Exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors

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Abstract

Catalytic reactors for carrying out endothermic or exothermic reactions are of great importance in the particular examples being reactors for the endothermic steam reforming of methanol and reactors for the exothermic catalytic combustion reaction. The present study aims to provide a fundamental understanding of the exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors. Particular emphasis is placed upon the simultaneous implementation of the endothermic steam reforming and the heat-supplying exothermic catalytic combustion such that the thermal stability of the reaction system is increased. The effect of catalyst layer thickness on the reaction characteristics is investigated in order to understand how to design and operate such reactors with high efficiency. The results indicate that unique jet design features can be implemented in order to suppress homogeneous combustion and promote heterogeneous catalytic combustion on the channel wall. Diffusion within these small pores in the catalyst layers is typically Knudsen in nature for gas phase systems, whereby the molecules collide with the walls of the pores more frequently than with other gas phase molecules. The composition in the combustion chamber is reacted to produce sufficient heat to sustain the micro-combustion process without energy input. The combustion and reforming processes can be stably and efficiently operated at lower temperatures, without the need for energy input to sustain or even to start the combustion process. Since a palladium component is alloyed with the zinc, generation of carbon monoxide due to the methanol decomposition reaction is suppressed. Direct heating is of considerable advantage as it largely overcomes the problems encountered with reaction rates being limited by the rate of heat transfer through the tube wall especially near the reformer entrance. The conventional methods are suitable for large scale hydrogen gas production, but they are not adequate for middle to small scale hydrogen gas production. As the channel dimension nears the quench diameter or drops below, the contribution of the unwanted gas phase homogeneous combustion reaction is reduced.

Keywords: Catalytic reactors; Reaction characteristics; Heat exchange; Carbon monoxide; Partial oxidation; Thermal stability

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1. Introduction

The availability of hydrogen is the fundamental condition for use of fuel cells in mobile and stationary applications. As the use of fuel cells is becoming more frequent, for example, in automobiles it makes sense to restrict the operation of the energy generating units of the automobile to one energy source, such as methanol, gasoline, or diesel fuel rather than feeding each energy generating unit from a different source of energy, such as one for the Otto carburetor engine for driving, diesel for the heating system, and methanol for the fuel cell for air conditioning and current supply [1, 2]. For this reason, attempts have been made to utilize the customary fuels for the production of the hydrogen needed for the fuel cell [3, 4]. It is a well-established process in industry to reform higher hydrocarbons or alcohols to hydrogen [5, 6]. However, when applying this reforming process to obtain hydrogen for fuel cells, the equipment known to date still is rather big and, therefore, ill-suited for employment in mobile installations [7, 8]. The cause of another problem in producing hydrogen for fuel cells by way of reforming higher hydrocarbons or alcohols is the complicated nature of the chemical processes that occur in reforming and the consequential difficulty of conducting the reaction [9, 10]. Known aggregates for reforming hydrocarbons or alcohols, therefore, comprise expensive means of control and regulation to handle the complicated reaction processes and thus are not suited for use in mobile installations, such as automobiles.

It is, therefore, necessary to provide an improved process and apparatus for reforming higher hydrocarbons or alcohols, such as gasoline, diesel fuel, methanol, or methane, that will facilitate hydrogen production for a fuel cell in mobile equipment, especially vehicles. The provision and utilization of a microreactor network with its microreactors and microchannels permit high selectivity in influencing the various partial reactions which are intricately interconnected in reforming hydrocarbons or alcohols [11, 12]. The small dimensions of the reaction spaces in the microreactors make it easier to regulate and keep under control the reactions taking place and, therefore, reduce the necessary expenditure for mechanical equipment [13, 14]. It is another advantage that the microreactor network is particularly well suited as a means for producing hydrogen for non-industrial applications [15, 16] because the space requirement of the apparatus has been reduced considerably in comparison with known industrial installations [17, 18]. Apart from application in mobile equipment, the hydrogen obtained from reforming also may be put to use, for example, in fuel cells for housing energy supply systems [19, 20]. The use of microreactors for in-situ and on-demand chemical

production is gaining increasing importance [21, 22] as the field of micro-reaction engineering matures from the stage of being regarded as a theoretical concept to a technology with significant industrial applications.

Various research groups have successfully developed microreactors for chemical processing applications such as partial oxidation of ammonia, nitration and chemical detection [23, 24]. One of the objectives of the research efforts is to demonstrate a working micro-reaction system for use as a sustained source of hydrogen fuel for proton exchange membrane fuel cells through catalytic steam reforming of methanol [25, 26]. The complete reformer-fuel cell unit is proposed as an alternative to conventional portable sources of electricity such as batteries for laptop computers and mobile phones due to its ability to provide an uninterrupted supply of electricity as long as a supply of methanol and water can be provided. Though considerable work already exists in the literature on the catalytic steam reforming of methanol for production of hydrogen using conventional reactors [27, 28], the use of microreactors for in-situ methanol reforming is a relatively new idea. Literature on the macro-scale steam reforming of methanol includes analysis of the reaction thermodynamics for prediction of optimum reactor temperature and feed compositions, catalyst characterization studies, and experimental studies on macro-scale pilot reactors [29, 30]. Results obtained in the study of methanol reforming in these conventional reactors form a good background for the development of prototype microreactors for this purpose [31, 32]. Silicon is considered a good material for fabrication of microreactors due to the high strength of the silicon-silicon bonds which results in the chemical inertness and thermal stability of silicon. Well established silicon micromachining techniques commonly used in the microelectronics industry facilitate easy fabrication of microchannels and other desired features on silicon substrates thus making silicon the preferred material for prototype microreactor fabrication.

The present study is focused primarily upon the exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors. The endothermic reaction is implemented in heat exchange with a heating medium. The endothermic reaction is implemented in heat exchange with an exothermic reaction. The exothermic reaction is implemented in heat exchange with a coolant. The design is described in the example of a process for the production of hydrogen from methanol and a compact reactor that is used in this case for simultaneous implementation of endothermic steam reforming and exothermic catalytic combustion, without being limited thereto. Such processes are essentially based on two catalytic reactions. First, a methanol-containing feedstock is sent into a process for catalytic steam reforming. This reaction is endothermic. The necessary heat for the reaction is supplied by catalytic combustion. The synthesis gas-containing reaction products of catalytic steam reforming are sent as feedstock into a process for further synthesis. Both the steam reforming and catalytic combustion reactions are implemented in compact reactors. Such compact reactors have several plates with flow channels, through which the respective gaseous and liquid media are sent. The media on the individual plates are in indirect heat exchange with one another and vary from plate to plate. The present study aims to provide a fundamental understanding of the exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors. Particular emphasis is placed upon the simultaneous implementation of the endothermic steam reforming and the heat-supplying exothermic catalytic combustion such that the thermal stability of the reaction system is increased.

2. Methods

Steam reforming is a process in which hydrogen is stripped from a hydrocarbon fuel by thermal energy provided by a combustor. In alcohol steam reforming, the feed stream contains steam and an alcohol or alcohols. In the present design, methanol, ethanol, and propanol are preferred with methanol being especially preferred. In an integrated reactor, combustion or heat generation should occur in close proximity to the endothermic reaction. Preferably, an exothermic reaction occurs in microchannels that are interleaved with microchannels in which there is an endothermic reaction. Co-flow of endothermic and exothermic reaction streams is preferred; however, cross-flow or countercurrent flow are also options. The heat of an exothermic reaction is conducted from the exothermic reaction to the endothermic reaction catalyst, where it drives the endothermic reaction. Preferably an exothermic reaction channel and endothermic reaction channel in the integrated reactors is a microchannel, that is, a channel having at least one dimension of 2 millimeters

or less. The use of channels having a minimum dimension of more than 2 mm may be less effective since heat and mass transfer limitations may be magnified. An integrated combustor can use the high surface area of reactor microchannels to remove heat as it is produced, thus keeping microreactor components from exceeding material temperature constraints while combusting with much less excess air or diluent than would be necessary for an external combustor. The flow rate of reactants will depend on the desired amount of hydrogen to be produced and on the minimum or maximum capacity of the steam reformer. The rate of combustion can be controlled to provide the desired amount of heat to a steam reforming reaction in an adjacent reforming chamber. The steam reforming reaction can be run over a broad pressure range from sub-ambient to very high. The alcohol steam reforming reaction is preferably carried out at temperatures of 200-400 °C, more preferably 220-300 °C, and in some cases 240-270 °C. In some preferred configurations, the combustion temperature is approximately the same as the average reformer temperature, that is, the average temperature of the reforming catalyst.

The design provides a method of conducting an endothermic reaction in an integrated combustion reaction, comprising: passing an endothermic reaction composition into at least one endothermic reaction chamber, passing a fuel and an oxidant into at least one exothermic reaction chamber wherein the fuel and oxidant each have a contact time in the combustion chamber of 50 milliseconds or less, wherein the exothermic reaction chamber comprises at least one exothermic reaction chamber wall that is adjacent at least one endothermic reaction chamber. The endothermic reaction chamber comprises an endothermic reaction catalyst in contact with at least the at least one endothermic reaction chamber wall that is adjacent at least one exothermic reaction chamber, and transferring heat from the at least one exothermic reaction chamber into the at least one endothermic reaction chamber at a rate as based on the internal surface area of the endothermic reaction chamber. The heat flux can be measured based on either a single exothermic reaction chamber or multiple chambers in a multi-chamber device. The reformate stream usually comprises hydrogen, carbon dioxide, and carbon monoxide. Proton exchange membrane fuel cells operate have a very low tolerance for carbon monoxide. They can generally tolerate carbon dioxide and some other gases such as nitrogen, but only up to a certain amount. Clean-up of a reformate stream can be performed, for example by a multi-step process consisting of water gas shift reactors, combined with selective oxidation and carbon monoxide methanation, or by the use of a hydrogen permeable membrane. Direct methanization of a reformate stream is important without first passing the reformate through a hydrogen-selective membrane, preferential oxidation, or water gas shift reactor. This is highly desirable since hydrogen-selective membranes are expensive, and additional process steps can be costly and result in lowered yield. Eliminating the requirement of a preferential oxidation also eliminates the need to add oxygen, including the need to vary oxygen content to account for fluctuations in carbon monoxide concentration. In preferred cases, the process adds heat to the steam reforming step but does not have additional heat exchangers or heat exchange steps for methanation or for other carbon monoxide-reducing steps.

The exothermic reaction chamber has an internal dimension of less than 0.8 mm and a volumetric heat flux, based on reaction chamber volume of greater than 8 Watts per cubic centimeter. Contact times in the exothermic and endothermic reaction chambers are preferably less than 600 milliseconds. Area heat flux for the area of either reaction chamber is preferably 0.8 Watts per square centimeter or more. The design provides a method of steam reforming in an integrated combustion-reforming reactor, comprising: step a) passing steam and hydrocarbon into at least one endothermic reaction chamber wherein the steam to carbon ratio is less than 2:1 with a pressure drop through the endothermic reaction chamber of less than 6000 kPa, step b) passing a fuel and an oxidant into at least one exothermic reaction chamber wherein the fuel and oxidant each have a contact time in the combustion chamber of 600 milliseconds or less, wherein the exothermic reaction chamber comprises at least one exothermic reaction chamber wall that is adjacent at least one endothermic reaction chamber, wherein the endothermic reaction chamber comprises an endothermic reaction catalyst in contact with at least the at least one endothermic reaction chamber wall that is adjacent at least one exothermic reaction chamber, step c) converting the steam and hydrocarbon to form carbon monoxide and hydrogen such that the at least one endothermic reaction chamber has an output demonstrating a conversion of at least 50 percent of the hydrocarbon with a selectivity to carbon monoxide of at least 50 percent. A

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device is characterized by operation for 200 or 500 hours and then cut open to reveal less than 0.08 gram of coke per each kilogram of the fuel processed.

The endothermic reaction chamber and the combustion chamber are separated by a thermally conductive wall. The endothermic reaction composition endothermically reacts to form products. Where not otherwise specified, the front of the combustion chamber is defined as where the flow of fuel contacts a combustion catalyst and an oxidant, and the back of the combustion chamber is defined as the last part of the reaction chamber that contains a combustion catalyst and is in direct thermal contact with an endothermic reaction chamber. The exhaust section is not in direct thermal contact with the endothermic reaction chamber. The design also provides a method of simultaneously conducting an endothermic and an exothermic reaction in an integrated combustion-reforming reactor, comprising: passing a mixture comprising hydrogen and methanol through a microchannel in an integrated combustion-reforming reactor; reacting the hydrogen and methanol with an oxidant to form water, carbon dioxide and carbon monoxide and produce heat, thus removing hydrogen and methanol from the mixture; wherein a greater percentage of methanol is removed from the mixture than the percentage of hydrogen removed from the mixture, as measured by comparing the levels of hydrogen and methanol in the mixture before passing through the microchannel with the levels of hydrogen and methanol at any point after passing through the microchannel. This is an extremely surprising result. The removing steps are by chemical reactions, not separation techniques.

An integrated combustion-reforming reactor refers to an integrated reactor that includes at least one combustion channel adjacent to at least one endothermic steam reforming reaction channel. During operation, a reactant enters a combustion or reaction chamber in a bulk flow path flowing past and in contact with a porous material or porous catalyst. In these cases, a portion of the reactant molecularly transversely diffuses into the porous catalyst and reacts to form a product or products, and then the products diffuse transversely into the bulk flow path and out of the reactor. The term bulk flow region or bulk flow path refers to open areas or open channels within the reaction chamber. A reaction chamber with a bulk flow path or region will contain a catalyst and there is a gap between the catalyst surface and a reaction chamber wall or a second catalyst surface. A contiguous bulk flow region allows rapid gas flow through the reaction chamber without large pressure drops. In preferred cases, there is laminar flow in the bulk flow region. Equilibrium conversion is defined in the classical manner, where the maximum attainable conversion is a function of the reactor temperature, pressure, and feed composition. For the case of hydrocarbon steam reforming reactions, the equilibrium conversion increases with increasing temperature and decreases with increasing pressure. Fuel flow to combustor can be initiated at this point. Once the fuel has begun reacting, the hydrogen flow is tapered off and the fuel flow is increased. The excess air should not be too much, since the extra air removes heat from the steam reformer. Air and methanol flows are adjusted until the steam reformer is at the desired temperature. The reformer fuel mixture flow is initiated at this point. Combustor flows are adjusted as necessary to maintain desired temperatures. Preferred forms of porous supports are foams and felts and these are preferably made of a thermally stable and conductive material.

The methanol conversion is calculated by using a carbon balance on the system. Reaction chamber volume is the internal volume of a reaction chamber either exothermic or endothermic. This volume includes the volume of the catalyst, the open flow volume if present and metal support ribs or fins if present within the reaction chamber volume. This volume does not include the reaction chamber walls. The reaction chamber volume must contain a catalyst somewhere within its cross-section and must be directly adjacent another reaction chamber for heat transport. This volume is used for calculations of endothermic reaction chamber volumetric heat flux, area heat flux, and endothermic reaction contact time. The reactor core volume is defined as the reaction chamber volume and all combustion chamber volume and the metal webs that separate the two chambers. The combustion chamber volume is defined as the chamber volume in which the exothermic heat generating reaction occurs and is adjacent to the reaction chamber volume. Perimeter metal is not included in reactor core volume. The reactor core volume does not include any preheat exchanger zone volume that may or may not be attached to the reactor core volume. The preheat exchanger zone may be attached to the reactor but does not contain an endothermic reaction catalyst along any plane that bisects the device orthogonal to the direction of flow. The use of electric heating for system start-up is eliminated

by following the subsequent procedure. Hydrogen and air are fed to combustor to initiate combustion and heat the vaporizers. Once the vaporizers are heated to approximately 80 °C, methanol is fed to the vaporizer. The hydrogen is slowly tapered off as the methanol feed is increased until only methanol and air are being fed to the combustor and the device is completely self-sustaining. The methanol-air mixture is adjusted until the steam reformer reaches the desired temperatures depending on the conditions being tested. The methanol-water solution feed is then initiated.

