates at low temperatures on the combustion side at which nitrogen oxides formation is negligible. The catalyst may be in the form of a flow-by structure such as a felt with an adjacent gap, a foam with an adjacent gap, a fin structure with gaps, a washcoat on any inserted substrate, or a gauze that is parallel to the flow direction with a corresponding gap for flow. The catalyst may be directly washcoated on the interior walls of the process microchannels, grown on the walls from solution, or coated in situ on a fin structure. The catalyst may be in the form of a single piece of porous contiguous material, or many pieces in physical contact. In one case, the catalyst is comprised of a contiguous material and has a contiguous porosity such that molecules can diffuse through the catalyst. In this case, the fluids flow through the catalyst rather than around it. The catalyst may comprise a porous support, an interfacial layer on the porous support, and a catalyst material on the interfacial layer. The interfacial layer may be solution deposited on the support or it may be deposited by chemical vapor deposition or physical vapor deposition. In one case, the catalyst has a porous support, a buffer layer, an interfacial layer, and a catalyst material. Any of the foregoing layers may be continuous or discontinuous as in the form of spots or dots, or in the form of a layer with gaps or holes. The porous support may be a porous ceramic or a metal foam. Other porous supports that may be used include carbides, nitrides, and composite materials. The buffer layer, when present, may have a different composition and density than both the porous support and the interfacial layers, and in one case has a coefficient of thermal expansion that is intermediate the thermal expansion coefficients of the porous support and the interfacial layer. The buffer layer may be a metal oxide or metal carbide.



Figure 6. Methanol mole fraction contour plots in the autothermal fixed bed reactor with structured catalysts and circular surface features.

The surface reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor are presented in Figure 7 with structured catalysts and square surface features. The equilibrium limited chemical process refers to a chemical process wherein at least one measure of the equilibrium extent of the chemical process exhibits substantial temperature dependence over the range of interest. Thermal communication between two areas means that heat can flow from one area to the other. The catalyst can be in the form of pellets or it can be a structured catalyst or monolith. The wall can be constructed from any material, but materials that offer low resistance to heat transfer such as metals and metallic alloys are preferred. In this configuration, heat is generated by combustion in the catalytic chamber and is transported very easily and efficiently though the wall to the reforming chamber where the heat demanding reforming reactions take place. Heat is generated where it is needed and does not have to overcome significant heat transfer resistances to reach the demand location resulting in high efficiencies. The heat integrated reformer can be easily integrated with a hydrogen producing process that typically consists of a feed pretreatment system to remove impurities from natural gas, heat recovery equipment to recover heat to preheat the feed and raise steam, one or more water gas shift reactors to convert carbon monoxide to hydrogen and pressure swing adsorption system to separate hydrogen from syngas. The waste stream from the pressure swing adsorption system can be used as fuel to the heat integrated reformer combustion side. Another advantage of the hydrogen production process based on a heat integrated reformer is that the makeup natural gas fuel that is normally supplied to ensure stable burner operation in flame-based reformers can be reduced or eliminated. In that case most of the fuel requirement can be supplied by the pressure swing adsorption waste stream. The fuel to the combustor can be any available and suitable fuel. Such fuels include methane, natural gas, propane, butane, methanol, ethanol, higher alcohols, and ethers. The fuels normally available in liquid form must be vaporized before entering the combustion zone. The same fuels can be fed to the reforming zone to undergo the hydrogen producing reforming reactions. Another potential fuel to the combustor is the hydrogen depleted off-gas from the anode of a fuel cell when the reformer is used as a part of a fuel processor producing hydrogen for a fuel cell. Yet another potential fuel to the combustor is the hydrogen depleted off-gas from the pressure swing adsorption or any other hydrogen purification devise when the reformer is used as a part of a fuel processor producing a hydrogen rich stream that feeds such a device to produce high purity hydrogen. In addition to hydrogen, the heat integrated reformer can be used in the production of ammonia, production of methanol, production of ethanol, production of oxo-alcohols and in general in processes where syngas is required. For some processes it may be advantageous to co-feed carbon dioxide in the reforming zone to promote the conversion to carbon monoxide. In yet another application, the heat integrated reformer can be used to produce hydrogen for fuel cells for the production of electricity. The reforming catalyst pellets can be supported in the autothermal fixed bed reactor by a suitable metal plate that is drilled to create holes that are sufficient large that present little resistance to reforming gas flow and keep the pellet catalyst in the desired location in the reactor. This metal plate also serves to distribute the reforming gas feed evenly along the radial dimension of the autothermal fixed bed reactor.



Figure 7. Surface reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor with structured catalysts and square surface features.

The surface reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor are presented in Figure 8 with structured catalysts and circular surface features. A microchannel reactor is preferably designed to achieve a temperature trajectory down the length of the reaction chamber that approaches a predetermined temperature trajectory [79, 80]. Typically, this predetermined temperature trajectory is substantially different from the temperature trajectory that will occur if the reaction is allowed to proceed adiabatically or isothermally [81, 82]. This predetermined temperature trajectory approaches a theoretically determined optimum temperature trajectory based on the reaction rate and design parameters specific to the particular application [83, 84]. Advantages of the process include the enhancement of reaction selectivity due to the dimensions of the microchannel reactor [85, 86]. In reactors of conventional dimension, reactions propagated homogeneously in the in the gaseous phase make a significant contribution to the overall make-up of the product [87, 88]. These reactions tend to be indiscriminate and often result in the production of undesirable by-products or hydrocarbon pyrolysis products. For example, if the reactant mixture contains propane, full and partial oxidation can take place as well as pyrolysis leading to the production of ethane and methane. One method to prepare the catalytic film that ensures good adhesion to the ferroalloy is to heat the ferroalloy sheet to elevated temperatures in air. During the heating, aluminum, which is a component of the ferroalloy, is diffusing out of the bulk of the alloy and forms an aluminum oxide surface layer. Upon this surface layer it is easy to coat alumina or other metal oxide supports for the desired dispersed metal phase which may be a precious or non-precious metal. Typical supports for reforming and combustion catalysts consist of oxides of aluminum, silicon, lanthanum, cerium, zirconium, calcium, potassium and sodium. The metal phase of reforming catalysts may contain nickel, cobalt, copper, platinum, rhodium and ruthenium. Nickel based catalysts are the most commonly used for reforming reactions. The presence of a catalyst and lower temperatures permit significantly higher space velocities to be used compared to flame-based reformers. Space velocity is defined as the ratio of the feed flow at standard conditions to the empty volume of the reactor. The catalyst on the reforming side can be a pellet catalyst or it can also be a structured catalyst on support. In the case of a pellet catalyst, space velocities similar to the ones used in flame-based reformers can be used. The suitable combustion and, where applicable, the reforming catalysts, can be prepared by coating a relatively thin catalytic film on the ferroalloy sheets. Suitable catalysts typically consist of a metal oxide film and one or multiple metal phases dispersed on the film. The most typical combustion catalysts support is high surface area aluminum oxide. A common dispersed metal phase catalyst is palladium or platinum and mixtures thereof. Coating of the catalysts support on the ferroalloy sheets can be accomplished by many techniques. After heating up so as to form the aluminum oxide layer at the surface, techniques such as dip coating from a solution of dispersed metal oxide particles or from a slurry which contains the metal oxide particles can be employed. Alternatively, catalyst can be deposited on the ferroallov sheets by spraving the catalytic components onto their surface. The catalyst support is then dried by calcination at elevated temperatures. The dispersed metal phase can be added to the support forming solution or slurry of the metal oxide particles or it can be added in a separate step from a solution of the desirable metal salt after the calcination step. The reformer reactor operates in the so-called co-current mode, namely combustion and reforming mixtures flow in the same direction. The same reactor configuration can be employed in operation in the so-called counter-current mode, namely combustion and reforming mixtures flowing in opposite directions. One or multiple baffles are placed inside the reactor and perpendicular to the tubes as to force the reacting mixture in a cross-flow multi-passage path through the reactor. This ensures higher fluid velocities, greater turbulence and better contact with the catalyst pellets which are outside tubes. This in turn results in lower mass transfer resistances in the fluid phase and higher reaction efficiencies while increasing the heat transfer rates as well. The products of the reforming reactions again exit the reactor through the flow passage.