Endothermic reaction chamber heat flux is defined as the endothermic reaction heat duty divided by the reaction chamber volume. Reactor core volume heat flux is defined as the endothermic reaction heat duty divided by the reactor core volume. Heat exchanger flux is defined as the total heat transferred to the cold streams divided by the heat exchanger core volume. Heat exchanger core volume is defined as the total heat exchanger volume inclusive of microchannels, ribs between microchannels, and the walls separating microchannels for all fluid streams transferring heat. The heat exchanger volume is inclusive of the heat exchanger zone. The heat exchanger core volume does not include the perimeter metal or manifolds or headers. The heat exchanger core volume does not include the endothermic reaction chamber nor any volume that could be included within any plane that bisects the endothermic reaction chamber orthogonal to the direction of flow. Average area heat flux is defined as the endothermic reaction heat duty divided by the area of the endothermic reaction chamber heat transfer surface. The endothermic heat transfer surface is defined by a planar area, which may be intermittent in the case of ribs or other structures in the endothermic reaction chamber, above which there is area for flow of reactants and below which there is a wall that separates the endothermic reaction chamber and the exothermic reaction chamber. This area is the path for heat transfer from the exothermic reaction chamber to the endothermic reaction chamber. The apparent equilibrium conversion temperature is the apparent temperature based on methane conversion or, more generally, hydrocarbon conversion or the temperature required to produce an equilibrium methane conversion equal to the measured methane conversion at the measured average process pressure. Average process pressure is assumed to be the average of the measured inlet and outlet pressures.

3. Results and discussion

The methanol mole fraction contour maps are illustrated in Figure 1 for the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. Channels refers to the generally accepted meaning and includes conduits and other means for directing the flow of a fluid. Channels include at least one opening, typically with an inlet and outlet, and may include other openings. Fluid communication between two areas means that a fluid can flow from one area to the other. Thermal communication between two areas means that heat can flow from one area to the other. Heat exchanger is a device or component designed such that heat can be transferred from one fluid to another. The heat source for the endothermic reaction is delivered directly to the wall in contact with the endothermic catalyst. This follows from the fact that metal conduction is a more efficient mode of heat transfer than either convective or radiative heat transfer. In contrast to premixed combustion, where the heat release will occur primarily in the homogeneous phase, combustion jets can direct a concentrated stream of air into a separate fuel channel stream. The two streams subsequently mix and undergo an oxidation reaction. In order to suppress homogeneous combustion and promote heterogeneous catalytic combustion on the channel wall, unique jet design features can be implemented. Important features include geometry, size, and relative location and spacing. The jets should not only impinge on the wall but also spread out the combustion oxidant as uniformly as possible along the entire width of the channel. Furthermore, heterogeneous combustion is preferably concentrated at the combustion wall in closest proximity to the endothermic reaction catalyst. Combustion on other walls represents a heat loss and furthermore has a disadvantageous impact on thermal stresses in the device. In order to raise the temperature of an endothermic steam reforming reaction and reduce the likelihood of coke formation at the beginning of the reactor zone or in the heat exchanger zone reactant or product channels, more air should be delivered for combustion against the wall at the beginning of the reactor zone. Concentration of jets in this region as well as application of non-circular jet orifices can successfully meet this objective. All the goals above are desired to be accomplished with a minimal pressure drop for both economic reasons as well as for the purposes of preserving back pressure in the

integrated combustion-reforming reactor device to ensure good flow distribution. To this end, a hybrid of circular and rectangular slot orifices can be implemented in the jet design. Alternatively, other non-rectangular non-circular jets could be used such as diamonds, triangles, semi-circles, quarter-moons, and the like. Computational fluid dynamics predictions indicate that a combination of these two jet geometries provide a more ideal heterogeneous fuel-oxidant mixture distribution on the combustion channel wall opposite the jet shim. It is recognized that other non-circular jet orifices could also be used at the entrance of the combustion zone or anywhere down the length of the reactor. It is also recognized that the combustion orifices could start before the reaction zone in the recuperative heat exchanger section to further preheat the reactants or further tailor the thermal profile of the device.
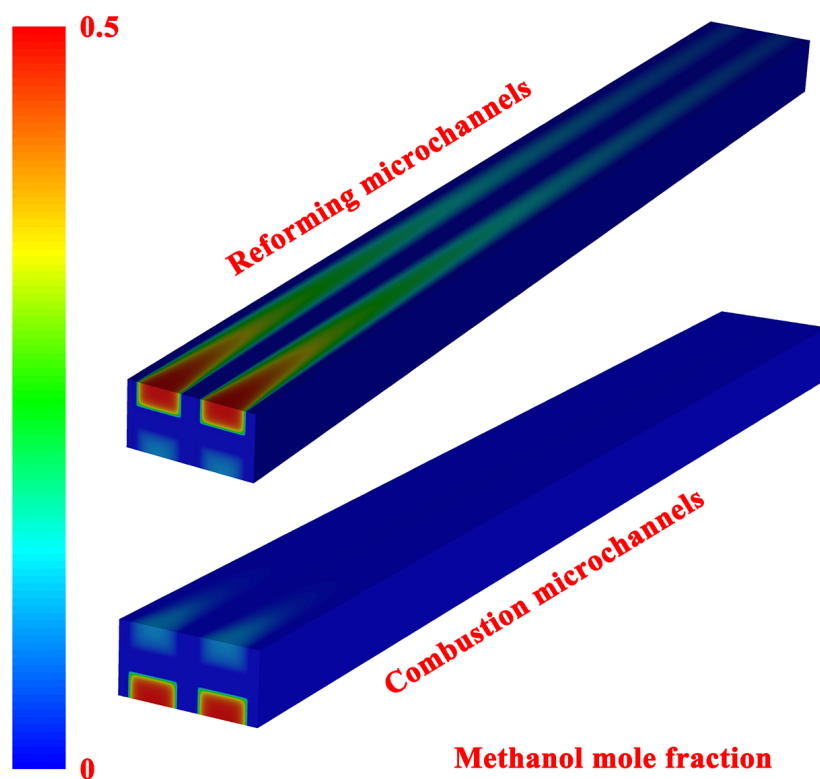

Figure 1. Methanol mole fraction contour maps in the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The hydrogen mole fraction contour maps are illustrated in Figure 2 for the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. Control of the relative proportion of homogenous and heterogeneous combustion can be achieved by manipulation of the jet design [33, 34]. Either homogeneous or heterogeneous combustion can be increased as needed depending upon the application. As an example, a microchannel combustor that does not include an endothermic reaction may be enhanced via jet design by promoting homogenous combustion to reduce methanol or carbon monoxide emissions or to provide a hot gas stream for subsequent use in a unit operation. The distribution of jet orifices may depend on the intended use of the device. Hydrogen burns immediately, thus, to avoid hot spots, the jets should be spaced more evenly over the combustion chamber. Methane, which burns more slowly, preferably has jets loaded near the front of the combustion chamber. When the fuel is syngas, the distribution of jets is intermediate. The endothermic and exothermic reaction chambers preferably contain catalysts [35, 36]. Catalysts suitable for catalyzing a

selected exothermic or endothermic reaction are well known to chemists and chemical engineers. Catalysts, especially an endothermic catalyst, can be a porous catalyst. Pore sizes in the range of about 0.6 to 600 microns enable molecules to diffuse molecularly through the materials under most gas phase catalysis conditions. The porous material can itself be a catalyst, but more preferably the porous material comprises a metal, ceramic or composite support having a layer or layers of a catalyst material or materials deposited thereon. The porosity can be geometrically regular as in a honeycomb or parallel pore structure, or porosity may be geometrically tortuous or random. The support of the porous material is a foam metal, foam ceramic, metal felt, or metal screen. The porous structures could be oriented in either a flow-by or flow-through orientation. The catalyst could also take the form of a metal gauze that is parallel to the direction of flow in a flow-by configuration. Alternatively, the catalyst support could also be formed from a dense metal shim or foil. A porous catalyst layer could be coated on the dense metal to provide sufficient active surface sites for reaction. An active catalyst metal or metal oxide could then be wash-coated either sequentially or concurrently to form the active catalyst structure. The dense metal foil or shim would form an insert structure that would be placed inside the reactor after bonding or forming the microchannel structure. Preferably, the catalyst inserts contact the wall or walls that are adjacent both the endothermic and exothermic reaction chambers. The porous catalyst could alternatively be affixed to the reactor wall through a coating process. The coating may contain a first porous layer to increase the number of active sites. Preferably, the pore diameter ranges from tens of nanometers to tens of microns. An active metal or metal oxide catalyst can then be sequentially or concurrently wash-coated on the first porous coating. The average pore size of the catalyst layers is preferably smaller than the average pore size of the support. Diffusion within these small pores in the catalyst layers is typically Knudsen in nature for gas phase systems, whereby the molecules collide with the walls of the pores more frequently than with other gas phase molecules. The catalyst, which is not necessarily porous, could also be applied by other methods such as wash coating. On metal surfaces, it is preferred to first apply a buffer layer by chemical vapor deposition and thermal oxidation, which improves adhesion of subsequent wash coats. The methanation catalyst can be a single material or a mixture of materials such as a methanation catalyst powder between methanation catalyst felts. A small reforming chamber, such as having a diameter of 0.8 mm or less provides superior results by enhancing uniformity of conditions such as reducing hot and cold spots and reducing channeling through a powdered catalyst. In this case, the reforming chamber is defined at one edge by the methanation catalyst. Where the catalysts are powders, there will not be a sharp delineation between reforming and methanation zones and some methanation catalyst powder will intermix with the reforming catalyst powder so that some methanation catalyst is present within the reforming chamber. The reforming chamber volume is defined by the volume where there is a significant amount of reforming catalyst such that a reforming reaction could take place under normal operating conditions. Methanol and water can be injected at room temperature into an inlet tube where they will be vaporized by heat conducted through the tube from the methanation and reforming catalysts. In practice, fuel processing systems may be significantly more complex. For example, heat from a combustor can also be used to supply heat for other processes such as steam generation that can be utilized for a steam reformer, autothermal reactor and water gas shift reactor. Heat loss is a function of surface area, lowering surface area for the same amount of heat reduces heat loss and puts thermal energy exactly where it is needed. Therefore, in some preferred designs, surface area is minimized. For example, in some environments, cylindrical reforming and combustion channels can perform better than planar geometries. Heat from the combustion chamber transfers through the thermally conductive wall into the endothermic reaction chamber and along the length of the endothermic reaction chamber where less than 8 percent of total heat flux into the endothermic reaction chamber is perpendicular to length.
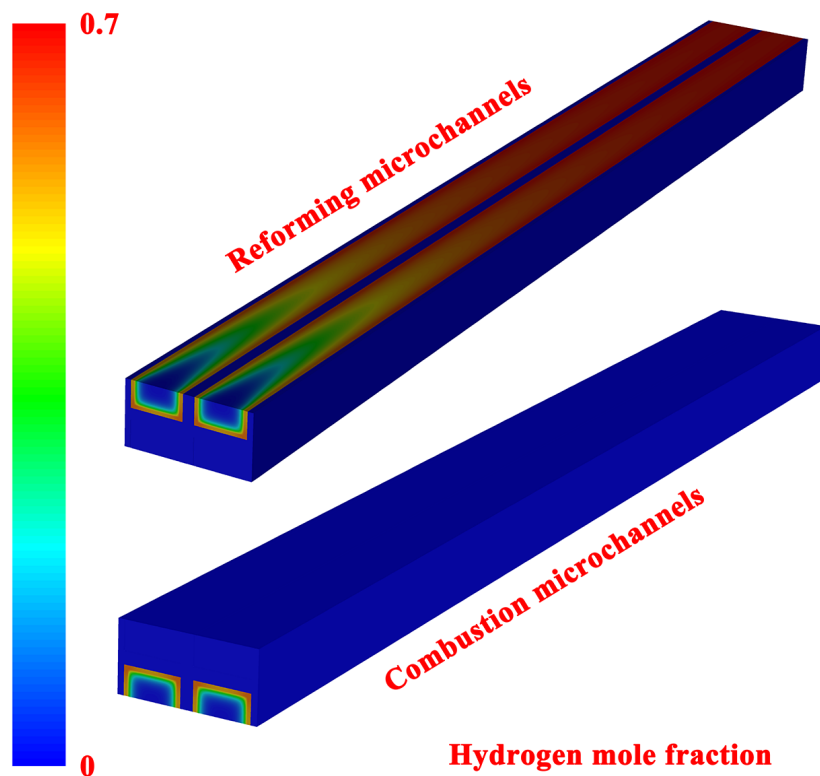
Figure 2. Hydrogen mole fraction contour maps in the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The chemical enthalpy profiles along the length of the integrated combustion-reforming reactor are illustrated in Figure 3 in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. The inlet and outlet of the combustion chamber are in fluid communication with combustion fuel and combustion exhaust channels, respectively, and the inlet and outlet of the reformation chamber are in fluid communication with reformation fuel and reformation products channels, respectively. The combustion fuel channel is disposed along the axis on a side of the combustion chamber opposite the reformation chamber. The reformation fuel channel is disposed along the axis on a side of the reformation chamber opposite the combustion chamber. The reformation products channel is disposed outside the reformation fuel channel with respect to the axis and on the side of the reformation chamber opposite the combustion chamber, and the combustion exhaust channel is disposed outside the reformation fuel channel with respect to the axis and on the side of the reformation chamber opposite the combustion chamber. The combustion catalyst comprises a porous matrix arranged such that sufficient mixture flows through the catalyst to maintain combustion at a temperature of at most about 548 K. The composition in the combustion chamber is reacted to produce sufficient heat to sustain the micro-combustion process without energy input. The combustion of a combustion fuel in a combustion chamber is maintained so as to transfer heat from the combustion chamber to the reforming chamber. The temperature difference between the combustion chamber and the reforming chamber is at most about 80 K. A composition comprising fuel and oxidant is passed into a combustion chamber and, simultaneous to the step of reacting steam and methanol, the fuel and oxidant in the combustion chamber are reacted to produce heat. The reforming chamber and the combustion chamber are separated by a thermally conductive layer. Heat is transferred from the combustion chamber to the reforming chamber. The average thermal transport dis-

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tance from the combustion chamber to the reforming chamber is 0.8 mm or less. This thermal transport distance is measured from the area within a combustion zone where combustion occurs. The above aspect of the design is typically associated with at least one of the following characteristics: at least 80 percent of the fuel is oxidized in the combustion chamber and the thermal efficiency of the method is at least 8 percent; hydrogen gas production of at least 60 standard cubic centimeters per minute hydrogen per cc of steam reformer volume; or hydrogen gas production of at least 0.8 standard cubic centimeters per minute hydrogen per cubic centimeter of device volume. The design provides a method of steam reforming that includes: passing a reformation gas through a reforming chamber, maintaining combustion of a combustion fuel in a combustion chamber so as to transfer heat from the combustion chamber to the reforming chamber. The reforming chamber is configured such that the volume of the chamber increases as a function of distance from a reaction chamber inlet; and reformation gas and products expand as they pass through the reforming chamber. A thermally conductive wall is disposed between the combustion chamber and the endothermic reaction chamber. The combustion catalyst is disposed on a side of the endothermic reaction chamber such that, during operation, heat from a combustion reaction on the combustion catalyst is transferred along the length of the reforming chamber. Length is the direction of a chamber that is parallel to flow through the chamber. Length, height and width are mutually perpendicular. Relatively short deviations in the direction of flow, such as flow from the tube toward and down the separator plate does not change the direction of length which is determined by the primary direction of flow through or past a catalyst. This aspect excludes parallel plate type configurations where a significant component of heat transfer is perpendicular to length. In this method, a fuel combusts on the catalyst and generates heat in the combustion chamber.
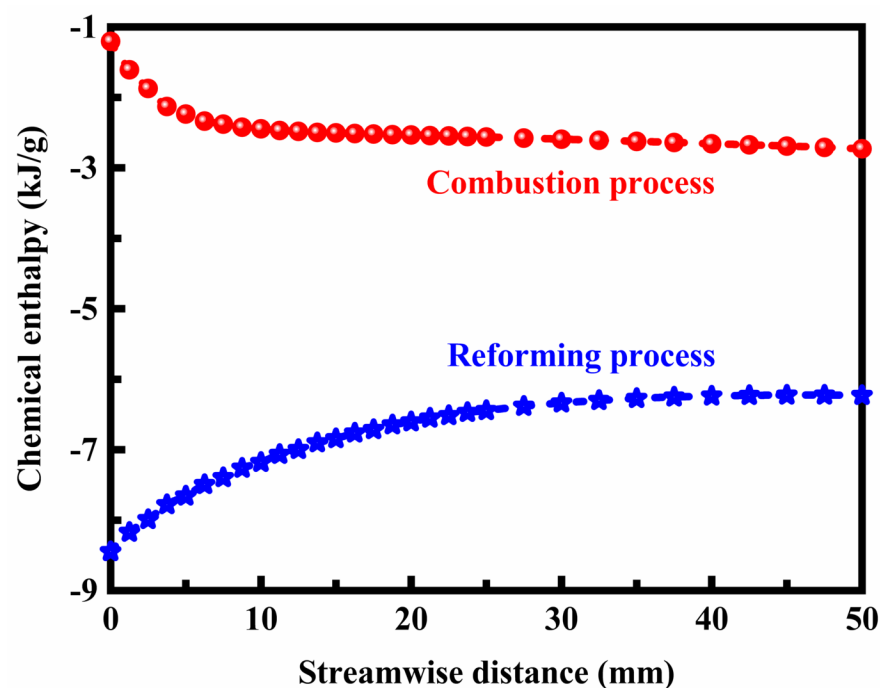