Figure 8. Surface reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor with structured catalysts and circular surface features.

4. Conclusions

The heat capacity, thermal conductivity, and viscosity of the mixture are calculated as a mass-weighted average of the values for each constituent. In addition, the material properties of each individual species are functions of the local temperature. When solving the species mass transport equations, binary mass diffusion coefficients are used directly. Only isotropic catalyst structures are considered and the permeability and inertial resistance factor are held constant. The effective thermal conductivity of the catalyst structure

system including the porous structure and intervening gas is calculated based upon the porosity of the porous medium, the fluid phase thermal conductivity, and the porous medium effective thermal conductivity as measured in air at ambient conditions. The major conclusions are summarized as follows:

- For catalytic thermal chemical reactions, both kinetic impediments are substantially reduced permitting realization of theoretical or near theoretical reaction kinetics.
- The heat transfer chamber is in thermal contact with the reaction chamber volume, the heat transfer chamber transferring heat at the enhanced heat transfer rate across the wall between the heat transfer chamber and the reaction chamber, thereby obtaining the enhanced production rate per reaction chamber volume for the thermal chemical reaction.
- Structured catalyst configurations result in high rates of heat transport from the oxidation side to the reforming side.
- Typically, combustion takes place at low or near-atmospheric pressure, although high pressure combustion is widely practiced.
- The heat that is generated on the combustion side is quickly transferred on the reforming side.
- The heat integrated reforming reactor offers several advantages over conventional flame-based reforming reactors. The incorporation of a simultaneous endothermic reaction to provide an improved heat sink may enable a typical heat flux of roughly an order of magnitude above the convective cooling heat flux.
- The wall can be constructed from any material, but materials that offer low resistance to heat transfer such as metals and metallic alloys are preferred. In this configuration, heat is generated by combustion in the catalytic chamber and is transported very easily and efficiently though the wall to the reforming chamber where the heat demanding reforming reactions take place.
- The presence of a catalyst and lower temperatures permit significantly higher space velocities to be used compared to flame-based reformers.

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Thermal chemical reaction characteristics of autothermal fixed bed reactors with

structured catalysts and different surface features

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Abstract

Conventional methods of producing a synthesis gas are expensive and complex installations. In order to overcome the complexity and expense of such installations, it is proposed to generate the synthesis gas within autothermal fixed bed reactors that utilize structured catalysts and different surface features to generate the heat necessary to support endothermic heating requirements of the steam reforming reactions. The present study is focused primarily upon the thermal chemical reaction characteristics of autothermal fixed-bed reactors with structured catalysts and different surface features. The heat capacity, thermal conductivity, and viscosity of the mixture are calculated as a mass-weighted average of the values for each constituent. In addition, the material properties of each individual species are functions of the local temperature. When solving the species mass transport equations, binary mass diffusion coefficients are used directly. Only isotropic catalyst structures are considered and the permeability and inertial resistance factor are held constant. The effective thermal conductivity of the catalyst structure system including the porous structure and intervening gas is calculated based upon the porosity of the porous medium, the fluid phase thermal conductivity, and the porous medium effective thermal conductivity as measured in air at ambient conditions. The present study aims to explore how to effectively generate the synthesis gas within autothermal fixed bed reactors that utilize structured catalysts and different surface features. Particular emphasis is placed upon the heat and mass transport phenomena involved in autothermal fixed bed steam reforming reactors. The results indicate that for catalytic thermal chemical reactions, both kinetic impediments are substantially reduced permitting realization of theoretical or near theoretical reaction kinetics. The heat transfer chamber is in thermal contact with the reaction chamber volume, the heat transfer chamber transferring heat at the enhanced heat transfer rate across the wall between the heat transfer chamber and the reaction chamber, thereby obtaining the enhanced production rate per reaction chamber volume for the thermal chemical reaction. Structured catalyst configurations result in high rates of heat transport from the oxidation side to the reforming side. Typically, combustion takes place at low or near-atmospheric pressure, although high pressure combustion is widely practiced. The heat that is generated on the combustion side is quickly transferred on the reforming side. The heat integrated reforming reactor offers several advantages over conventional flame-based reforming reactors. The incorporation of a simultaneous endothermic reaction to provide an improved heat sink may enable a typical heat flux of roughly an order of magnitude above the convective cooling heat flux. The wall can be constructed from any material, but materials that offer low resistance to heat transfer such as metals and metallic alloys are preferred. In this configuration, heat is generated by combustion in the catalytic chamber and is transported very easily and efficiently though the wall to the reforming chamber where the heat demanding reforming reactions take place. The presence of a catalyst and lower temperatures permit significantly higher space velocities to be used compared to flame-based reformers. Keywords: Hydrocarbons; Reactors; Structures; Properties; Reforming; Combustion