Figure 3. Chemical enthalpy profiles along the length of the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The sensible enthalpy profiles along the length of the integrated combustion-reforming reactor are illustrated in Figure 4 in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. The present design can provide numerous advantages. First, light-weight and compact energy sources can be obtained [37, 38]. Further, the rapid heat and mass transfer in a small

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device can enable the use of extremely active catalysts, catalyst which are active at low temperature, and catalysts with high throughput per volume [39, 40]. It is also possible to control process conditions, such as operating temperature, very precisely, so that high performance can be attained. The fuel combustion and steam reforming processes can be stably and efficiently operated at lower temperatures, without the need for energy input to sustain or even to start the micro-combustion process. In some instances, the micro-combustor is started with hydrogen or vapors such as methanol. Heat losses can be effectively controlled and reduced. Another advantage is that the simplicity of the design and the materials used enable mass production at competitive costs. Advantages can also include higher conversions, lower carbon monoxide selectivity, and simplicity of design. Another advantage that results from small size is better control of heating and uniformity of temperature in a reaction zone. Another advantage is an extremely fast response time, that is, a change in fluid flow can result in a nearly instantaneous change in temperature. Further, the micro-combustor or micro-reformer can be part of an efficient integrated system, which can reform lower hydrocarbons and even higher hydrocarbons that require higher processing temperature, such as butane. Carbon dioxide selectivity over carbon monoxide, a poison to fuel cells, of the steam reforming process is high, so that it is possible to avoid or reduce requirements for removing carbon monoxide after reforming and before supplying the gas to the fuel cell, thereby greatly simplifying the overall system and reducing system size. Since catalytic combustion is used, stable low temperature performance is easily attained for the combustor to provide uninterrupted operational heat for vaporizers and steam reformer units so they may operate in a steady optimum manner. The low temperature operation and manufacturing made possible by the design allows a greater choice of insulating materials, enables greater use of materials with dissimilar thermal expansion coefficients, and enables manufacture on semiconductor chips. The combustors and reformers can be made from plastic. There are numerous advantages of manufacturing in plastic including low weight and less required insulation. Additional advantages include: more design options, cheap high-volume manufacturing, eliminating the need for expensive manufacturing machines compared to the equipment used in silicon processing, and inexpensive materials. A thermal cycle is heating a device up to operational temperature, operating the device at an operating temperature and observing the results, and cooling the device to about room temperature. Thermal efficiency is calculated by dividing the lower heating value of the hydrogen in the reformats stream by the total heating value of the methanol fed the reformer plus the heating value of the fuel fed to the combustor. Volume of a combustor, combustion chamber, reformer chamber or reformer, unless otherwise indicated, refers to the internal volume where reaction substantially occurs but not adjacent material. Where a catalyst is present, the volume includes at least the catalyst volume and catalyst void fraction. Volume of a device, unless otherwise indicated, refers to the combustor and reformer volume and the volume of any intervening and integral components such as heat exchangers, preheaters, vaporization chambers, and recuperators. By directing the flow in this manner, a temperature gradient is established between the center and the outer edges of the catalyst bed with the highest temperature at the center of the thermally conductive transverse separator plate located between the two reactor chambers; thus, minimizing heat loss through the reactor walls. That a fuel combusts on the combustion catalyst means contacting a fuel with a solid catalyst, including within a porous catalyst or over a catalyst coating. The efficiency could be substantially improved by removing the thermocouple and by use of improved insulator materials such as metallized polyimide, and it is believed that with these improvements the devices can be thermally efficient. The steam may be introduced by direct injection of steam and by saturation of the feedstock by contact of the latter with a stream of heated water. The amount of steam introduced is preferably such as to give a steam ratio in the range 2 to 3.5 moles of steam per gram atom of methanol carbon in the feedstock.
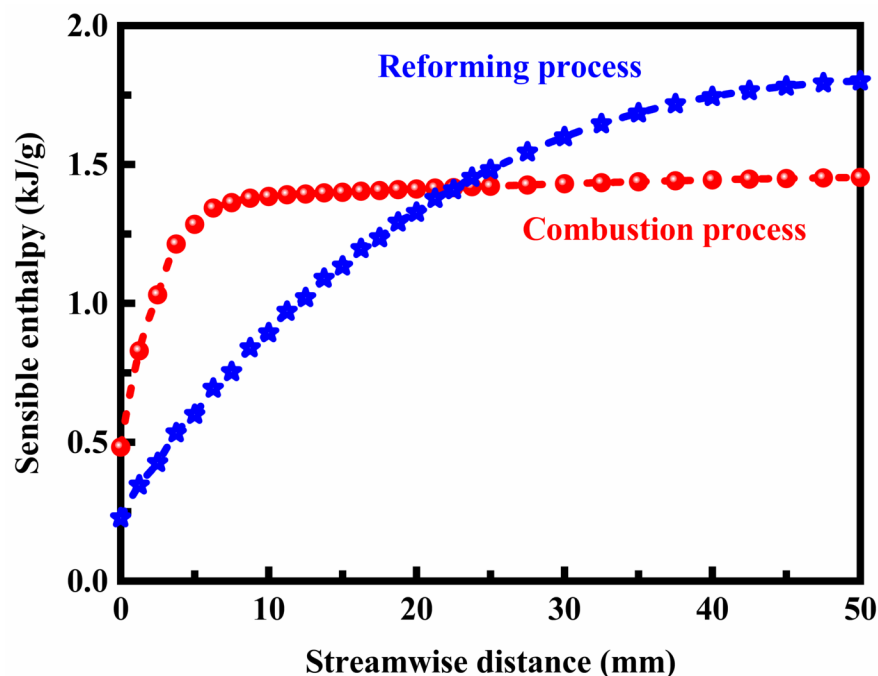
Figure 4. Sensible enthalpy profiles along the length of the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The temperature contour maps are illustrated in Figure 5 for the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. In the steam reformation of methanol, methanol is reacted with water to give hydrogen and carbon dioxide and also carbon monoxide. In addition to industrial processes for synthesis gas production, in particular applications in mobile systems such as fuel cells are of importance. Fuel cells require hydrogen which can be produced by steam-reforming methanol. For vehicle drives or mobile fuel cells, for example, it is of importance here to be able to carry out the steam reformation in a small reactor of low weight. This is made possible, in particular, by catalysts which catalyze the reaction of methanol and water and have a high activity with low volume. In this case it is useful to make up the catalysts in tablet form, in which case the tablets are to have very small dimensions, in order to achieve a high bulk density and a high ratio of surface area to volume. Also, a copper-based catalyst is excellent in low temperature activity and selectivity, but has the problem of heat resistance. In particular, since the activity and the selectivity are extremely reduced under the high temperature in excess of 300 °C, it is difficult to use such catalyst for a long time under the high temperature. In addition to this, metallic copper as active species is oxidized and sintered under the atmosphere containing the oxygen to cause the reduction in the activity. In contrast, a palladium-based catalyst that has strong resistance against the high temperature oxidizing atmosphere has the problem that it promotes the decomposition reaction of the methanol and thus generates a large quantity of carbon monoxide that is injurious to the fuel cell. It is an object of the present design to provide a methanol reforming catalyst capable of maintaining a high activity with good stability even in a high temperature and oxygen atmosphere while suppressing carbon monoxide generation. Since a palladium component is alloyed with the zinc, generation of carbon monoxide due to the methanol decomposition reaction is suppressed. Also, since both the palladium-zinc alloy and the metal oxide as the support are stable in the high temperature oxidizing atmosphere, the partial oxidation reaction as the exothermic reaction using the oxygen gas is proceeded simultaneously with the steam reforming reaction as the endothermic reaction or prior to the steam reforming reaction. That is, auto thermal reaction that proceeds the steam reforming reaction by utilizing

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the heat generated by the partial oxidation reaction is proceeded stably. A fuel cell of the present design comprises the methanol reforming apparatus, a fuel cell, a pipe supplying a gas reformed by the reforming apparatus to the fuel cell, and a pipe supplying an oxygen-containing gas to the fuel cell. Since the reforming apparatus having the above methanol reforming catalyst is used, the size reduction of the overall fuel cell system can be achieved. Therefore, the fuel cell system is suitable for the fuel cell system which is installed in the mobile body such as a car and a ship whose apparatus size is limited. The steam reforming reaction is an endothermic reaction and is normally affected by passing a mixture of the desulphurized methanol feedstock and steam through tubes containing a steam reforming catalyst, normally nickel supported on a shaped support such as rings of alumina or a calcium aluminate cement, while strongly heating the tubes. The tubes are usually heated in a furnace fueled with a suitable methanol-containing stream; alternatively, the tubes may be located within a high temperature convective heat exchange reformer. In this type of heat exchange reformer, the catalyst is disposed in tubes extending between a pair of tube sheets through a heat exchange zone. Reactants are fed to a zone above the upper tube sheet and pass through the tubes and into a zone beneath the lower tube sheet. The heating medium, for example the hot product of combusting a fuel with air, is passed through the zone between the two tube sheets.
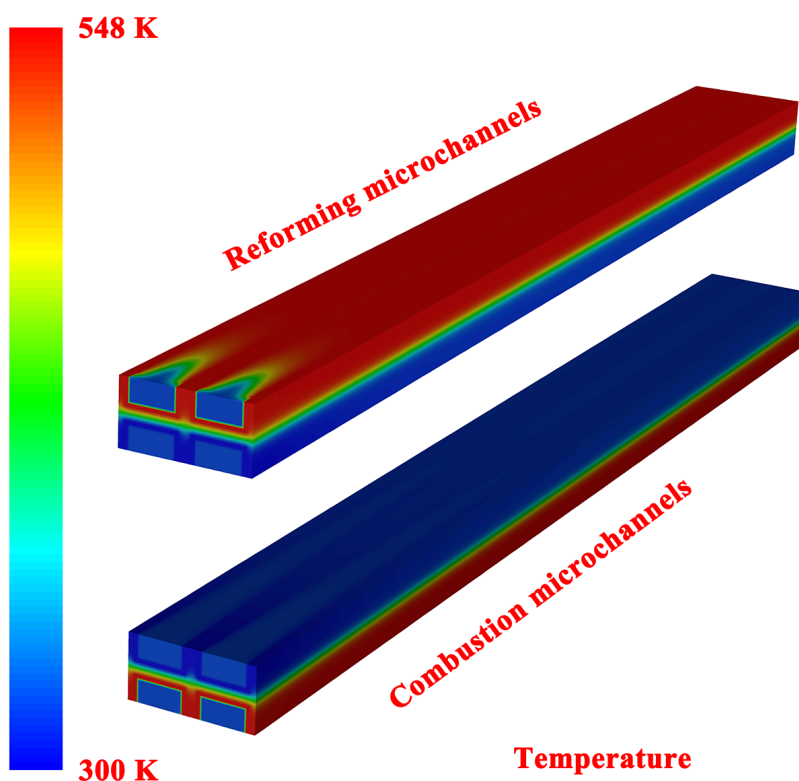

Figure 5. Temperature contour maps in the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The steam mole fraction contour maps are illustrated in Figure 6 for the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. For efficient operation of the steam reforming reaction, large surface areas are required to transfer the heat from the combusted gases to the tubes [41, 42]. In reformers presently used for steam reforming small diameter reaction tubes are clustered closely together in the furnace so that heat transfer from the combusting gases in the reactor into the catalyst packed tubes is optimized [43, 44]. The use

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of a plurality of tubes to accomplish heat transfer contributes to the large size and high cost of the reformer. In fuel cell systems in which the reformer and the fuel cell are fully integrated, namely the combustion gases for the reforming reaction are derived from the fuel cell exhaust, the shell side heat transfer coefficient between the hot gas and the tube is characteristically low and hence, the rate of reaction is limited primarily by the rate of heat transfer. This problem is particularly severe at the reactor entrance as the rate of the endothermic reaction is very high, and thus, the amount of heat required is very high while the shell side heat transfer coefficient is often low as the mechanical design of typical reactors often allows the gases in the shell to be relatively stagnant near the tube entrances. This leads to a drop in the overall efficiency as a large portion of each reactor tube operates at an undesirably low temperature. Thus, in order to effect complete conversion, the reformer must be relatively large and expensive. It is the primary object of the present study to provide a novel process and apparatus for the production of hydrogen by steam reforming of methanol that can be accomplished with a thermally efficient reformer of reduced size and cost which can be integrated with a fuel cell power system or used as a standalone hydrogen generator. Production of hydrogen by steam reforming of methanol or other hydrocarbon fuels is accomplished in a reformer of substantially reduced size by superheating a gaseous mixture of water and methanol to a temperature of about 548 K and then passing the superheated gaseous mixture over a catalyst bed contained in a reformer. At least a substantial portion of the heat for the endothermic steam-methanol reforming reaction is provided by the sensible heat in the superheated steam-methanol stream augmented by heat transferred through the tube wall depending on the overall system considerations. The concept of providing a substantial portion of the heat for the endothermic reforming reaction by sensible heat in the superheated steam-methanol stream is referred to hence forth as direct heating. Direct heating is of considerable advantage as it largely overcomes the problems encountered with reaction rates being limited by the rate of heat transfer through the tube wall especially near the reformer entrance and thus, for a given conversion, the reactor may be smaller, more efficient and less expensive. High steam-to-methanol ratios are required for direct heated reformers. The relatively large amounts of steam passed through the bed continuously clean the catalyst by removing ethanol and suppressing production of carbon monoxide and retard catalyst poisoning thereby enhancing catalyst stability. Direct heated reformers are particularly suitable for integration with fuel cells as the heat and fuel values contained in exhaust stream from each component can be utilized in the other. Hydrogen contained in the exhaust gas from the fuel cell anode may be burned to superheat the methanol-water mixture being fed to the reformer. Once the reactor is warmed up, the entire fuel requirements for the system are provided by the methanol being fed to the reformer. In order to accommodate the endothermicity of the reforming reaction, at least a major portion of the heat required for reforming is provided to the reformer as sensible heat contained in the superheated gases. Thus, when methanol and steam vapors contact a catalyst such as a combination of zinc oxide and copper oxide at a temperature of about 548 K at atmospheric or higher pressure, methanol decomposes to carbon monoxide and hydrogen and the carbon monoxide and steam react according to the well-known water gas shift reaction to form carbon dioxide and hydrogen. High exhaust gas temperatures may be indicative of unreacted fuel entering the exhaust chamber while low exhaust gas temperatures are indicative of a low fuel feed rate, or an unreactive catalyst bed. The efficiency decreased because the thermal losses as a percent of the total amount of power fed to the device increases as the size is reduced. In reactor configurations comprising solid catalyst particles disposed as a bed outside a plurality of heat transfer tubes, the layout of such heat transfer tubes is of critical importance, since it would be desirable to achieve a uniform temperature distribution across the radial direction of the reactor.
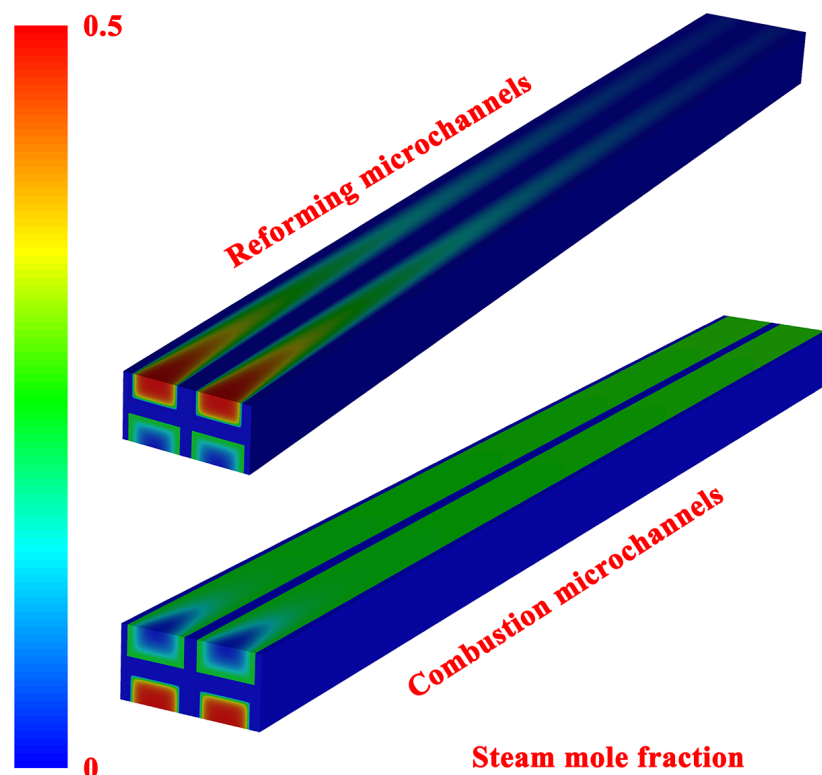
Figure 6. Steam mole fraction contour maps in the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The effect of catalyst layer thickness on the methanol conversion is illustrated in Figure 7 in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. Within the reformer, the methanol and steam react endothermically at high temperature to produce a gaseous product consisting primarily of steam, hydrogen, and carbon dioxide. Methanol is passed with steam over a catalyst at pressure typically ranging from 14.7 to 150 psia and temperatures in the range of about 373 K to about 548 K. Typical steam to methanol mole ratio are in the range of about 2.5:1 to about 4:1. The conversion of methanol may be affected in one pass over the catalyst bed contained in the reformer. Conventional methods for the production of hydrogen gas include steam reforming of hydrocarbons [45, 46]. According to the usual method, carbon monoxide and carbon dioxide are removed from a reformed gas containing hydrogen gas, carbon monoxide and carbon dioxide obtained by the above methods so as to produce hydrogen gas [47, 48]. The conventional methods have several drawbacks in that the price of the raw material hydrocarbons continues to rise, and the supply of the raw material hydrocarbons is in unstable conditions, desulfurization of the raw materials is required, and a high reaction temperature of 1100-1300 K is required for the steam reforming process. Consequently, the conventional methods are suitable for large scale hydrogen gas production, but they are not adequate for middle to small scale hydrogen gas production. In contrast, hydrogen gas production by the steam reforming of methanol has various advantages in that the reaction temperature is relatively low, separation of hydrogen gas from the reformed gas is easy, and no desulfurization is required because methanol is the raw material. Also, the method can easily cope with large to small scale plants, since it uses inexpensive and easily transportable methanol as the raw material. The steam reforming reaction of methanol yields a wet gas containing condensable components such as methanol and water, and a reformed gas. After the reaction, the reformed gas containing hydrogen and carbon dioxide

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is taken out by cooling of the wet gas. Here, an industrial problem is the treatment of the condensed liquid. Conventionally, the condensed liquid is disposed without treatment or the condensed liquid obtained by vapor-liquid separation treatment is recycled to the reaction system so as to make reuse of the condensed liquid together with the raw material methanol and water. However, the former has a big problem from the view-point of pollution since the condensed liquid contains a considerable number of organic components such as unreacted methanol and high boiling point components. In the latter, a trace amount of ethanol contained in the raw material methanol accumulates because it is hardly converted by the usual reaction method. If the treated condensed liquid is reused in the reforming reaction system, it is necessary to adjust the amount of water so as to make the methanol-water ratio at a predetermined value. Therefore, if steam reforming of methanol is continuously carried out, a portion or the whole of a predetermined amount of raw material water may be allotted for water to be added to the condensed liquid. The steam reforming reaction of methanol which discharges the condensed liquid or makes reuse of the treated condensed liquid should not particularly be limited, but the reaction is usually carried out as follows. Known catalysts are used for the steam reforming reaction of methanol. For example, they include copper catalysts such as those containing copper oxides, chromium oxides and manganese oxides. The conditions of steam reforming reaction of methanol vary with the catalysts used, and cannot absolutely be specified. The reformed gas mainly contains hydrogen gas and carbon dioxide gas. When carbon dioxide gas is removed from the reformed gas by a conventional method such as absorptive removal with an aqueous sodium carbonate solution, an aqueous potassium carbonate solution or an aqueous monoethanolamide solution, a high purity of hydrogen gas is obtained. Also, when the condensed liquid is reused after treatment for the steam reforming reaction of methanol, it has no bad effect due to ethanol and high boiling point components on the reaction. The conversion of methanol is usually maintained high. The durability of catalysts is increased, and the process causes no pollution.
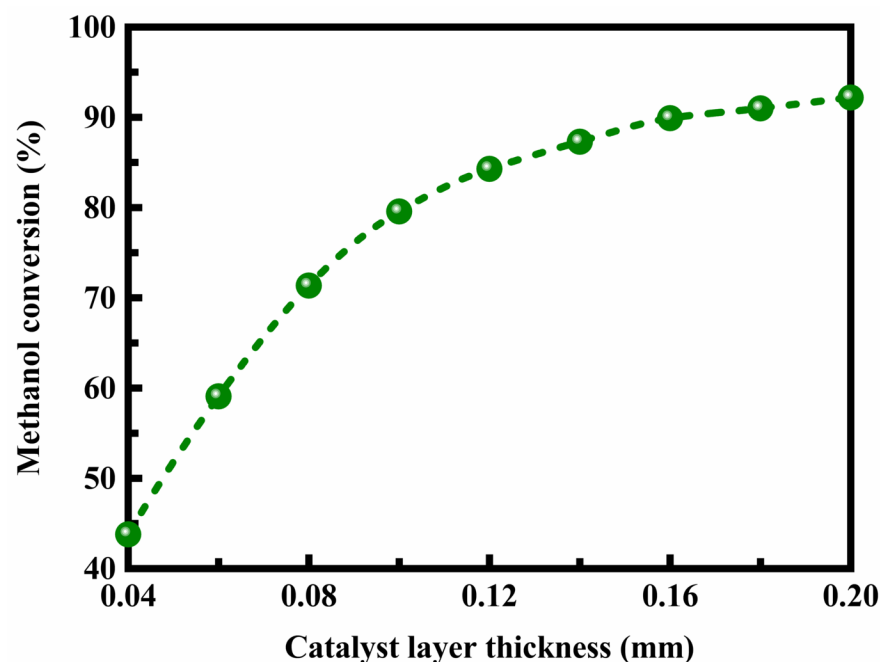

Figure 7. Effect of catalyst layer thickness on the methanol conversion of the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The effect of catalyst layer thickness on the hydrogen yield is illustrated in Figure 8 in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction.

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The process comprises contacting a gas phase comprising methanol and steam, with a solid catalyst. The gas phase may or may not comprise other gases, in addition to the methanol and steam. For instance, the gas phase may comprise an inert gas, for example, nitrogen or argon, which could for example be present as a carrier gas. The inert gas, when present, is typically nitrogen. Additionally, or alternatively, the gas phase may further comprise oxygen. Blending oxygen or air into the gas phase may encourage combustion and may also balance the total thermodynamic requirements of the non-syngas direct steam reforming system. Thus, the gas phase may further comprise oxygen or air. The gases in the gas phase may be pre-mixed, namely mixed together before the mixture is brought into contact with the catalyst. Alternatively, the gases can be fed into a reactor separately, so that the reactant gases are mixed together in the presence of the solid catalyst. The exothermic and endothermic reaction channel flows are in the same direction, although in this design, the reformer flow enters and leaves in a direction perpendicular to the direction of flow during reaction to accommodate manifolding connections on a different face of the device than the combustion flow manifolding. At a given reactor length or height it is not difficult to obtain nearly uniform ratios of catalyst area to heat transfer area and thereby uniform temperature distribution in the interior of the catalyst bed cross section, namely toward the center of the reactor. This ratio can be kept constant if, for instance, the tube pitch is kept constant for the same heat transfer tube diameter. By tube pitch is meant the center-to-center distance of neighboring tubes. Even a change from for instance triangular pitch in the center of the bed to a rectangular pitch near the periphery of the bed can be obtained without experiencing too large variations in the ratio of catalyst area to heat transfer area. However, at the periphery of the heated or cooled catalyst bed, the surrounding external reactor wall defining the periphery of the reactor does not heat nor cool the catalyst bed. The peripheral heat transfer tubes are preferably positioned in direct contact with the external reactor wall. The peripheral heat transfer tubes may be simple tubes having a single wall and may be shaped so that they have a substantially semi-circular or triangular cross-section. Other types of tube can be envisaged, for example double-tubes. The temperature toward the external reactor wall can be kept at about the same level as in the center of the reactor. Note that the catalytic combustion is most likely accompanied by some homogeneous combustion in the flow-by gap. The outermost steam reforming channels are sized to have half the flow of the inner channels since the outer channels received only half of the heat. Each outermost channel has catalyst only against the innermost wall and is designed to admit roughly half the flow going through a full channel for a given pressure drop. Some process characteristics of some preferred processes include the following factors: Operate safely at a fuel: oxygen ratio near stoichiometric for the use of combustion as the exothermic reaction. This reduces the required air which improves the overall system thermal efficiency and reduces the required duty for the external air blower or compressor. Operate steam reforming at short contact times or conversely at high gas hourly space velocities. This is required to create a compact device. Operate with a high heat flux. This is required to operate at short contact times. Operate with a low pressure drop per unit length of reactor. This enables a higher productivity per unit volume. Optional: quench-inhibit gas phase reactions. As the channel dimension nears the quench diameter or drops below, the contribution of the unwanted gas phase homogeneous combustion reaction is reduced. The devices may be made of materials such as plastic, metal, ceramic and composites, depending on the desired characteristics. Walls separating the device from the environment may be thermally insulating; however, the walls separating adjacent exothermic and endothermic reaction chambers should be thermally conductive. The devices can be made by forming chambers within a single block of material, by joining multiple components, and by stacking and bonding shims. A preferred integrated reactor body can be made from a single block of metal. Its channels could be created with a wire electric discharge machining in the main body, and the headers and footers could be made separately and welded on, adding to the flexibility of the design. Wire electric discharge machining is used to create slots or holes in a block of metal that are the microchannels through which flow passes and a unit operation occurs. Sinker electric discharge machining, laser machining, and in some larger channels conventional milling can also be used to make channels from a single block of metal. The aperture-containing shims can be formed by processes including: conventional machining, wire electric discharge machining, laser cutting, photochemical machining, electrochemical machining, molding, water jet, stamping, etching and combinations thereof. For low cost, stamping is especially desirable. Alternately, laser welding shims could join the devices or sheets to form seals between flow paths. Devices could alternatively

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be joined by the use of adhesives. The combustion chamber and reforming chamber are oriented so that heat is transferred from the combustion chamber into the reforming chamber. Both the combustor and reformer should have a separate preheater or a preheat zone integrated within the device in which reactants are preheated prior to contacting a catalyst.
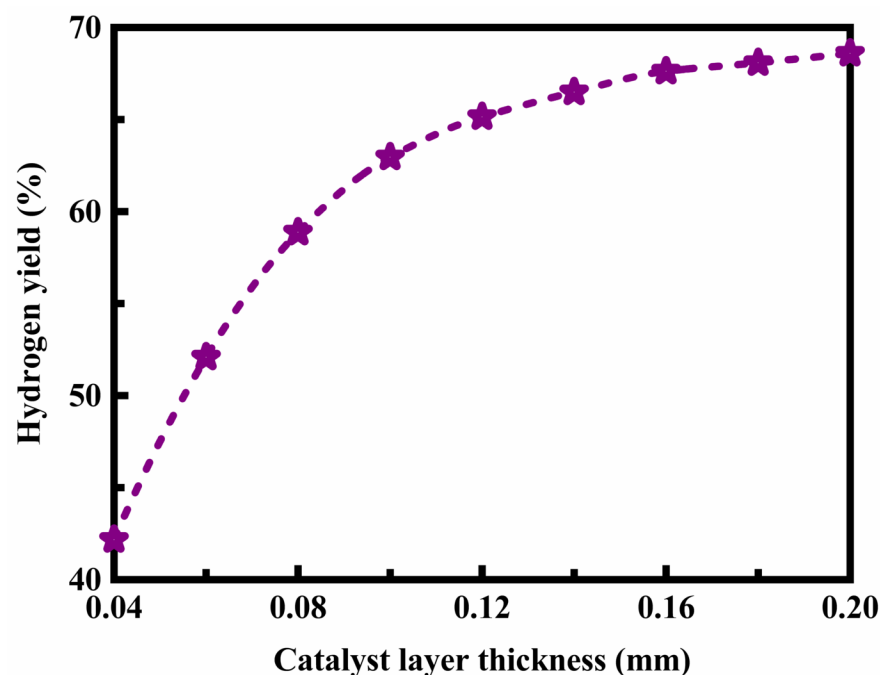

Figure 8. Effect of catalyst layer thickness on the hydrogen yield of the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

4. Conclusions

The present study aims to provide a fundamental understanding of the exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors. Particular emphasis is placed upon the simultaneous implementation of the endothermic steam reforming and the heat-supplying exothermic catalytic combustion such that the thermal stability of the reaction system is increased. The effect of catalyst layer thickness on the reaction characteristics is investigated in order to understand how to design and operate such reactors with high efficiency. The major conclusions are summarized as follows:

- Unique jet design features can be implemented in order to suppress homogeneous combustion and promote heterogeneous catalytic combustion on the channel wall.
- Diffusion within these small pores in the catalyst layers is typically Knudsen in nature for gas phase systems, whereby the molecules collide with the walls of the pores more frequently than with other gas phase molecules.
- The composition in the combustion chamber is reacted to produce sufficient heat to sustain the micro-combustion process without energy input.
- The combustion and reforming processes can be stably and efficiently operated at lower temperatures, without the need for energy input to sustain or even to start the combustion process.
- Since a palladium component is alloyed with the zinc, generation of carbon monoxide due to the methanol decomposition reaction is suppressed.
- Direct heating is of considerable advantage as it largely overcomes the problems encountered with

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reaction rates being limited by the rate of heat transfer through the tube wall especially near the reformer entrance and thus, for a given conversion, the reactor may be smaller, more efficient and less expensive.

- The conventional methods are suitable for large scale hydrogen gas production, but they are not adequate for middle to small scale hydrogen gas production.
- As the channel dimension nears the quench diameter or drops below, the contribution of the unwanted gas phase homogeneous combustion reaction is reduced.

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Exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors

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Abstract

Catalytic reactors for carrying out endothermic or exothermic reactions are of great importance in the particular examples being reactors for the endothermic steam reforming of methanol and reactors for the exothermic catalytic combustion reaction. The present study aims to provide a fundamental understanding of the exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors. Particular emphasis is placed upon the simultaneous implementation of the endothermic steam reforming and the heat-supplying exothermic catalytic combustion such that the thermal stability of the reaction system is increased. The effect of catalyst layer thickness on the reaction characteristics is investigated in order to understand how to design and operate such reactors with high efficiency. The results indicate that unique jet design features can be implemented in order to suppress homogeneous combustion and promote heterogeneous catalytic combustion on the channel wall. Diffusion within these small pores in the catalyst layers is typically Knudsen in nature for gas phase systems, whereby the molecules collide with the walls of the pores more frequently than with other gas phase molecules. The composition in the combustion chamber is reacted to produce sufficient heat to sustain the micro-combustion process without energy input. The combustion and reforming processes can be stably and efficiently operated at lower temperatures, without the need for energy input to sustain or even to start the combustion process. Since a palladium component is alloyed with the zinc, generation of carbon monoxide due to the methanol decomposition reaction is suppressed. Direct heating is of considerable advantage as it largely overcomes the problems encountered with reaction rates being limited by the rate of heat transfer through the tube wall especially near the reformer entrance. The conventional methods are suitable for large scale hydrogen gas production, but they are not adequate for middle to small scale hydrogen gas production. As the channel dimension nears the quench diameter or drops below, the contribution of the unwanted gas phase homogeneous combustion reaction is reduced.

Keywords: Catalytic reactors; Reaction characteristics; Heat exchange; Carbon monoxide; Partial oxidation; Thermal stability

1. Introduction

The availability of hydrogen is the fundamental condition for use of fuel cells in mobile and stationary applications. As the use of fuel cells is becoming more frequent, for example, in automobiles it makes sense to restrict the operation of the energy generating units of the automobile to one energy source, such as methanol, gasoline, or diesel fuel rather than feeding each energy generating unit from a different source of energy, such as one for the Otto carburetor engine for driving, diesel for the heating system, and methanol for the fuel cell for air conditioning and current supply [1, 2]. For this reason, attempts have been made to utilize the customary fuels for the production of the hydrogen needed for the fuel cell [3, 4]. It is a well-established process in industry to reform higher hydrocarbons or alcohols to hydrogen [5, 6]. However, when applying this reforming process to obtain hydrogen for fuel cells, the

equipment known to date still is rather big and, therefore, ill-suited for employment in mobile installations [7, 8]. The cause of another problem in producing hydrogen for fuel cells by way of reforming higher hydrocarbons or alcohols is the complicated nature of the chemical processes that occur in reforming and the consequential difficulty of conducting the reaction [9, 10]. Known aggregates for reforming hydrocarbons or alcohols, therefore, comprise expensive means of control and regulation to handle the complicated reaction processes and thus are not suited for use in mobile installations, such as automobiles.