1. Introduction

Synthesis gas, or syngas, is a mixture of gases prepared as feedstock for a chemical reaction; for example, carbon monoxide and hydrogen to make hydrocarbons or organic chemicals, or hydrogen and nitrogen to make ammonia [1, 2]. Syngas may be produced for use with a Fischer-Tropsch process [3, 4]. The synthetic production of hydrocarbons by the catalytic reaction of carbon monoxide and hydrogen is known and is generally referred to as the Fischer-Tropsch reaction [5, 6]. Numerous catalysts have been used in carrying out the reaction, and at relatively low to medium pressure and temperatures, both saturated and unsaturated hydrocarbons can be produced [7, 8]. The synthesis reaction is very exothermic and temperature sensitive whereby temperature control is required to maintain a desired hydrocarbon product selectivity. Two basic methods have been employed for producing the synthesis gas utilized as feedstock in the Fischer-Tropsch reaction. The two methods are steam reforming, wherein one or more light hydrocarbons such as methane or ethane are reacted with steam over a catalyst to form carbon monoxide and hydrogen [9, 10], and partial oxidation, wherein one or more light hydrocarbons are combusted or reacted sub-stoichiometrically to produce synthesis gas [11, 12]. The steam reforming reaction is endothermic and a catalyst containing nickel is often utilized [9, 10]. The hydrogen to carbon monoxide ratio of the synthesis gas produced by steam reforming of methane is approximately 3:1. Partial oxidation is the non-catalytic, sub-stoichiometric combustion of light hydrocarbons such as methane or ethane to produce the synthesis gas [11, 12]. The partial oxidation reaction is typically carried out using high purity oxygen. High purity oxygen can be quite expensive. The hydrogen to carbon monoxide ratio of synthesis gas produced by the partial oxidation of methane is approximately 2:1. In some situations, these approaches may be combined.

A combination of partial oxidation and steam reforming, known as autothermal reforming [13, 14], wherein air is used as a source of oxygen for the partial oxidation reaction has also been used for producing synthesis gas heretofore [13, 14]. In low pressure hydrocarbon synthesis processes, autothermal reforming with air is utilized to produce synthesis gas [15, 16]. Autothermal reforming is a combination of partial oxidation and steam reforming where the exothermic heat of the partial oxidation supplies the necessary heat for the endothermic steam reforming reaction [15, 16]. The autothermal reforming process can be carried out in a relatively inexpensive refractory lined carbon steel vessel whereby low cost is typically involved [17, 18]. The autothermal process results in a lower hydrogen to carbon monoxide ratio in the synthesis gas than does steam reforming alone. That is the steam reforming reaction with methane results in a ratio of about 3:1 while the partial oxidation of methane results in a ratio of about 2:1. The optimum ratio for the hydrocarbon synthesis reaction carried out at low or medium pressure over a cobalt catalyst is 2:1. When the feed to the autothermal reforming process is a mixture of light hydrocarbons such as a natural gas stream, some form of additional control is desired to maintain the ratio of hydrogen to carbon monoxide in the synthesis gas at the optimum ratio of about 2:1. In producing a product from the synthesis unit, a residue gas is frequently produced [19, 20]. For some processes, the use of this gas to create energy has been suggested [19, 20]. Systems that have utilized the residue gas have required numerous additional components and steps to do so [21, 22]. In producing a synthesis gas for a chemical process, it is desirable to produce the synthesis gas as efficiently as possible [21, 22]. The ability to develop a process with low capital expense may be an imperative to development of large-scale systems.

Synthesis gas containing hydrogen and carbon monoxide is produced for a variety of industrial applications, for example, the production of hydrogen, chemicals and synthetic fuel production. Conventionally, the synthesis gas is produced in a fired reformer in which natural gas and steam is reformed to the synthesis gas in catalyst filled reformer tubes [23, 24]. The endothermic heating requirements for steam methane reforming reactions occurring within the reformer tubes are provided

by burners firing into the furnace that are fueled by part of the natural gas. In order to increase the hydrogen content of the synthesis gas, the synthesis gas can be subjected to water-gas shift reactions to react residual steam in the synthesis gas with the carbon monoxide [23, 24]. Such steam methane reformers are optimized for hydrogen production and typically are fed with a reactant stream containing hydrocarbons and steam at a steam-to-carbon ratio of 1.5 to 3.5, depending on the quantity of carbon dioxide in the reactant stream, to thereby produce the synthesis gas at a hydrogen to carbon monoxide ratio of 3 or higher [25, 26]. This is not optimum for the production of synthesis gas for synthetic fuel production where a hydrogen to carbon monoxide ratio of 1.8 to 2.0 within the synthesis gas is more desirable [27, 28]. Consequently, where synthetic fuel production is a desired use of the synthesis gas, an autothermal reformer is typically used in which the steam-to-carbon ratio of the feed to create additional steam and heat to reform the hydrocarbons contained in the feed to the synthesis gas. For a large-scale installation, an air separation plant may be required to supply the oxygen.

Conventional methods of producing a synthesis gas are expensive and complex installations. In order to overcome the complexity and expense of such installations, it has been proposed to generate the synthesis gas within reactors that utilize an oxygen transport membrane to supply oxygen and thereby generate the heat necessary to support endothermic heating requirements of the steam methane reforming reactions [29, 30]. A typical oxygen transport membrane has a dense layer that, while being impervious to air or other oxygen containing gas, will transport oxygen ions when subjected to an elevated operational temperature and a difference in oxygen partial pressure across the membrane. This difference in oxygen partial pressure can be produced by compressing the supplied air or from combustion of hydrocarbons fed to a permeate side of the membrane and supported by permeated oxygen or a combination of the two methods [31, 32]. For example, a reactant gas feed is combined with steam. The reactant gas feed can be natural gas or other hydrocarbon containing gas. This combined feed stream is then heated and introduced into an adiabatic pre-reformer to produce an intermediate stream that contains carbon monoxide, carbon dioxide, steam, hydrogen, and methane. The intermediate stream can be combined with carbon dioxide and steam. The resulting reactant stream is then introduced with air into reactant and oxidant sides, respectively, of an oxygen transport membrane reformer [33, 34]. The oxygen transport membrane reformer has an oxygen transport membrane separating the reactant and oxidant sides of the reformer. The reactant gas reacts with oxygen that has permeated through the oxygen transport membrane to produce a synthesis gas. Preferably a reforming catalyst is applied to at least a portion of the reactant side surface of oxygen transport membrane or packed into the reactant side to promote the reforming reactions [35, 36]. In an integrated system, an oxygen transport membrane reformer is connected to a downstream reactor such as a Fischer-Tropsch reactor to produce a liquid product. The presence of the pre-reforming stage will prevent the breakdown of higher order hydrocarbons present in the reactant feed stream and the resulting carbon deposition that would otherwise occur had the higher order hydrocarbons been fed directly to the reactor [37, 38]. Such carbon deposition will degrade reforming catalyst used in connection with the oxygen transport membrane reactor.

Heat is supplied to an endothermic reforming reaction inside a reaction passage separated from an air passage by an oxygen transport membrane [39, 40]. A reactant gas, for example, methane flows through the reaction passage is combusted with permeated oxygen to provide the heat to support the reforming reaction [39, 40]. Further heat is supplied to the reforming reaction by either combusting a fuel with retentate or a fuel with a second permeate produced by another oxygen transport membrane or within a combustion passage. Alternatively, an oxygen transport membrane can be situated between an air passage and a combustion passage and a barrier is located between the combustion passage and the reaction passage [41, 42]. In such case, the oxygen transport membrane supplies oxygen permeated to

support combustion of a fuel in the combustion passage and thereby generate heat that is transferred to the reaction passage [41, 42]. A staged reactor system has a sequential arrangement of reactor stages to produce a synthesis gas product. Each of the reactor stages has an oxidant side separated from a reactant side by an oxygen transport membrane [43, 44]. The reactant sides are linked together so that a reactant stream containing methane and steam is introduced into the system and sequentially reacted with oxygen permeating through the membrane to produce a synthesis gas product for use in a downstream reactor [45, 46]. Catalyst beds can be located within the reactant side of the reactor stages or can be positioned between the reactor stages.

Both steam and a reactant gas from a downstream process utilizing the synthesis gas can be introduced into the feed between stages [47, 48]. The presence of the multiple stages allows the temperature within each of the reaction stages to be controlled to prevent the oxygen transport membrane from being degraded and to control the deposition of soot throughout the membrane system [47, 48]. Staged reactor systems can employ oxygen transport membranes in which the air or other oxygen containing stream fed to each of the stages can be controlled to control the temperatures and conversation that can be obtained in producing a synthesis gas. The problem with all of these reactor systems is that an oxygen transport membrane will operate at high temperatures of about 900 °C to about 1100 °C. Where hydrocarbons such as methane and also higher order hydrocarbons are subjected to such temperatures, carbon formation will occur [49, 50]. Additionally, where oxygen is supplied by an oxygen transport membrane, the area of the membrane is distributed throughout the reactor [51, 52]. As such, the oxygen is not generally available at the entrance to the reactor [53, 54]. This also results in an aggravated carbon formation problem at the entrance that is especially the case at low steam-to-carbon ratios. In any case, a reactant containing methane and steam will produce a relatively low oxygen flux across the membrane resulting in the membrane area required for such a reactor to be larger and it will add to the expense and complexity in such a reactor [55, 56]. Additionally, a steam methane reforming catalyst must be periodically replaced. In these reactor designs where the catalyst is employed adjacent to the oxygen transport membrane, catalyst replacement becomes an expensive if not impractical exercise [57, 58]. It is therefore necessary to provide a method and apparatus in which the oxygen transport membrane is not directly used to react the steam and methane components of the reactant feed, but rather, to generate the heat required to support endothermic heating requirements of steam methane reforming reactions within a separate reactor.

Conventional methods of producing a synthesis gas are expensive and complex installations. In order to overcome the complexity and expense of such installations, it is proposed to generate the synthesis gas within autothermal fixed bed reactors that utilize structured catalysts and different surface features to generate the heat necessary to support endothermic heating requirements of the steam reforming reactions. The present study is focused primarily upon the thermal chemical reaction characteristics of autothermal fixed bed reactors with structured catalysts and different surface features. The heat capacity, thermal conductivity, and viscosity of the mixture are calculated as a mass-weighted average of the values for each constituent. In addition, the material properties of each individual species are functions of the local temperature. When solving the species mass transport equations, binary mass diffusion coefficients are used directly. Only isotropic catalyst structures are considered and the permeability and inertial resistance factor are held constant. The effective thermal conductivity of the catalyst structure system including the porous structure and intervening gas is calculated based upon the porosity of the porous medium, the fluid phase thermal conductivity, and the porous medium effective thermal conductivity as measured in air at ambient conditions. The present study aims to explore how to effectively generate the synthesis gas within autothermal fixed bed reactors that utilize structured catalysts and different surface features. Particular emphasis is placed upon the heat and mass transport phenomena involved in autothermal fixed bed steam reforming reactors.

2. Methods

The methanol steam reforming reaction in a microchannel reactor is the focus of this study. The water gas shift reaction also is included as it occurs on the steam reforming catalyst. In the endothermic microchannel steam reforming reactor, heat is provided by combustion in adjacent microchannels. In the present study, the performance of the steam reforming channel is evaluated and a constant temperature thermal boundary condition is imposed on the wall to simulate the adjacent combustion. These simulations do not consider the effect of external heat transfer resistance outside of the reforming channel. This assumption will become more significant as the reaction is further intensified. Pressure is set at 8 bar at the outlet, unless specified otherwise. Constant temperature is imposed on the channel walls. For all the cases considered, the wall temperature is the same as the feed temperature. The catalyst structure is modeled as porous media where chemical reactions take place. The complex interaction between mass and heat transfer, as well as chemical reactions within the catalyst structure, lead to internal catalyst temperature and species concentration distributions. An entrance length equal to 20 times the open channel gap is imposed upstream of the catalyst to avoid an entrance region effect in comparing reactor performance under different variables. For commercial microchannel reactors of interest, a heat exchanger is upstream of the reactor section for preheat and thus the flow field is fully developed and laminar. The higher grid line density within the catalyst structure reflects the understanding that temperature and species concentrations gradients inside the catalyst structure will be greater than those in the flow-by gap. Six meshes of the same structure are built with varying level of refinement to verify the mesh independency of the computational fluid dynamics solution.

The mixture of interest is composed of methanol, steam, hydrogen, carbon monoxide, and carbon dioxide. Ideal gas is assumed in calculating the density of the mixture. The heat capacity, thermal conductivity, and viscosity of the mixture are calculated as a mass-weighted average of the values for each constituent. In addition, the material properties of each individual species are assumed to be, in general, functions of the local temperature. The exception to this is the mass diffusivity of each individual species. For part of the modeling cases, when the reactor wall temperature and the feed inlet temperature are specified at 260 °C, the mass diffusivity of each species is assumed to be independent of the temperature. When solving the species mass transport equations, binary mass diffusion coefficients are used directly. In other words, a dilute system is assumed and considered reasonable as excess steam is present. For flow simulation in the catalyst structure, Darcy's law is used. The following parameters are provided to the computational fluid dynamics code: permeability and inertial resistance factor. These parameters may be defined differently based upon different coordinate directions. In the present study, only isotropic catalyst structures are considered and the permeability and inertial resistance factor are held constant. The effective thermal conductivity of the catalyst structure system including the porous structure and intervening gas is calculated based upon the porosity of the porous medium, the fluid phase thermal conductivity, and the porous medium effective thermal conductivity as measured in air at ambient conditions.

When molecules diffuse through a porous material, their effective diffusivity through the porous network is reduced relative to their diffusivity when they diffuse in an open volume. A high porosity factor value favors diffusion. However, it is not desirable to greatly increase the porosity, since this porosity does not participate in the adsorption capacity. In general, both the bulk and Knudsen diffusion are assumed to contribute to the mass transport rate within the pore volume. For equimolar binary counter-diffusion, the effective diffusivity is calculated based upon the effective diffusivity within the porous medium, the bulk diffusivity in the pore, and the Knudsen diffusivity. The bulk diffusivity of each species in the pores of the porous medium is affected by the connection of the pores of different sizes. A simple parallel pore model yields for the effective bulk diffusivity based upon the molecular

mass diffusivity of species and the tortuosity factor of the porous medium. The tortuosity factor is a property of the adsorbent and does not depend on the diffusing molecule. This factor takes into account the diffusion length when the molecules diffuse through a three-dimensional porous space constituted of pores that are interconnected via restrictions, relative to rectilinear cylindrical pores with the same mean pore diameter. The catalyst support structure of interest in this study possesses larger than average pore size compared to a catalyst pellet. The contribution from the Knudsen diffusion is calculated to be relatively small. The tortuosity factor is not known for the felt-like porous catalyst support structure, and as such this parameter is allowed to vary in the simulation matrix.