It is, therefore, necessary to provide an improved process and apparatus for reforming higher hydrocarbons or alcohols, such as gasoline, diesel fuel, methanol, or methane, that will facilitate hydrogen production for a fuel cell in mobile equipment, especially vehicles. The provision and utilization of a microreactor network with its microreactors and microchannels permit high selectivity in influencing the various partial reactions which are intricately interconnected in reforming hydrocarbons or alcohols [11, 12]. The small dimensions of the reaction spaces in the microreactors make it easier to regulate and keep under control the reactions taking place and, therefore, reduce the necessary expenditure for mechanical equipment [13, 14]. It is another advantage that the microreactor network is particularly well suited as a means for producing hydrogen for non-industrial applications [15, 16] because the space requirement of the apparatus has been reduced considerably in comparison with known industrial installations [17, 18]. Apart from application in mobile equipment, the hydrogen obtained from reforming also may be put to use, for example, in fuel cells for housing energy supply systems [19, 20]. The use of microreactors for in-situ and on-demand chemical production is gaining increasing importance [21, 22] as the field of micro-reaction engineering matures from the stage of being regarded as a theoretical concept to a technology with significant industrial applications.

Various research groups have successfully developed microreactors for chemical processing applications such as partial oxidation of ammonia, nitration and chemical detection [23, 24]. One of the objectives of the research efforts is to demonstrate a working micro-reaction system for use as a sustained source of hydrogen fuel for proton exchange membrane fuel cells through catalytic steam reforming of methanol [25, 26]. The complete reformer-fuel cell unit is proposed as an alternative to conventional portable sources of electricity such as batteries for laptop computers and mobile phones due to its ability to provide an uninterrupted supply of electricity as long as a supply of methanol and water can be provided. Though considerable work already exists in the literature on the catalytic steam reforming of methanol for production of hydrogen using conventional reactors [27, 28], the use of microreactors for in-situ methanol reforming is a relatively new idea. Literature on the macro-scale steam reforming of methanol includes analysis of the reaction thermodynamics for prediction of optimum reactor temperature and feed compositions, catalyst characterization studies, and experimental studies on macro-scale pilot reactors [29, 30]. Results obtained in the study of methanol reforming in these conventional reactors form a good background for the development of prototype microreactors for this purpose [31, 32]. Silicon is considered a good material for fabrication of microreactors due to the high strength of the silicon-silicon bonds which results in the chemical inertness and thermal stability of silicon. Well established silicon micromachining techniques commonly used in the microelectronics industry facilitate easy fabrication of microchannels and other desired features on silicon substrates thus making silicon the preferred material for prototype microreactor fabrication.

The present study is focused primarily upon the exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors. The endothermic reaction is implemented in heat exchange with a heating medium. The endothermic reaction is implemented in heat exchange with an exothermic reaction. The exothermic reaction is implemented in heat exchange with a coolant. The design is described in the example of a process for the production of hydrogen from methanol and a compact reactor that is used in this case for simultaneous implementation of endothermic

steam reforming and exothermic catalytic combustion, without being limited thereto. Such processes are essentially based on two catalytic reactions. First, a methanol-containing feedstock is sent into a process for catalytic steam reforming. This reaction is endothermic. The necessary heat for the reaction is supplied by catalytic combustion. The synthesis gas-containing reaction products of catalytic steam reforming are sent as feedstock into a process for further synthesis. Both the steam reforming and catalytic combustion reactions are implemented in compact reactors. Such compact reactors have several plates with flow channels, through which the respective gaseous and liquid media are sent. The media on the individual plates are in indirect heat exchange with one another and vary from plate to plate. The present study aims to provide a fundamental understanding of the exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors. Particular emphasis is placed upon the simultaneous implementation of the endothermic steam reforming and the heat-supplying exothermic catalytic combustion such that the thermal stability of the reaction system is increased.

2. Methods

Steam reforming is a process in which hydrogen is stripped from a hydrocarbon fuel by thermal energy provided by a combustor. In alcohol steam reforming, the feed stream contains steam and an alcohol or alcohols. In the present design, methanol, ethanol, and propanol are preferred with methanol being especially preferred. In an integrated reactor, combustion or heat generation should occur in close proximity to the endothermic reaction. Preferably, an exothermic reaction occurs in microchannels that are interleaved with microchannels in which there is an endothermic reaction. Co-flow of endothermic and exothermic reaction streams is preferred; however, cross-flow or countercurrent flow are also options. The heat of an exothermic reaction is conducted from the exothermic reaction to the endothermic reaction catalyst, where it drives the endothermic reaction. Preferably an exothermic reaction channel and endothermic reaction channel in the integrated reactors is a microchannel, that is, a channel having at least one dimension of 2 millimeters or less. The use of channels having a minimum dimension of more than 2 mm may be less effective since heat and mass transfer limitations may be magnified. An integrated combustor can use the high surface area of reactor microchannels to remove heat as it is produced, thus keeping microreactor components from exceeding material temperature constraints while combusting with much less excess air or diluent than would be necessary for an external combustor. The flow rate of reactants will depend on the desired amount of hydrogen to be produced and on the minimum or maximum capacity of the steam reformer. The rate of combustion can be controlled to provide the desired amount of heat to a steam reforming reaction in an adjacent reforming chamber. The steam reforming reaction can be run over a broad pressure range from sub-ambient to very high. The alcohol steam reforming reaction is preferably carried out at temperatures of 200-400 °C, more preferably 220-300 °C, and in some cases 240-270 °C. In some preferred configurations, the combustion temperature is approximately the same as the average reformer temperature, that is, the average temperature of the reforming catalyst.

The design provides a method of conducting an endothermic reaction in an integrated combustion reaction, comprising: passing an endothermic reaction composition into at least one endothermic reaction chamber, passing a fuel and an oxidant into at least one exothermic reaction chamber wherein the fuel and oxidant each have a contact time in the combustion chamber of 50 milliseconds or less, wherein the exothermic reaction chamber comprises at least one exothermic reaction chamber wall that is adjacent at least one endothermic reaction chamber. The endothermic reaction chamber comprises an endothermic reaction catalyst in contact with at least the at least one endothermic reaction chamber wall that is adjacent at least one exothermic reaction chamber, and transferring heat from the at least one exothermic reaction chamber into the at least one endothermic reaction chamber at a rate as based on the internal surface area

of the endothermic reaction chamber. The heat flux can be measured based on either a single exothermic reaction chamber or multiple chambers in a multi-chamber device. The reformate stream usually comprises hydrogen, carbon dioxide, and carbon monoxide. Proton exchange membrane fuel cells operate have a very low tolerance for carbon monoxide. They can generally tolerate carbon dioxide and some other gases such as nitrogen, but only up to a certain amount. Clean-up of a reformate stream can be performed, for example by a multi-step process consisting of water gas shift reactors, combined with selective oxidation and carbon monoxide methanation, or by the use of a hydrogen permeable membrane. Direct methanization of a reformate stream is important without first passing the reformate through a hydrogen-selective membrane, preferential oxidation, or water gas shift reactor. This is highly desirable since hydrogen-selective membranes are expensive, and additional process steps can be costly and result in lowered yield. Eliminating the requirement of a preferential oxidation also eliminates the need to add oxygen, including the need to vary oxygen content to account for fluctuations in carbon monoxide concentration. In preferred cases, the process adds heat to the steam reforming step but does not have additional heat exchangers or heat exchange steps for methanation or for other carbon monoxide-reducing steps.

The exothermic reaction chamber has an internal dimension of less than 0.8 mm and a volumetric heat flux, based on reaction chamber volume of greater than 8 Watts per cubic centimeter. Contact times in the exothermic and endothermic reaction chambers are preferably less than 600 milliseconds. Area heat flux for the area of either reaction chamber is preferably 0.8 Watts per square centimeter or more. The design provides a method of steam reforming in an integrated combustion-reforming reactor, comprising: step a) passing steam and hydrocarbon into at least one endothermic reaction chamber wherein the steam to carbon ratio is less than 2:1 with a pressure drop through the endothermic reaction chamber of less than 6000 kPa, step b) passing a fuel and an oxidant into at least one exothermic reaction chamber wherein the fuel and oxidant each have a contact time in the combustion chamber of 600 milliseconds or less, wherein the exothermic reaction chamber comprises at least one exothermic reaction chamber wall that is adjacent at least one endothermic reaction chamber, wherein the endothermic reaction chamber comprises an endothermic reaction catalyst in contact with at least the at least one endothermic reaction chamber wall that is adjacent at least one exothermic reaction chamber, step c) converting the steam and hydrocarbon to form carbon monoxide and hydrogen such that the at least one endothermic reaction chamber has an output demonstrating a conversion of at least 50 percent of the hydrocarbon with a selectivity to carbon monoxide of at least 50 percent. A device is characterized by operation for 200 or 500 hours and then cut open to reveal less than 0.08 gram of coke per each kilogram of the fuel processed.

The endothermic reaction chamber and the combustion chamber are separated by a thermally conductive wall. The endothermic reaction composition endothermically reacts to form products. Where not otherwise specified, the front of the combustion chamber is defined as where the flow of fuel contacts a combustion catalyst and an oxidant, and the back of the combustion chamber is defined as the last part of the reaction chamber that contains a combustion catalyst and is in direct thermal contact with an endothermic reaction chamber. The exhaust section is not in direct thermal contact with the endothermic reaction chamber. The design also provides a method of simultaneously conducting an endothermic and an exothermic reaction in an integrated combustion-reforming reactor, comprising: passing a mixture comprising hydrogen and methanol through a microchannel in an integrated combustion-reforming reactor; reacting the hydrogen and methanol with an oxidant to form water, carbon dioxide and carbon monoxide and produce heat, thus removing hydrogen and methanol from the mixture; wherein a greater percentage of methanol is removed from the mixture than the percentage of hydrogen removed from the mixture, as measured by comparing the levels of hydrogen and methanol in the mixture before passing through the microchannel with the levels of hydrogen and methanol at any point after passing through

the microchannel. This is an extremely surprising result. The removing steps are by chemical reactions, not separation techniques.

An integrated combustion-reforming reactor refers to an integrated reactor that includes at least one combustion channel adjacent to at least one endothermic steam reforming reaction channel. During operation, a reactant enters a combustion or reaction chamber in a bulk flow path flowing past and in contact with a porous material or porous catalyst. In these cases, a portion of the reactant molecularly transversely diffuses into the porous catalyst and reacts to form a product or products, and then the products diffuse transversely into the bulk flow path and out of the reactor. The term bulk flow region or bulk flow path refers to open areas or open channels within the reaction chamber. A reaction chamber with a bulk flow path or region will contain a catalyst and there is a gap between the catalyst surface and a reaction chamber wall or a second catalyst surface. A contiguous bulk flow region allows rapid gas flow through the reaction chamber without large pressure drops. In preferred cases, there is laminar flow in the bulk flow region. Equilibrium conversion is defined in the classical manner, where the maximum attainable conversion is a function of the reactor temperature, pressure, and feed composition. For the case of hydrocarbon steam reforming reactions, the equilibrium conversion increases with increasing temperature and decreases with increasing pressure. Fuel flow to combustor can be initiated at this point. Once the fuel has begun reacting, the hydrogen flow is tapered off and the fuel flow is increased. The excess air should not be too much, since the extra air removes heat from the steam reformer. Air and methanol flows are adjusted until the steam reformer is at the desired temperature. The reformer fuel mixture flow is initiated at this point. Combustor flows are adjusted as necessary to maintain desired temperatures. Preferred forms of porous supports are foams and felts and these are preferably made of a thermally stable and conductive material.

The methanol conversion is calculated by using a carbon balance on the system. Reaction chamber volume is the internal volume of a reaction chamber either exothermic or endothermic. This volume includes the volume of the catalyst, the open flow volume if present and metal support ribs or fins if present within the reaction chamber volume. This volume does not include the reaction chamber walls. The reaction chamber volume must contain a catalyst somewhere within its cross-section and must be directly adjacent another reaction chamber for heat transport. This volume is used for calculations of endothermic reaction chamber volumetric heat flux, area heat flux, and endothermic reaction contact time. The reactor core volume is defined as the reaction chamber volume and all combustion chamber volume and the metal webs that separate the two chambers. The combustion chamber volume is defined as the chamber volume in which the exothermic heat generating reaction occurs and is adjacent to the reaction chamber volume. Perimeter metal is not included in reactor core volume. The reactor core volume does not include any preheat exchanger zone volume that may or may not be attached to the reactor core volume. The preheat exchanger zone may be attached to the reactor but does not contain an endothermic reaction catalyst along any plane that bisects the device orthogonal to the direction of flow. The use of electric heating for system start-up is eliminated by following the subsequent procedure. Hydrogen and air are fed to combustor to initiate combustion and heat the vaporizers. Once the vaporizers are heated to approximately 80 °C, methanol is fed to the vaporizer. The hydrogen is slowly tapered off as the methanol feed is increased until only methanol and air are being fed to the combustor and the device is completely self-sustaining. The methanol-air mixture is adjusted until the steam reformer reaches the desired temperatures depending on the conditions being tested. The methanol-water solution feed is then initiated.

Endothermic reaction chamber heat flux is defined as the endothermic reaction heat duty divided by the reaction chamber volume. Reactor core volume heat flux is defined as the endothermic reaction heat duty divided by the reactor core volume. Heat exchanger flux is defined as the total heat transferred to the cold streams divided by the heat exchanger core volume. Heat exchanger core volume is defined as

the total heat exchanger volume inclusive of microchannels, ribs between microchannels, and the walls separating microchannels for all fluid streams transferring heat. The heat exchanger volume is inclusive of the heat exchanger zone. The heat exchanger core volume does not include the perimeter metal or manifolds or headers. The heat exchanger core volume does not include the endothermic reaction chamber nor any volume that could be included within any plane that bisects the endothermic reaction chamber orthogonal to the direction of flow. Average area heat flux is defined as the endothermic reaction heat duty divided by the area of the endothermic reaction chamber heat transfer surface. The endothermic heat transfer surface is defined by a planar area, which may be intermittent in the case of ribs or other structures in the endothermic reaction chamber, above which there is area for flow of reactants and below which there is a wall that separates the endothermic reaction chamber and the exothermic reaction chamber. This area is the path for heat transfer from the exothermic reaction chamber to the endothermic reaction chamber. The apparent equilibrium conversion temperature is the apparent temperature based on methane conversion or, more generally, hydrocarbon conversion or the temperature required to produce an equilibrium methane conversion equal to the measured methane conversion at the measured average process pressure. Average process pressure is assumed to be the average of the measured inlet and outlet pressures.