Limited production rates may result from longer residence time which is typically seconds to minutes in conventional thermal chemical reaction vessels [59, 60]. As it is conventionally defined, residence time is equal to the volume of the reaction zone divided by the inlet volumetric flow rate of reactants at the reaction system's temperature and pressure. The reaction zone is the total volume of the catalyst and surrounding area through which reactants and products flow [61, 62]. In the water gas shift reaction, carbon monoxide and water are converted to carbon dioxide and hydrogen. Conventionally, this reaction suffers from multiple-second residence times when carried out in fixed bed reactors [63, 64]. Theoretical kinetics suggests that residence times on the order of milliseconds could, theoretically, be obtained [65, 66]. There are two kinetic retarding aspects to conventional reactors. The first is a diffusion limitation as reactants diffuse into and out of a catalyst-bearing porous pellet and the second is a heat transfer limitation which is a combination of heat transfer parameters of catalyst supports and overall reactor geometry. Because the water gas shift reaction is critical to a multi-reactor fuel processing system that supports distributed energy production through the use of a fuel cell, there is a need for a smaller, faster water gas shift reactor [67, 68]. The term microchannel reactor may refer to an apparatus comprising a plurality of process microchannels wherein a process may be conducted. The process may be a steam reforming reaction process. The process microchannels may be operated in parallel. The microchannel reactor may include a header or manifold assembly for providing for the flow of fluid into the process microchannels, and a footer or manifold assembly providing for the flow of fluid out of the process microchannels. The microchannel reactor may comprise one or more heat exchange channels adjacent to and in thermal contact with the process microchannels. The heat exchange channels provide heating and cooling for the fluids in the process microchannels. The heat exchange channels may be combustion channels. The heat exchange channels and combustion channels may be microchannels. The term volume with respect to volume within a process microchannel may include all volume in the process microchannel a process fluid may flow through or flow by. This volume may include volume within surface features that may be positioned in the process microchannel and adapted for the flow of fluid in a flow-through manner or in a flow-by manner. The term thermal contact may refer to two bodies, for example, two channels, that may or may not be in physical contact with each other or adjacent to each other but still exchange heat with each other. One body in thermal contact with another body may heat or cool the other body.

3. Results and discussion

The hydrogen mole fraction contour plots in the autothermal fixed bed reactor are illustrated in Figure 1 with structured catalysts and square surface features. The term surface feature may refer to a depression in a channel wall and a projection from a channel wall that disrupts flow within the channel. The surface features may have a depth, a width, and for non-circular surface features a length. The surface features may be used to disrupt flow and create advective flow at an angle to the bulk flow direction. Each of the microchannels may have a cross-section having any shape, for example, a square, rectangle, circle, and semi-circle. These features cooperate with the reaction kinetics in terms of transferring heat at a rate sufficient to avoid substantial impediment of the kinetics. For a heat transfer

chamber in thermal contact with the reaction chamber volume, the heat transfer chamber transfers heat at an enhanced heat transfer rate across a wall between the heat transfer chamber and the reaction chamber, thereby obtaining the enhanced production rate per reaction chamber volume for the thermal chemical reaction wherein a ratio of the enhanced production rate per reaction chamber volume to a conventional production rate per conventional reaction chamber volume for the thermal chemical reaction is at least 2. These features are effective for both catalytic and non-catalytic thermal chemical reactions. For catalytic chemical reactions, addition of a catalyst upon the porous insert permits flow of reactants past catalyst sites rather than limiting reactant motion to diffusion as in conventional systems. Thus, for catalytic thermal chemical reactions, both kinetic impediments are substantially reduced permitting realization of theoretical or near theoretical reaction kinetics. In a thermal chemical reaction, the rate of production, namely reaction kinetics, is limited by the rate of heat transfer either to or from the reaction site. In order to obtain an enhanced heat transfer rate and thereby an enhanced production rate, the reaction chamber of the autothermal fixed bed reactor has a porous insert within the reaction chamber volume wherein the reaction chamber volume with the porous insert has a mean porosity less than 0.8 and a transport distance no greater than 0.8 mm, thereby transferring reaction heat at an enhanced heat transfer rate through the porous insert.



Figure 1. Hydrogen mole fraction contour plots in the autothermal fixed bed reactor with structured catalysts and square surface features.

The hydrogen mole fraction contour plots in the autothermal fixed bed reactor are illustrated in Figure 2 with structured catalysts and circular surface features. The surface features may have two or more layers stacked on top of each other or intertwined in a three-dimensional pattern. The pattern in each discrete layer may be the same or different. Flow may rotate in each layer or only in one layer. Sub-layers, which may not be adjacent to the bulk flow path of the channel, may be used to create additional surface area. The flow may rotate in the first level of surface features and diffuse molecularly into the second or more sublayers to promote reaction. Three-dimensional surface features may be made via metal casting, laser cutting, etching, ablation, or other processes where varying

patterns may be broken into discrete planes as if stacked on top of one another. The porous insert may be a powder, a porous monolith, metal or ceramic foam, honeycomb, tube bank, stacked microchannel assembly, fibers, or combinations thereof. In view of the cost of replacing spent catalyst, for catalytic reactors, it is preferred that the porous insert be removable from the reaction chamber. The porous insert may be arranged to provide single or multiple flow passages for reactants through the reaction chamber volume. The porous insert may rest on or contact raised features formed on the interior surfaces of the reaction chamber. For catalytic thermal chemical reactions, a preferred porous insert is a porous support with a catalyst material thereon. More preferred is a porous insert with a solution deposited interfacial layer between the porous support and the catalyst material. A more preferred porous insert has a buffer layer between the porous support and the interfacial layer. The heat transfer chamber is in thermal contact with the reaction chamber volume, the heat transfer chamber transferring heat at the enhanced heat transfer rate across the wall between the heat transfer chamber and the reaction chamber, thereby obtaining the enhanced production rate per reaction chamber volume for the thermal chemical reaction. The method of making the preferred catalyst has the steps of selecting a porous support, vapor depositing a buffer layer on the porous support, solution depositing an interfacial layer thereon, and depositing a catalyst metal onto the interfacial layer. When a metal foam is used as the porous support, the metal foam is etched prior to vapor depositing the buffer layer. Etching is preferably with an acid. Optionally a catalyst layer may be deposited onto the interfacial layer.