3. Results and discussion

The methanol mole fraction contour maps are illustrated in Figure 1 for the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. Channels refers to the generally accepted meaning and includes conduits and other means for directing the flow of a fluid. Channels include at least one opening, typically with an inlet and outlet, and may include other openings. Fluid communication between two areas means that a fluid can flow from one area to the other. Thermal communication between two areas means that heat can flow from one area to the other. Heat exchanger is a device or component designed such that heat can be transferred from one fluid to another. The heat source for the endothermic reaction is delivered directly to the wall in contact with the endothermic catalyst. This follows from the fact that metal conduction is a more efficient mode of heat transfer than either convective or radiative heat transfer. In contrast to premixed combustion, where the heat release will occur primarily in the homogeneous phase, combustion jets can direct a concentrated stream of air into a separate fuel channel stream. The two streams subsequently mix and undergo an oxidation reaction. In order to suppress homogeneous combustion and promote heterogeneous catalytic combustion on the channel wall, unique jet design features can be implemented. Important features include geometry, size, and relative location and spacing. The jets should not only impinge on the wall but also spread out the combustion oxidant as uniformly as possible along the entire width of the channel. Furthermore, heterogeneous combustion is preferably concentrated at the combustion wall in closest proximity to the endothermic reaction catalyst. Combustion on other walls represents a heat loss and furthermore has a disadvantageous impact on thermal stresses in the device. In order to raise the temperature of an endothermic steam reforming reaction and reduce the likelihood of coke formation at the beginning of the reactor zone or in the heat exchanger zone reactant or product channels, more air should be delivered for combustion against the wall at the beginning of the reactor zone. Concentration of jets in this region as well as application of non-circular jet orifices can successfully meet this objective. All the goals above are desired to be accomplished with a minimal pressure drop for both economic reasons as well as for the purposes of preserving back pressure in the integrated combustion-reforming reactor device to ensure good flow distribution. To this end, a hybrid of circular and rectangular slot orifices can be implemented in the jet design. Alternatively, other non-rectangular non-circular jets could be used such as diamonds, triangles, semi-circles, quarter-moons, and the like. Computational fluid dynamics predictions indicate that a

combination of these two jet geometries provide a more ideal heterogeneous fuel-oxidant mixture distribution on the combustion channel wall opposite the jet shim. It is recognized that other non-circular jet orifices could also be used at the entrance of the combustion zone or anywhere down the length of the reactor. It is also recognized that the combustion orifices could start before the reaction zone in the recuperative heat exchanger section to further preheat the reactants or further tailor the thermal profile of the device.
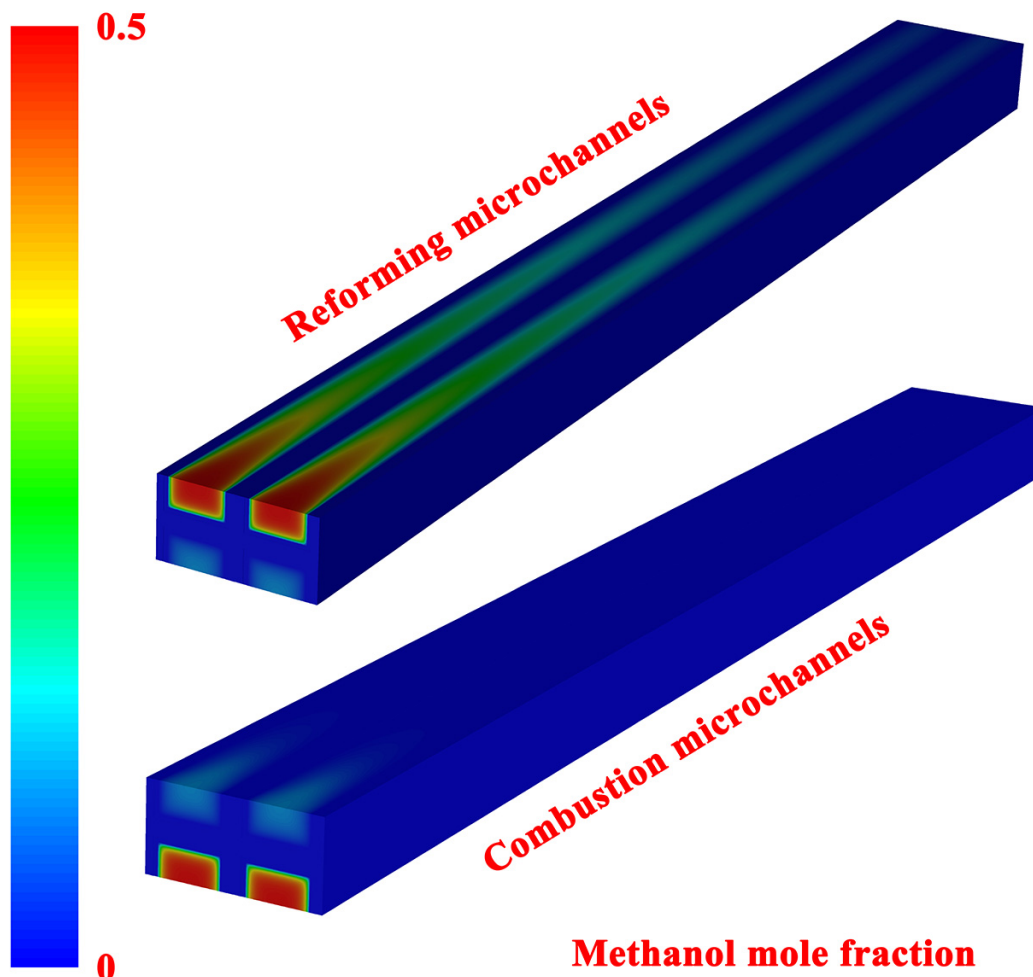

Figure 1. Methanol mole fraction contour maps in the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The hydrogen mole fraction contour maps are illustrated in Figure 2 for the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. Control of the relative proportion of homogenous and heterogeneous combustion can be achieved by manipulation of the jet design [33, 34]. Either homogeneous or heterogeneous combustion can be increased as needed depending upon the application. As an example, a microchannel combustor that does not include an endothermic reaction may be enhanced via jet design by promoting homogenous combustion to reduce methanol or carbon monoxide emissions or to provide a hot gas stream for subsequent use in a unit operation. The distribution of jet orifices may depend on the intended use of the device. Hydrogen burns immediately, thus, to avoid hot spots, the jets should be spaced more evenly over the combustion chamber. Methane, which burns more slowly, preferably has jets loaded near the front of the combustion chamber. When the fuel is syngas, the distribution of jets is intermediate. The endothermic and exothermic reaction chambers preferably contain catalysts [35, 36]. Catalysts suitable for catalyzing a selected exothermic or endothermic reaction are

well known to chemists and chemical engineers. Catalysts, especially an endothermic catalyst, can be a porous catalyst. Pore sizes in the range of about 0.6 to 600 microns enable molecules to diffuse molecularly through the materials under most gas phase catalysis conditions. The porous material can itself be a catalyst, but more preferably the porous material comprises a metal, ceramic or composite support having a layer or layers of a catalyst material or materials deposited thereon. The porosity can be geometrically regular as in a honeycomb or parallel pore structure, or porosity may be geometrically tortuous or random. The support of the porous material is a foam metal, foam ceramic, metal felt, or metal screen. The porous structures could be oriented in either a flow-by or flow-through orientation. The catalyst could also take the form of a metal gauze that is parallel to the direction of flow in a flow-by configuration. Alternatively, the catalyst support could also be formed from a dense metal shim or foil. A porous catalyst layer could be coated on the dense metal to provide sufficient active surface sites for reaction. An active catalyst metal or metal oxide could then be wash-coated either sequentially or concurrently to form the active catalyst structure. The dense metal foil or shim would form an insert structure that would be placed inside the reactor after bonding or forming the microchannel structure. Preferably, the catalyst inserts contact the wall or walls that are adjacent both the endothermic and exothermic reaction chambers. The porous catalyst could alternatively be affixed to the reactor wall through a coating process. The coating may contain a first porous layer to increase the number of active sites. Preferably, the pore diameter ranges from tens of nanometers to tens of microns. An active metal or metal oxide catalyst can then be sequentially or concurrently wash-coated on the first porous coating. The average pore size of the catalyst layers is preferably smaller than the average pore size of the support. Diffusion within these small pores in the catalyst layers is typically Knudsen in nature for gas phase systems, whereby the molecules collide with the walls of the pores more frequently than with other gas phase molecules. The catalyst, which is not necessarily porous, could also be applied by other methods such as wash coating. On metal surfaces, it is preferred to first apply a buffer layer by chemical vapor deposition and thermal oxidation, which improves adhesion of subsequent wash coats. The methanation catalyst can be a single material or a mixture of materials such as a methanation catalyst powder between methanation catalyst felts. A small reforming chamber, such as having a diameter of 0.8 mm or less provides superior results by enhancing uniformity of conditions such as reducing hot and cold spots and reducing channeling through a powdered catalyst. In this case, the reforming chamber is defined at one edge by the methanation catalyst. Where the catalysts are powders, there will not be a sharp delineation between reforming and methanation zones and some methanation catalyst powder will intermix with the reforming catalyst powder so that some methanation catalyst is present within the reforming chamber. The reforming chamber volume is defined by the volume where there is a significant amount of reforming catalyst such that a reforming reaction could take place under normal operating conditions. Methanol and water can be injected at room temperature into an inlet tube where they will be vaporized by heat conducted through the tube from the methanation and reforming catalysts. In practice, fuel processing systems may be significantly more complex. For example, heat from a combustor can also be used to supply heat for other processes such as steam generation that can be utilized for a steam reformer, autothermal reactor and water gas shift reactor. Heat loss is a function of surface area, lowering surface area for the same amount of heat reduces heat loss and puts thermal energy exactly where it is needed. Therefore, in some preferred designs, surface area is minimized. For example, in some environments, cylindrical reforming and combustion channels can perform better than planar geometries. Heat from the combustion chamber transfers through the thermally conductive wall into the endothermic reaction chamber and along the length of the endothermic reaction chamber where less than 8 percent of total heat flux into the endothermic reaction chamber is perpendicular to length.
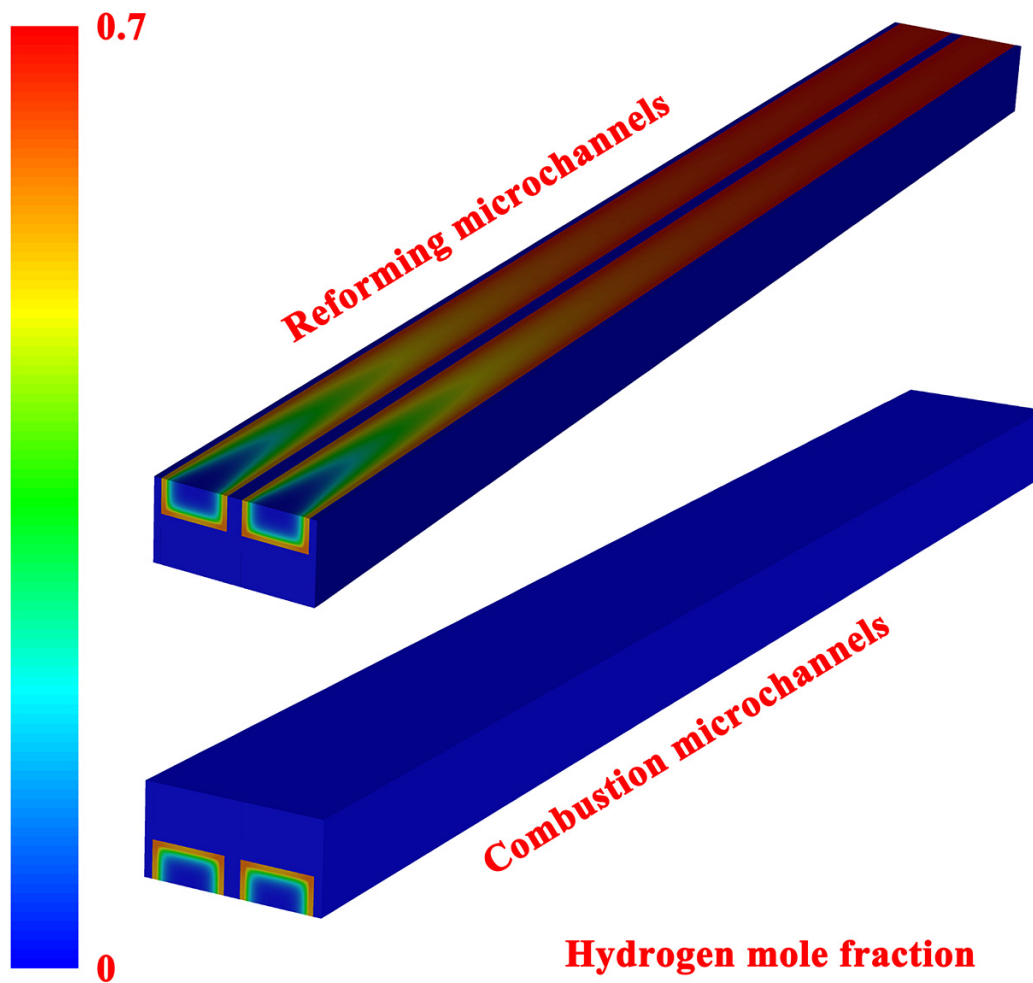
Figure 2. Hydrogen mole fraction contour maps in the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The chemical enthalpy profiles along the length of the integrated combustion-reforming reactor are illustrated in Figure 3 in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. The inlet and outlet of the combustion chamber are in fluid communication with combustion fuel and combustion exhaust channels, respectively, and the inlet and outlet of the reformation chamber are in fluid communication with reformation fuel and reformation products channels, respectively. The combustion fuel channel is disposed along the axis on a side of the combustion chamber opposite the reformation chamber. The reformation fuel channel is disposed along the axis on a side of the reformation chamber opposite the combustion chamber. The reformation products channel is disposed outside the reformation fuel channel with respect to the axis and on the side of the reformation chamber opposite the combustion chamber, and the combustion exhaust channel is disposed outside the reformation fuel channel with respect to the axis and on the side of the reformation chamber opposite the combustion chamber. The combustion catalyst comprises a porous matrix arranged such that sufficient mixture flows through the catalyst to maintain combustion at a temperature of at most about 548 K. The composition in the combustion chamber is reacted to produce sufficient heat to sustain the micro-combustion process without energy input. The combustion of a combustion fuel in a combustion chamber is maintained so as to transfer heat from the combustion chamber to the reforming chamber. The temperature difference between the combustion chamber and the reforming chamber is at most about 80 K. A composition comprising fuel and oxidant is passed into a combustion chamber and, simultaneous to the step of reacting steam and methanol, the fuel and oxidant in the combustion chamber are reacted

to produce heat. The reforming chamber and the combustion chamber are separated by a thermally conductive layer. Heat is transferred from the combustion chamber to the reforming chamber. The average thermal transport distance from the combustion chamber to the reforming chamber is 0.8 mm or less. This thermal transport distance is measured from the area within a combustion zone where combustion occurs. The above aspect of the design is typically associated with at least one of the following characteristics: at least 80 percent of the fuel is oxidized in the combustion chamber and the thermal efficiency of the method is at least 8 percent; hydrogen gas production of at least 60 standard cubic centimeters per minute hydrogen per cc of steam reformer volume; or hydrogen gas production of at least 0.8 standard cubic centimeters per minute hydrogen per cubic centimeter of device volume. The design provides a method of steam reforming that includes: passing a reformation gas through a reforming chamber, maintaining combustion of a combustion fuel in a combustion chamber so as to transfer heat from the combustion chamber to the reforming chamber. The reforming chamber is configured such that the volume of the chamber increases as a function of distance from a reaction chamber inlet; and reformation gas and products expand as they pass through the reforming chamber. A thermally conductive wall is disposed between the combustion chamber and the endothermic reaction chamber. The combustion catalyst is disposed on a side of the endothermic reaction chamber such that, during operation, heat from a combustion reaction on the combustion catalyst is transferred along the length of the reforming chamber. Length is the direction of a chamber that is parallel to flow through the chamber. Length, height and width are mutually perpendicular. Relatively short deviations in the direction of flow, such as flow from the tube toward and down the separator plate does not change the direction of length which is determined by the primary direction of flow through or past a catalyst. This aspect excludes parallel plate type configurations where a significant component of heat transfer is perpendicular to length. In this method, a fuel combusts on the catalyst and generates heat in the combustion chamber.
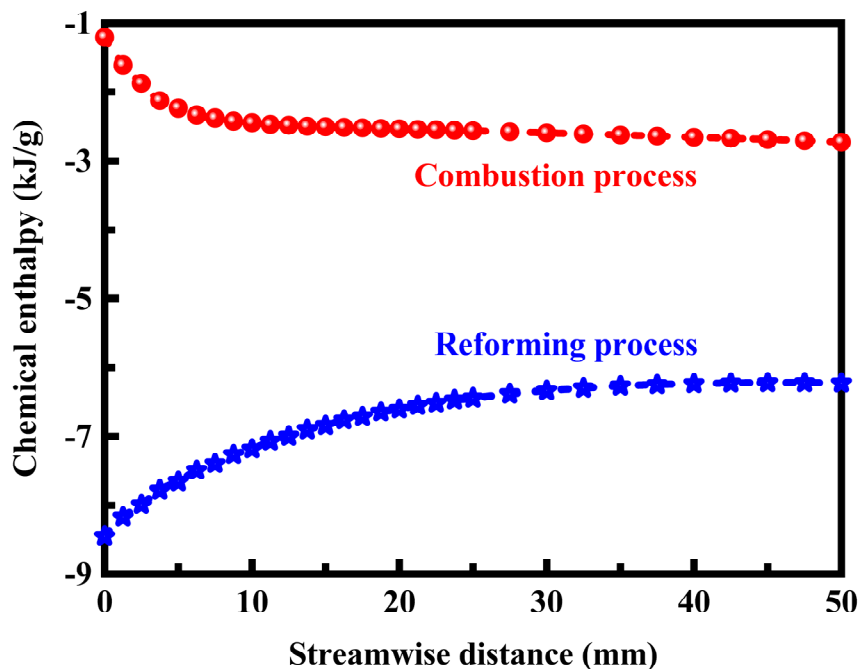