Figure 2. Hydrogen mole fraction contour plots in the autothermal fixed bed reactor with structured catalysts and circular surface features.

The bulk reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor are presented in Figure 3 with structured catalysts and square surface features. The length and width of a surface feature may be defined in the same way as the length and width of a channel. The depth of the surface features may correspond to the direction of stacking a stacked and bonded microchannel device with surface features formed on or in the sheet surfaces. The dimensions for the surface features may refer the maximum dimension of a surface feature. All of the

reforming reactions are endothermic, requiring substantial amounts of heat input which must be covered by an external heat supply. The heat deficit becomes even larger since the reactions take place at temperatures in the range of 200-280 °C, which means that the reactants must be heated-up to such temperatures. The required heat is typically supplied by placing the catalyst containing tubes of the reactor in rows inside a fired furnace. The high temperature of the flame necessitates that the combustion burners must be placed at a sufficient distance from the reforming tubes to prevent the tubes from high temperature exposure which could destroy the tubes. This is a rather inefficient arrangement since the hydrogen producing reforming reaction forms a small part of overall reactor. Materials limitations also dictate the avoidance of extremely high temperatures for the reforming reactor tubes, further limiting the ability to place the combustion burners in close proximity to the reforming tubes. All these mean that traditional steam methane reforming reactor configurations are very large and new configurations must be developed to decrease the size and the cost of such systems. In a reformer, tubes are coated with a combustion catalyst on the outer surface and a reforming catalyst on the inner surface. Structured catalyst configurations result in high rates of heat transport from the oxidation side to the reforming side. However, in such a configuration catalyst replacement is a problem. A reactor consists of a bundle of small diameter ceramic or metallic tubes enclosed in a thermally insulated vessel. Catalysts are deposited on the internal and external surfaces of the tubes and heat is transferred across the tube walls. Part of the tubes of the autothermal fixed bed reactor may not be covered by catalyst and may act as heat exchange zones. Although this system resulted in a compact configuration the replacement of the catalyst is problematic and as a result the whole reactor must be replaced when the catalyst effectiveness for either the combustion or the reforming reaction declines.



Figure 3. Bulk reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor with structured catalysts and square surface features.

The bulk reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor are presented in Figure 4 with structured catalysts and circular surface features. A surface feature may comprise a recess or a protrusion based on the projected area at the base of the surface feature or the top of the surface feature. If the area at the top of the surface feature is the same or exceeds the area at the base of the surface feature, then the surface feature may be considered to be recessed. If the area at the base of the surface feature exceeds the area at the top of the surface feature exceeds the area at the top of the surface feature, then it may be considered to be protruded. For this description, the surface features may be

described as recessed although it is to be understood that by changing the aspect ratio of the surface feature it may be alternatively defined as a protrusion. The temperatures and pressures of the two streams entering the combustor and the reformer, respectively, need not be the same. Typically, combustion takes place at low or near-atmospheric pressure, although high pressure combustion is widely practiced. For a process microchannel defined by walls that intersect only the tops of the surface features, especially for a flat channel, all surface features may be defined as recessed and it is to be understood that a similar channel could be created by protruding surface features from the base of a channel with a cross section that includes the base of the surface features. As a feature, the integrated combustor-steam reformer assembly includes a tubular section defined by a cylindrical wall and a housing defining an axially extending concentric annular passage in heat transfer relation to each other. A fuel-air mixture is supplied to the tubular section. The inside wall of the tubular section is in contact with a ferroalloy sheet coated with a catalyst that induces the combustion reaction in the feed. A fuel-steam mixture is supplied to the annular passage. The annular passage is either filled with a suitable catalyst in pellet form which promotes the reformation reaction, or it contains, in close contact with the tube, ferroalloy sheets coated with the reforming catalyst. Reforming can take place at pressures somewhat above atmospheric to moderately high. The cylindrical wall of the tubular section should be of sufficient strength to allow for the pressure differential between the two streams. It is also apparent that different geometries can be used instead of cylindrical shapes should they offer advantages in particular applications. The composition of the mixture entering the combustor should be such as to ensure complete combustion of the fuel. Although a stoichiometric ratio of air to fuel is sufficient, higher ratios can be employed. It is typical practice to provide a higher than stoichiometric steam-to-fuel ratio to minimize possible side reactions that can cause carbon formation to the detriment of the catalyst and the reactor. The structured combustion catalyst can preferably be in the form of a corrugated metal foil made of a high temperature resistant metal or metal alloy. A metal alloy such as an alloy with the formula ferroalloy, can be used for high temperature combustion catalyst support. The corrugated foil is supported on a rod or tube placed inside tube. The corrugated foil is wrapped on the tube or rod so that the corrugated channels run parallel to the axis of the tube. Reforming takes place on the catalyst placed in reforming zone enclosed between tube and reactor wall.



Figure 4. Bulk reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor with structured catalysts and circular surface features.

The methanol mole fraction contour plots in the autothermal fixed bed reactor are illustrated in Figure 5 with structured catalysts and square surface features. For some reactions, for example certain single reactions that are chemically irreversible or endothermic, maximizing the reaction temperature is often desired because both kinetics and conversion increase with increasing temperature. However, for many reactions, trade-offs exist between kinetics, equilibrium, and reaction selectivity. For example, reversible exothermic chemical reactions generally exhibit improved reaction kinetics but lower equilibrium conversion with increasing temperature. Lowering the reaction temperature favors higher conversion but typically requires more catalyst and a larger reactor. Accordingly, more efficient utilization of catalyst and reactor resources for a desired conversion likely requires a non-uniform temperature trajectory for the reactants as they progress through the reaction process. For a single reversible exothermic reaction, a theoretical optimum temperature trajectory would start at a high temperature to take advantage of fast kinetics and proceed in monotonically decreasing fashion to lower temperatures to improve conversion. There are also reasons related to energy efficiency to control the temperature trajectory of chemical reactions. For both endothermic and exothermic chemical reactions, greater thermodynamic reversibility, and therefore greater system efficiently can theoretically be achieved with reaction temperature control. Thermal chemical reactions are those chemical reactions that produce or consume heat. Examples of thermal chemical reactions include hydrocarbon conversion reactions such as steam reforming, water-gas shift reactions and combustion. The methanol steam reforming reaction is usually carried out in the presence of a catalyst at temperatures up to about 280 °C. Because the intrinsic kinetics of a thermal chemical reaction can be much faster than the heat transfer rate between the reaction vessel and the thermal sink, source or environment, the actual rate of product production is slower than the intrinsic rate. Intrinsic kinetics means the rate at which products could theoretically be formed at the catalyst surface. The major advantage is the heat integration between the combustion and the reforming zones. Combustion takes place on the catalytic film which is coated on the structured catalyst placed on one side of the wall separating the two zones. The heat that is generated on the combustion side is quickly transferred and used on the reforming side. This rapid heat transfer is critical in maintaining the combustion side catalyst at temperatures below 300 °C and, more preferably, below 280 °C. These temperatures ensure acceptable catalyst life and permit the use of a very compact combustion zone which allows the reactor assembly to be dramatically smaller compared with a flame-based reformer which needs to maintain a significant distance between the flame generation and the reforming sections. The lower temperatures also allow the use of less expensive alloys for the construction of the reactor. The lower temperatures also mean no nitrogen oxide emissions as their formation requires much higher temperatures. When employing a quench type reformer, preheated process gas of methanol and steam is introduced in a first bed with the reforming catalyst and partially converted to a gas containing hydrogen. A part of the hydrogen is then oxidized with oxygen containing atmosphere being introduced into the partial reformed process gas from the top catalyst bed and oxidized in a bed of oxidation catalyst arranged between the top catalyst bed and a subsequent fixed bed of reforming catalyst. Heat evolving from the exothermic oxidation reaction proceeding in the oxidation catalyst bed is, thereby, transferred to the reacting process gas in an amount sufficient to maintain the endothermic reforming reactions in subsequent reforming catalyst bed. The oxygen containing atmosphere may be added to the process gas in several steps, whereby each step is performed. The oxygen containing atmosphere for use in the process, may be any atmosphere containing oxygen in an amount sufficient to the oxidation of the required amount of hydrogen in order to provide the necessary heat for the endothermic reforming reactions at a reasonable reaction rate. The oxygen containing atmosphere may be pure oxygen, oxygen-enriched air, or oxygen depleted air. An advantage by using air or oxygen depleted air in the above process will be that valuable ammonia synthesis gas is produced in the process.



Figure 5. Methanol mole fraction contour plots in the autothermal fixed bed reactor with structured catalysts and square surface features.

The methanol mole fraction contour plots in the autothermal fixed bed reactor are illustrated in Figure 6 with structured catalysts and circular surface features. The heat exchange channels comprise process channels wherein an endothermic reaction is conducted. These heat exchange process channels may be microchannels. Examples of endothermic reactions that may be conducted in the heat exchange channels include steam reforming and dehydrogenation reactions. The heat integrated reforming reactor offers several advantages over conventional flame-based reforming reactors. The incorporation of a simultaneous endothermic reaction to provide an improved heat sink may enable a typical heat flux of roughly an order of magnitude above the convective cooling heat flux. The catalytic combustion takes place at lower temperatures that permit close coupling of the combustion and reforming zones. In a flame-based reformer the flame must be at a significant distance from the tube containing the reforming catalyst to prevent the tube from melting [69, 70]. As a result, the integrated reforming reactor is several times smaller than a flame based reforming reactor and consequently has a much lower capital and installation cost [71, 72]. The flame-based reformers can consist of hundreds of tubes and burners and a sophisticated feed flow distribution system is required to distribute the combustion feed and reforming feed to all burners and tubes evenly [73, 74]. The heat integrated reformer has a single inlet for the reforming and single inlet for the combustion feed gases which results in simple and inexpensive feed flow system [75, 76]. The flame reformers even with the use of low nitrogen oxides burners still produce significant emissions of nitrogen oxides in the combustion gases that have to be controlled with a separate selective catalytic reduction catalyst and ammonia injection [77, 78]. The heat integrated reformer operates at low temperatures on the combustion side at which nitrogen oxides formation is negligible. The catalyst may be in the form of a flow-by structure such as a felt with an adjacent gap, a foam with an adjacent gap, a fin structure with gaps, a washcoat on any inserted substrate, or a gauze that is parallel to the flow direction with a corresponding gap for flow. The catalyst may be directly washcoated on the interior walls of the process microchannels, grown on the

walls from solution, or coated in situ on a fin structure. The catalyst may be in the form of a single piece of porous contiguous material, or many pieces in physical contact. In one case, the catalyst is comprised of a contiguous material and has a contiguous porosity such that molecules can diffuse through the catalyst. In this case, the fluids flow through the catalyst rather than around it. The catalyst may comprise a porous support, an interfacial layer on the porous support, and a catalyst material on the interfacial layer. The interfacial layer may be solution deposited on the support or it may be deposited by chemical vapor deposition or physical vapor deposition. In one case, the catalyst has a porous support, a buffer layer, an interfacial layer, and a catalyst material. Any of the foregoing layers may be continuous or discontinuous as in the form of spots or dots, or in the form of a layer with gaps or holes. The porous support may be a porous ceramic or a metal foam. Other porous supports that may be used include carbides, nitrides, and composite materials. The buffer layer, when present, may have a different composition and density than both the porous support and the interfacial layers, and in one case has a coefficient of thermal expansion that is intermediate the thermal expansion coefficients of the porous support and the interfacial layer. The buffer layer may be a metal oxide or metal carbide.



Figure 6. Methanol mole fraction contour plots in the autothermal fixed bed reactor with structured catalysts and circular surface features.

The surface reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor are presented in Figure 7 with structured catalysts and square surface features. The equilibrium limited chemical process refers to a chemical process wherein at least one measure of the equilibrium extent of the chemical process exhibits substantial temperature dependence over the range of interest. Thermal communication between two areas means that heat can flow from one area to the other. The catalyst can be in the form of pellets or it can be a structured catalyst or monolith. The wall can be constructed from any material, but materials that offer low resistance to heat transfer such as metals and metallic alloys are preferred. In this configuration, heat is generated by combustion in the catalytic chamber and is transported very easily and efficiently though the wall to the reforming chamber where the heat demanding reforming reactions take place. Heat is generated where

it is needed and does not have to overcome significant heat transfer resistances to reach the demand location resulting in high efficiencies. The heat integrated reformer can be easily integrated with a hydrogen producing process that typically consists of a feed pretreatment system to remove impurities from natural gas, heat recovery equipment to recover heat to preheat the feed and raise steam, one or more water gas shift reactors to convert carbon monoxide to hydrogen and pressure swing adsorption system to separate hydrogen from syngas. The waste stream from the pressure swing adsorption system can be used as fuel to the heat integrated reformer combustion side. Another advantage of the hydrogen production process based on a heat integrated reformer is that the makeup natural gas fuel that is normally supplied to ensure stable burner operation in flame-based reformers can be reduced or eliminated. In that case most of the fuel requirement can be supplied by the pressure swing adsorption waste stream. The fuel to the combustor can be any available and suitable fuel. Such fuels include methane, natural gas, propane, butane, methanol, ethanol, higher alcohols, and ethers. The fuels normally available in liquid form must be vaporized before entering the combustion zone. The same fuels can be fed to the reforming zone to undergo the hydrogen producing reforming reactions. Another potential fuel to the combustor is the hydrogen depleted off-gas from the anode of a fuel cell when the reformer is used as a part of a fuel processor producing hydrogen for a fuel cell. Yet another potential fuel to the combustor is the hydrogen depleted off-gas from the pressure swing adsorption or any other hydrogen purification devise when the reformer is used as a part of a fuel processor producing a hydrogen rich stream that feeds such a device to produce high purity hydrogen. In addition to hydrogen, the heat integrated reformer can be used in the production of ammonia, production of methanol, production of ethanol, production of oxo-alcohols and in general in processes where syngas is required. For some processes it may be advantageous to co-feed carbon dioxide in the reforming zone to promote the conversion to carbon monoxide. In yet another application, the heat integrated reformer can be used to produce hydrogen for fuel cells for the production of electricity. The reforming catalyst pellets can be supported in the autothermal fixed bed reactor by a suitable metal plate that is drilled to create holes that are sufficient large that present little resistance to reforming gas flow and keep the pellet catalyst in the desired location in the reactor. This metal plate also serves to distribute the reforming gas feed evenly along the radial dimension of the autothermal fixed bed reactor.