Figure 3. Chemical enthalpy profiles along the length of the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The sensible enthalpy profiles along the length of the integrated combustion-reforming reactor are illustrated in Figure 4 in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. The present design can provide numerous advantages. First,

light-weight and compact energy sources can be obtained [37, 38]. Further, the rapid heat and mass transfer in a small device can enable the use of extremely active catalysts, catalyst which are active at low temperature, and catalysts with high throughput per volume [39, 40]. It is also possible to control process conditions, such as operating temperature, very precisely, so that high performance can be attained. The fuel combustion and steam reforming processes can be stably and efficiently operated at lower temperatures, without the need for energy input to sustain or even to start the micro-combustion process. In some instances, the micro-combustor is started with hydrogen or vapors such as methanol. Heat losses can be effectively controlled and reduced. Another advantage is that the simplicity of the design and the materials used enable mass production at competitive costs. Advantages can also include higher conversions, lower carbon monoxide selectivity, and simplicity of design. Another advantage that results from small size is better control of heating and uniformity of temperature in a reaction zone. Another advantage is an extremely fast response time, that is, a change in fluid flow can result in a nearly instantaneous change in temperature. Further, the micro-combustor or micro-reformer can be part of an efficient integrated system, which can reform lower hydrocarbons and even higher hydrocarbons that require higher processing temperature, such as butane. Carbon dioxide selectivity over carbon monoxide, a poison to fuel cells, of the steam reforming process is high, so that it is possible to avoid or reduce requirements for removing carbon monoxide after reforming and before supplying the gas to the fuel cell, thereby greatly simplifying the overall system and reducing system size. Since catalytic combustion is used, stable low temperature performance is easily attained for the combustor to provide uninterrupted operational heat for vaporizers and steam reformer units so they may operate in a steady optimum manner. The low temperature operation and manufacturing made possible by the design allows a greater choice of insulating materials, enables greater use of materials with dissimilar thermal expansion coefficients, and enables manufacture on semiconductor chips. The combustors and reformers can be made from plastic. There are numerous advantages of manufacturing in plastic including low weight and less required insulation. Additional advantages include: more design options, cheap high-volume manufacturing, eliminating the need for expensive manufacturing machines compared to the equipment used in silicon processing, and inexpensive materials. A thermal cycle is heating a device up to operational temperature, operating the device at an operating temperature and observing the results, and cooling the device to about room temperature. Thermal efficiency is calculated by dividing the lower heating value of the hydrogen in the reformats stream by the total heating value of the methanol fed the reformer plus the heating value of the fuel fed to the combustor. Volume of a combustor, combustion chamber, reformer chamber or reformer, unless otherwise indicated, refers to the internal volume where reaction substantially occurs but not adjacent material. Where a catalyst is present, the volume includes at least the catalyst volume and catalyst void fraction. Volume of a device, unless otherwise indicated, refers to the combustor and reformer volume and the volume of any intervening and integral components such as heat exchangers, preheaters, vaporization chambers, and recuperators. By directing the flow in this manner, a temperature gradient is established between the center and the outer edges of the catalyst bed with the highest temperature at the center of the thermally conductive transverse separator plate located between the two reactor chambers; thus, minimizing heat loss through the reactor walls. That a fuel combusts on the combustion catalyst means contacting a fuel with a solid catalyst, including within a porous catalyst or over a catalyst coating. The efficiency could be substantially improved by removing the thermocouple and by use of improved insulator materials such as metallized polyimide, and it is believed that with these improvements the devices can be thermally efficient. The steam may be introduced by direct injection of steam and by saturation of the feedstock by contact of the latter with a stream of heated water. The amount of steam introduced is preferably such as to give a steam ratio in the range 2 to 3.5 moles of steam per gram atom of methanol carbon in the feedstock.
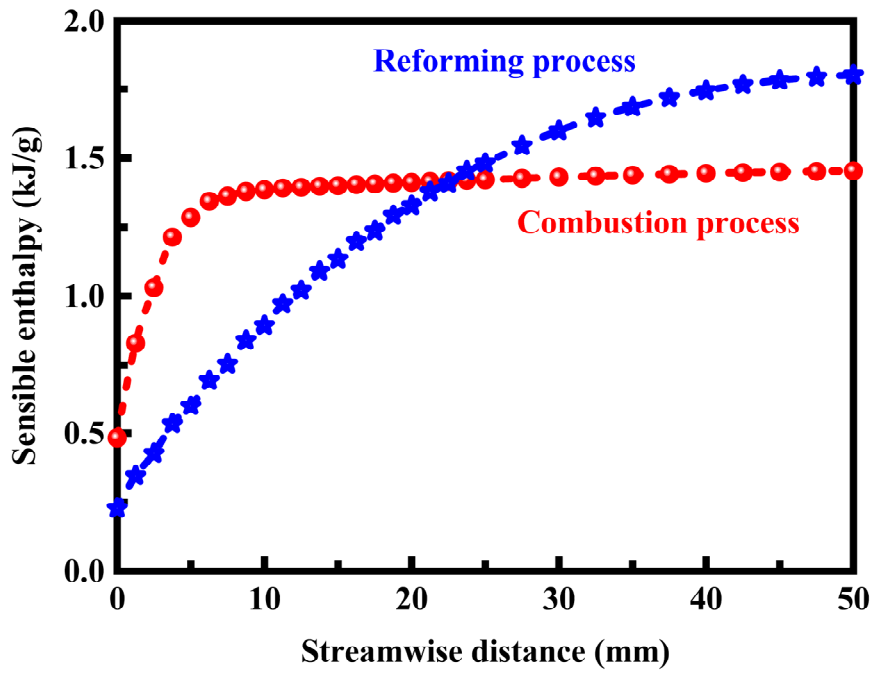
Figure 4. Sensible enthalpy profiles along the length of the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The temperature contour maps are illustrated in Figure 5 for the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. In the steam reformation of methanol, methanol is reacted with water to give hydrogen and carbon dioxide and also carbon monoxide. In addition to industrial processes for synthesis gas production, in particular applications in mobile systems such as fuel cells are of importance. Fuel cells require hydrogen which can be produced by steam-reforming methanol. For vehicle drives or mobile fuel cells, for example, it is of importance here to be able to carry out the steam reformation in a small reactor of low weight. This is made possible, in particular, by catalysts which catalyze the reaction of methanol and water and have a high activity with low volume. In this case it is useful to make up the catalysts in tablet form, in which case the tablets are to have very small dimensions, in order to achieve a high bulk density and a high ratio of surface area to volume. Also, a copper-based catalyst is excellent in low temperature activity and selectivity, but has the problem of heat resistance. In particular, since the activity and the selectivity are extremely reduced under the high temperature in excess of 300 °C, it is difficult to use such catalyst for a long time under the high temperature. In addition to this, metallic copper as active species is oxidized and sintered under the atmosphere containing the oxygen to cause the reduction in the activity. In contrast, a palladium-based catalyst that has strong resistance against the high temperature oxidizing atmosphere has the problem that it promotes the decomposition reaction of the methanol and thus generates a large quantity of carbon monoxide that is injurious to the fuel cell. It is an object of the present design to provide a methanol reforming catalyst capable of maintaining a high activity with good stability even in a high temperature and oxygen atmosphere while suppressing carbon monoxide generation. Since a palladium component is alloyed with the zinc, generation of carbon monoxide due to the methanol decomposition reaction is suppressed. Also, since both the palladium-zinc alloy and the metal oxide as the support are stable in the high temperature oxidizing atmosphere, the partial oxidation reaction as the exothermic reaction using the oxygen gas is proceeded simultaneously with the steam reforming reaction as the endothermic reaction or prior to the steam reforming reaction. That is, auto thermal reaction that proceeds the steam reforming reaction by utilizing the heat generated by the partial oxidation reaction is proceeded stably. A fuel cell of the present

design comprises the methanol reforming apparatus, a fuel cell, a pipe supplying a gas reformed by the reforming apparatus to the fuel cell, and a pipe supplying an oxygen-containing gas to the fuel cell. Since the reforming apparatus having the above methanol reforming catalyst is used, the size reduction of the overall fuel cell system can be achieved. Therefore, the fuel cell system is suitable for the fuel cell system which is installed in the mobile body such as a car and a ship whose apparatus size is limited. The steam reforming reaction is an endothermic reaction and is normally affected by passing a mixture of the desulphurized methanol feedstock and steam through tubes containing a steam reforming catalyst, normally nickel supported on a shaped support such as rings of alumina or a calcium aluminate cement, while strongly heating the tubes. The tubes are usually heated in a furnace fueled with a suitable methanol-containing stream; alternatively, the tubes may be located within a high temperature convective heat exchange reformer. In this type of heat exchange reformer, the catalyst is disposed in tubes extending between a pair of tube sheets through a heat exchange zone. Reactants are fed to a zone above the upper tube sheet and pass through the tubes and into a zone beneath the lower tube sheet. The heating medium, for example the hot product of combusting a fuel with air, is passed through the zone between the two tube sheets.
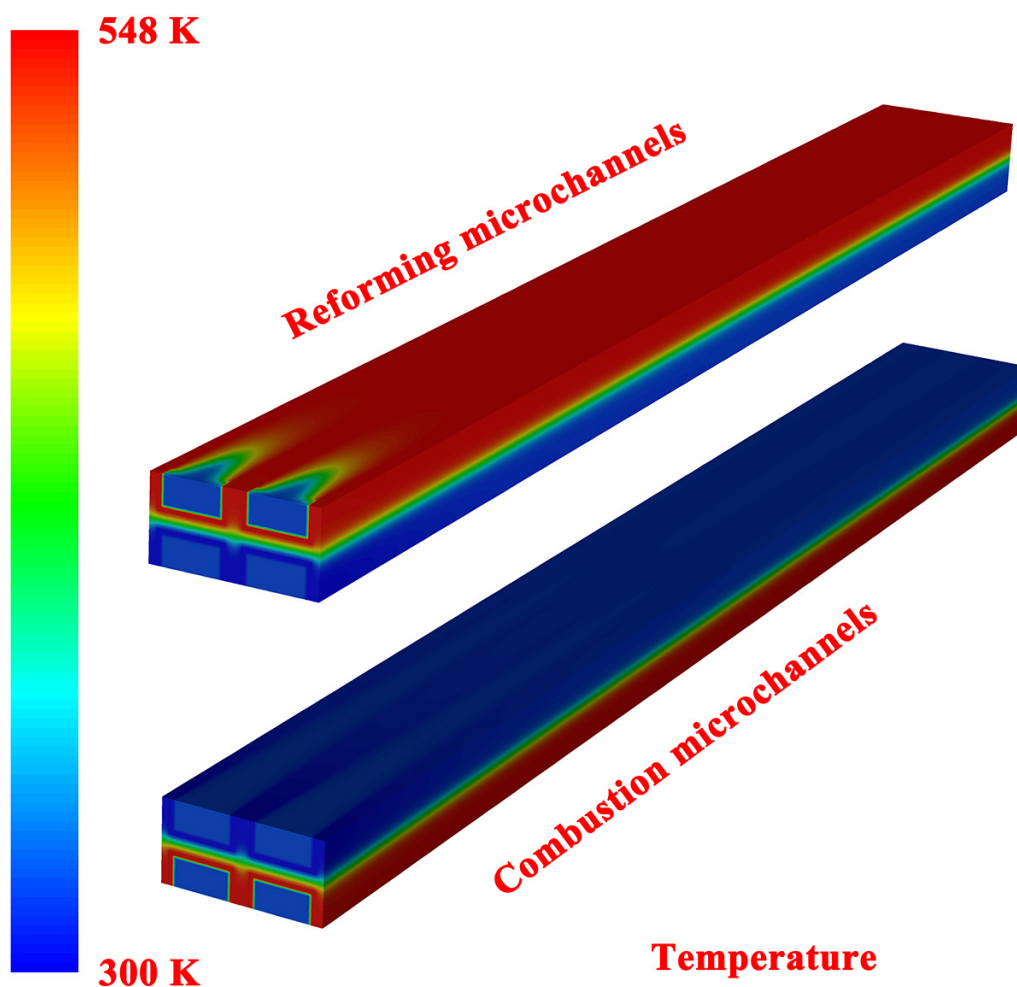

Figure 5. Temperature contour maps in the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The steam mole fraction contour maps are illustrated in Figure 6 for the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. For efficient operation of the steam reforming reaction, large surface areas are required to transfer the heat from the combusted gases to the tubes [41, 42]. In reformers

presently used for steam reforming small diameter reaction tubes are clustered closely together in the furnace so that heat transfer from the combusting gases in the reactor into the catalyst packed tubes is optimized [43, 44]. The use of a plurality of tubes to accomplish heat transfer contributes to the large size and high cost of the reformer. In fuel cell systems in which the reformer and the fuel cell are fully integrated, namely the combustion gases for the reforming reaction are derived from the fuel cell exhaust, the shell side heat transfer coefficient between the hot gas and the tube is characteristically low and hence, the rate of reaction is limited primarily by the rate of heat transfer. This problem is particularly severe at the reactor entrance as the rate of the endothermic reaction is very high, and thus, the amount of heat required is very high while the shell side heat transfer coefficient is often low as the mechanical design of typical reactors often allows the gases in the shell to be relatively stagnant near the tube entrances. This leads to a drop in the overall efficiency as a large portion of each reactor tube operates at an undesirably low temperature. Thus, in order to effect complete conversion, the reformer must be relatively large and expensive. It is the primary object of the present study to provide a novel process and apparatus for the production of hydrogen by steam reforming of methanol that can be accomplished with a thermally efficient reformer of reduced size and cost which can be integrated with a fuel cell power system or used as a standalone hydrogen generator. Production of hydrogen by steam reforming of methanol or other hydrocarbon fuels is accomplished in a reformer of substantially reduced size by superheating a gaseous mixture of water and methanol to a temperature of about 548 K and then passing the superheated gaseous mixture over a catalyst bed contained in a reformer. At least a substantial portion of the heat for the endothermic steam-methanol reforming reaction is provided by the sensible heat in the superheated steam-methanol stream augmented by heat transferred through the tube wall depending on the overall system considerations. The concept of providing a substantial portion of the heat for the endothermic reforming reaction by sensible heat in the superheated steam-methanol stream is referred to hence forth as direct heating. Direct heating is of considerable advantage as it largely overcomes the problems encountered with reaction rates being limited by the rate of heat transfer through the tube wall especially near the reformer entrance and thus, for a given conversion, the reactor may be smaller, more efficient and less expensive. High steam-to-methanol ratios are required for direct heated reformers. The relatively large amounts of steam passed through the bed continuously clean the catalyst by removing ethanol and suppressing production of carbon monoxide and retard catalyst poisoning thereby enhancing catalyst stability. Direct heated reformers are particularly suitable for integration with fuel cells as the heat and fuel values contained in exhaust stream from each component can be utilized in the other. Hydrogen contained in the exhaust gas from the fuel cell anode may be burned to superheat the methanol-water mixture being fed to the reformer. Once the reactor is warmed up, the entire fuel requirements for the system are provided by the methanol being fed to the reformer. In order to accommodate the endothermicity of the reforming reaction, at least a major portion of the heat required for reforming is provided to the reformer as sensible heat contained in the superheated gases. Thus, when methanol and steam vapors contact a catalyst such as a combination of zinc oxide and copper oxide at a temperature of about 548 K at atmospheric or higher pressure, methanol decomposes to carbon monoxide and hydrogen and the carbon monoxide and steam react according to the well-known water gas shift reaction to form carbon dioxide and hydrogen. High exhaust gas temperatures may be indicative of unreacted fuel entering the exhaust chamber while low exhaust gas temperatures are indicative of a low fuel feed rate, or an unreactive catalyst bed. The efficiency decreased because the thermal losses as a percent of the total amount of power fed to the device increases as the size is reduced. In reactor configurations comprising solid catalyst particles disposed as a bed outside a plurality of heat transfer tubes, the layout of such heat transfer tubes is of critical importance, since it would be desirable to achieve a uniform temperature distribution across the radial direction of the reactor.
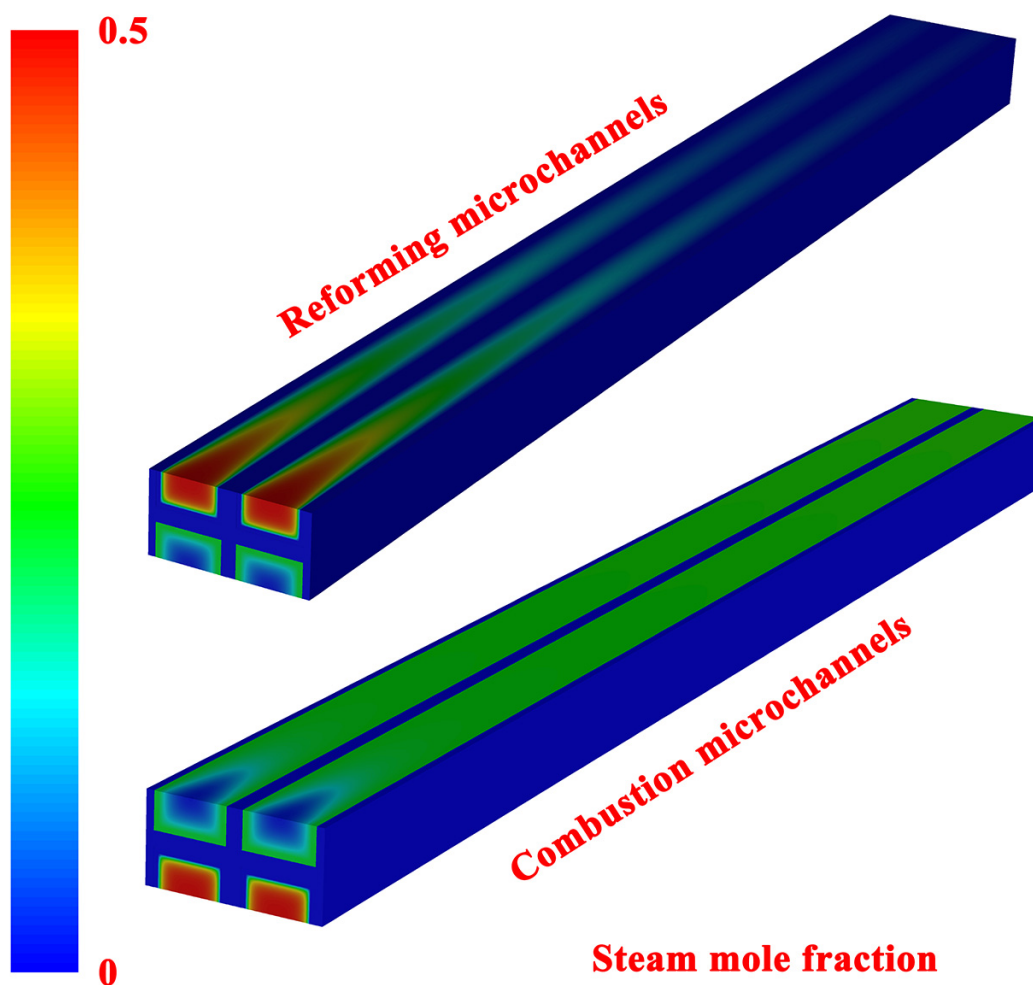
Figure 6. Steam mole fraction contour maps in the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The effect of catalyst layer thickness on the methanol conversion is illustrated in Figure 7 in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. Within the reformer, the methanol and steam react endothermically at high temperature to produce a gaseous product consisting primarily of steam, hydrogen, and carbon dioxide. Methanol is passed with steam over a catalyst at pressure typically ranging from 14.7 to 150 psia and temperatures in the range of about 373 K to about 548 K. Typical steam to methanol mole ratio are in the range of about 2.5:1 to about 4:1. The conversion of methanol may be affected in one pass over the catalyst bed contained in the reformer. Conventional methods for the production of hydrogen gas include steam reforming of hydrocarbons [45, 46]. According to the usual method, carbon monoxide and carbon dioxide are removed from a reformed gas containing hydrogen gas, carbon monoxide and carbon dioxide obtained by the above methods so as to produce hydrogen gas [47, 48]. The conventional methods have several drawbacks in that the price of the raw material hydrocarbons continues to rise, and the supply of the raw material hydrocarbons is in unstable conditions, desulfurization of the raw materials is required, and a high reaction temperature of 1100-1300 K is required for the steam reforming process. Consequently, the conventional methods are suitable for large scale hydrogen gas production, but they are not adequate for middle to small scale hydrogen gas production. In contrast, hydrogen gas production by the steam reforming of methanol has various advantages in that the reaction temperature is relatively low, separation of hydrogen gas from the reformed gas is easy, and no desulfurization is required because methanol is the raw material. Also, the method can easily cope with large to small scale plants, since it

uses inexpensive and easily transportable methanol as the raw material. The steam reforming reaction of methanol yields a wet gas containing condensable components such as methanol and water, and a reformed gas. After the reaction, the reformed gas containing hydrogen and carbon dioxide is taken out by cooling of the wet gas. Here, an industrial problem is the treatment of the condensed liquid. Conventionally, the condensed liquid is disposed without treatment or the condensed liquid obtained by vapor-liquid separation treatment is recycled to the reaction system so as to make reuse of the condensed liquid together with the raw material methanol and water. However, the former has a big problem from the view-point of pollution since the condensed liquid contains a considerable number of organic components such as unreacted methanol and high boiling point components. In the latter, a trace amount of ethanol contained in the raw material methanol accumulates because it is hardly converted by the usual reaction method. If the treated condensed liquid is reused in the reforming reaction system, it is necessary to adjust the amount of water so as to make the methanol-water ratio at a predetermined value. Therefore, if steam reforming of methanol is continuously carried out, a portion or the whole of a predetermined amount of raw material water may be allotted for water to be added to the condensed liquid. The steam reforming reaction of methanol which discharges the condensed liquid or makes reuse of the treated condensed liquid should not particularly be limited, but the reaction is usually carried out as follows. Known catalysts are used for the steam reforming reaction of methanol. For example, they include copper catalysts such as those containing copper oxides, chromium oxides and manganese oxides. The conditions of steam reforming reaction of methanol vary with the catalysts used, and cannot absolutely be specified. The reformed gas mainly contains hydrogen gas and carbon dioxide gas. When carbon dioxide gas is removed from the reformed gas by a conventional method such as absorptive removal with an aqueous sodium carbonate solution, an aqueous potassium carbonate solution or an aqueous monoethanolamide solution, a high purity of hydrogen gas is obtained. Also, when the condensed liquid is reused after treatment for the steam reforming reaction of methanol, it has no bad effect due to ethanol and high boiling point components on the reaction. The conversion of methanol is usually maintained high. The durability of catalysts is increased, and the process causes no pollution.
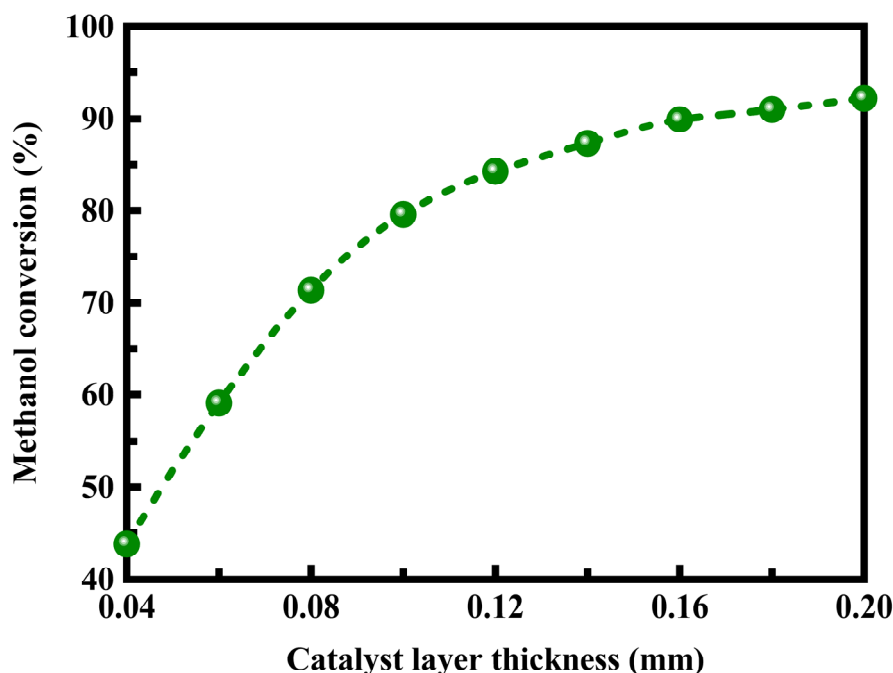

Figure 7. Effect of catalyst layer thickness on the methanol conversion of the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

The effect of catalyst layer thickness on the hydrogen yield is illustrated in Figure 8 in which

combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam reforming reaction. The process comprises contacting a gas phase comprising methanol and steam, with a solid catalyst. The gas phase may or may not comprise other gases, in addition to the methanol and steam. For instance, the gas phase may comprise an inert gas, for example, nitrogen or argon, which could for example be present as a carrier gas. The inert gas, when present, is typically nitrogen. Additionally, or alternatively, the gas phase may further comprise oxygen. Blending oxygen or air into the gas phase may encourage combustion and may also balance the total thermodynamic requirements of the non-syngas direct steam reforming system. Thus, the gas phase may further comprise oxygen or air. The gases in the gas phase may be pre-mixed, namely mixed together before the mixture is brought into contact with the catalyst. Alternatively, the gases can be fed into a reactor separately, so that the reactant gases are mixed together in the presence of the solid catalyst. The exothermic and endothermic reaction channel flows are in the same direction, although in this design, the reformer flow enters and leaves in a direction perpendicular to the direction of flow during reaction to accommodate manifolding connections on a different face of the device than the combustion flow manifolding. At a given reactor length or height it is not difficult to obtain nearly uniform ratios of catalyst area to heat transfer area and thereby uniform temperature distribution in the interior of the catalyst bed cross section, namely toward the center of the reactor. This ratio can be kept constant if, for instance, the tube pitch is kept constant for the same heat transfer tube diameter. By tube pitch is meant the center-to-center distance of neighboring tubes. Even a change from for instance triangular pitch in the center of the bed to a rectangular pitch near the periphery of the bed can be obtained without experiencing too large variations in the ratio of catalyst area to heat transfer area. However, at the periphery of the heated or cooled catalyst bed, the surrounding external reactor wall defining the periphery of the reactor does not heat nor cool the catalyst bed. The peripheral heat transfer tubes are preferably positioned in direct contact with the external reactor wall. The peripheral heat transfer tubes may be simple tubes having a single wall and may be shaped so that they have a substantially semi-circular or triangular cross-section. Other types of tube can be envisaged, for example double-tubes. The temperature toward the external reactor wall can be kept at about the same level as in the center of the reactor. Note that the catalytic combustion is most likely accompanied by some homogeneous combustion in the flow-by gap. The outermost steam reforming channels are sized to have half the flow of the inner channels since the outer channels received only half of the heat. Each outermost channel has catalyst only against the innermost wall and is designed to admit roughly half the flow going through a full channel for a given pressure drop. Some process characteristics of some preferred processes include the following factors: Operate safely at a fuel: oxygen ratio near stoichiometric for the use of combustion as the exothermic reaction. This reduces the required air which improves the overall system thermal efficiency and reduces the required duty for the external air blower or compressor. Operate steam reforming at short contact times or conversely at high gas hourly space velocities. This is required to create a compact device. Operate with a high heat flux. This is required to operate at short contact times. Operate with a low pressure drop per unit length of reactor. This enables a higher productivity per unit volume. Optional: quench-inhibit gas phase reactions. As the channel dimension nears the quench diameter or drops below, the contribution of the unwanted gas phase homogeneous combustion reaction is reduced. The devices may be made of materials such as plastic, metal, ceramic and composites, depending on the desired characteristics. Walls separating the device from the environment may be thermally insulating; however, the walls separating adjacent exothermic and endothermic reaction chambers should be thermally conductive. The devices can be made by forming chambers within a single block of material, by joining multiple components, and by stacking and bonding shims. A preferred integrated reactor body can be made from a single block of metal. Its channels could be created with a wire electric discharge machining in the main body, and the headers and footers could be made separately and welded on, adding to the flexibility of the design. Wire electric discharge

machining is used to create slots or holes in a block of metal that are the microchannels through which flow passes and a unit operation occurs. Sinker electric discharge machining, laser machining, and in some larger channels conventional milling can also be used to make channels from a single block of metal. The aperture-containing shims can be formed by processes including: conventional machining, wire electric discharge machining, laser cutting, photochemical machining, electrochemical machining, molding, water jet, stamping, etching and combinations thereof. For low cost, stamping is especially desirable. Alternately, laser welding shims could join the devices or sheets to form seals between flow paths. Devices could alternatively be joined by the use of adhesives. The combustion chamber and reforming chamber are oriented so that heat is transferred from the combustion chamber into the reforming chamber. Both the combustor and reformer should have a separate preheater or a preheat zone integrated within the device in which reactants are preheated prior to contacting a catalyst.
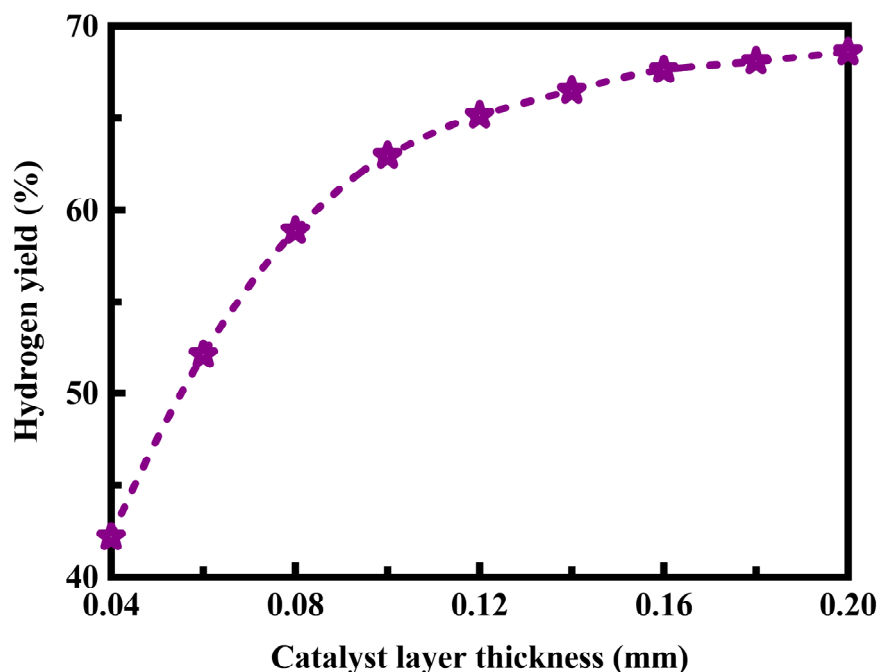

Figure 8. Effect of catalyst layer thickness on the hydrogen yield of the integrated combustion-reforming reactor in which combustion chambers are in direct thermal contact to reaction chambers for an endothermic steam-methanol reforming reaction.

4. Conclusions

The present study aims to provide a fundamental understanding of the exothermic and endothermic reaction characteristics and operation methods of integrated combustion-reforming reactors. Particular emphasis is placed upon the simultaneous implementation of the endothermic steam reforming and the heat-supplying exothermic catalytic combustion such that the thermal stability of the reaction system is increased. The effect of catalyst layer thickness on the reaction characteristics is investigated in order to understand how to design and operate such reactors with high efficiency. The major conclusions are summarized as follows:

- Unique jet design features can be implemented in order to suppress homogeneous combustion and promote heterogeneous catalytic combustion on the channel wall.
- Diffusion within these small pores in the catalyst layers is typically Knudsen in nature for gas phase systems, whereby the molecules collide with the walls of the pores more frequently than with other gas phase molecules.
- The composition in the combustion chamber is reacted to produce sufficient heat to sustain the micro-combustion process without energy input.

- The combustion and reforming processes can be stably and efficiently operated at lower temperatures, without the need for energy input to sustain or even to start the combustion process.
- Since a palladium component is alloyed with the zinc, generation of carbon monoxide due to the methanol decomposition reaction is suppressed.
- Direct heating is of considerable advantage as it largely overcomes the problems encountered with reaction rates being limited by the rate of heat transfer through the tube wall especially near the reformer entrance and thus, for a given conversion, the reactor may be smaller, more efficient and less expensive.
- The conventional methods are suitable for large scale hydrogen gas production, but they are not adequate for middle to small scale hydrogen gas production.
- As the channel dimension nears the quench diameter or drops below, the contribution of the unwanted gas phase homogeneous combustion reaction is reduced.

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