Figure 7. Surface reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor with structured catalysts and square surface features.

The surface reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor are presented in Figure 8 with structured catalysts and circular surface features. A microchannel reactor is preferably designed to achieve a temperature trajectory down the length of the reaction chamber that approaches a predetermined temperature trajectory [79, 80]. Typically, this predetermined temperature trajectory is substantially different from the temperature trajectory that will occur if the reaction is allowed to proceed adiabatically or isothermally [81, 82]. This predetermined temperature trajectory approaches a theoretically determined optimum temperature trajectory based on the reaction rate and design parameters specific to the particular application [83, 84]. Advantages of the process include the enhancement of reaction selectivity due to the dimensions of the microchannel reactor [85, 86]. In reactors of conventional dimension, reactions propagated homogeneously in the in the gaseous phase make a significant contribution to the overall make-up of the product [87, 88]. These reactions tend to be indiscriminate and often result in the production of undesirable by-products or hydrocarbon pyrolysis products. For example, if the reactant mixture contains propane, full and partial oxidation can take place as well as pyrolysis leading to the production of ethane and methane. One method to prepare the catalytic film that ensures good adhesion to the ferroalloy is to heat the ferroalloy sheet to elevated temperatures in air. During the heating, aluminum, which is a component of the ferroalloy, is diffusing out of the bulk of the alloy and forms an aluminum oxide surface layer. Upon this surface layer it is easy to coat alumina or other metal oxide supports for the desired dispersed metal phase which may be a precious or non-precious metal. Typical supports for reforming and combustion catalysts consist of oxides of aluminum, silicon, lanthanum, cerium, zirconium, calcium, potassium and sodium. The metal phase of reforming catalysts may contain nickel, cobalt, copper, platinum, rhodium and ruthenium. Nickel based catalysts are the most commonly used for reforming reactions. The presence of a catalyst and lower temperatures permit significantly higher space velocities to be used compared to flame-based reformers. Space velocity is defined as the ratio of the feed flow at standard conditions to the empty volume of the reactor. The catalyst on the reforming side can be a pellet catalyst or it can also be a structured catalyst on support. In the case of a pellet catalyst, space velocities similar to the ones used in flame-based reformers can be used. The suitable combustion and, where applicable, the reforming catalysts, can be prepared by coating a relatively thin catalytic film on the ferroalloy sheets. Suitable catalysts typically consist of a metal oxide film and one or multiple metal phases dispersed on the film. The most typical combustion catalysts support is high surface area aluminum oxide. A common dispersed metal phase catalyst is palladium or platinum and mixtures thereof. Coating of the catalysts support on the ferroalloy sheets can be accomplished by many techniques. After heating up so as to form the aluminum oxide layer at the surface, techniques such as dip coating from a solution of dispersed metal oxide particles or from a slurry which contains the metal oxide particles can be employed. Alternatively, catalyst can be deposited on the ferroalloy sheets by spraying the catalytic components onto their surface. The catalyst support is then dried by calcination at elevated temperatures. The dispersed metal phase can be added to the support forming solution or slurry of the metal oxide particles or it can be added in a separate step from a solution of the desirable metal salt after the calcination step. The reformer reactor operates in the so-called co-current mode, namely combustion and reforming mixtures flow in the same direction. The same reactor configuration can be employed in operation in the so-called counter-current mode, namely combustion and reforming mixtures flowing in opposite directions. One or multiple baffles are placed inside the reactor and perpendicular to the tubes as to force the reacting mixture in a cross-flow multi-passage path through the reactor. This ensures higher fluid velocities, greater turbulence and better contact with the catalyst pellets which are outside tubes. This in turn results in lower mass transfer resistances in the fluid phase and higher reaction efficiencies while increasing the heat transfer rates as well. The products of the reforming reactions again exit the reactor through the flow passage.



Figure 8. Surface reactant mole fraction profiles at different temperatures along the length of the autothermal fixed bed reactor with structured catalysts and circular surface features.

4. Conclusions

The heat capacity, thermal conductivity, and viscosity of the mixture are calculated as a mass-weighted average of the values for each constituent. In addition, the material properties of each individual species are functions of the local temperature. When solving the species mass transport equations, binary mass diffusion coefficients are used directly. Only isotropic catalyst structures are considered and the permeability and inertial resistance factor are held constant. The effective thermal conductivity of the catalyst structure system including the porous structure and intervening gas is calculated based upon the porosity of the porous medium, the fluid phase thermal conductivity, and the porous medium effective thermal conductivity as measured in air at ambient conditions. The major conclusions are summarized as follows:

- For catalytic thermal chemical reactions, both kinetic impediments are substantially reduced permitting realization of theoretical or near theoretical reaction kinetics.
- The heat transfer chamber is in thermal contact with the reaction chamber volume, the heat transfer chamber transferring heat at the enhanced heat transfer rate across the wall between the heat transfer chamber and the reaction chamber, thereby obtaining the enhanced production rate per reaction chamber volume for the thermal chemical reaction.
- Structured catalyst configurations result in high rates of heat transport from the oxidation side to the reforming side.
- Typically, combustion takes place at low or near-atmospheric pressure, although high pressure combustion is widely practiced.
- The heat that is generated on the combustion side is quickly transferred on the reforming side.
- The heat integrated reforming reactor offers several advantages over conventional flame-based reforming reactors. The incorporation of a simultaneous endothermic reaction to provide an improved heat sink may enable a typical heat flux of roughly an order of magnitude above the convective cooling heat flux.
- The wall can be constructed from any material, but materials that offer low resistance to heat transfer such as metals and metallic alloys are preferred. In this configuration, heat is generated by

combustion in the catalytic chamber and is transported very easily and efficiently though the wall to the reforming chamber where the heat demanding reforming reactions take place.

• The presence of a catalyst and lower temperatures permit significantly higher space velocities to be used compared to flame-based reformers.

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