Compact Steam-Methane Reforming for the Production of Hydrogen in Continuous Flow Microreactor Systems

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ABSTRACT: The implementation of fuel cell deployment requires efficient conversion of fuels into hydrogen in a distributed energy system. Fortunately, continuous flow and microreactor technology provide unique opportunities for the portable production of hydrogen. This study focuses on determining the operation space for a thermally integrated methane reforming system, thereby providing a theoretical basis for the design and optimization of such systems. The steam-methane reforming over rhodium coupled with methane combustion over platinum in a thermally integrated microchannel reactor arranged with rectangular-shaped protuberances was studied numerically in order to improve its operability and stability. Computational fluid dynamic simulations were carried out with detailed reaction mechanisms to identify conditions for the maximum hydrogen yield and the highest output power. Various operating lines were presented, and various performance metrics were evaluated accordingly. The results indicated that the efficient production of hydrogen is made possible through improving transport performance for highly active catalysts. The flow disturbance elements designed for the reactor are of great benefit to intensification of the reforming process. There exists a trade-off between fuel utilization and output power. Autothermal operation advantages from improved transport performance in small physical dimensions were demonstrated for the system, but careful thermal management is always necessary to ensure its efficient and stable operation. The thermal conductivity of the wall separating the exothermic and endothermic reactions plays a significant role in determining the performance of the system. Highly active catalysts are required to intensify the overall reforming process and to achieve efficient thermal management. Adjustment of fluid velocities can serve as a convenient means to achieve efficient operation of the system.

1. INTRODUCTION

Flow chemistry, the science of running a reaction in continuous mode, has become increasingly important in the field of chemical production. When reactions are highly exothermic or endothermic, chemical processes are inherently limited by heat transfer. Microchannel reactors have received significant attention due to potential advantages they offer over conventional process equipment in terms of improved transport performance. Small physical dimensions associated with very high surface area-to-volume ratios can significantly enhance heat and mass transport in a microchannel reactor, thereby enabling compact operations. This transport characteristic also has the advantage of promoting the application of new reaction pathways and catalysts to reduce capital and operating costs, and to improve the energy efficiency and product yield.

Microreactor technology is becoming increasingly available commercially, thanks to microfabrication technology providers such as Velocys, Microinnova, mikroglas, Ehrfeld, Siemens, Heatric, IMM, IMT, FZK, CPC, and Dai Nippon Screen. This list is by no means exhaustive. Microchannel reactors may offer distinct advantages in process development and chemical production. Such microchemical systems are usually a continuous flow reactor. Microchannel reactors involve microfabricated structures to allow flow chemistry to be performed at the microscale. Continuous flow technology can offer a number of advantages for chemical production. Microchannel reactors can benefit from such technology to allow chemical reactions to be conducted in a safer and more efficient way.

The production of hydrogen can be achieved through a number of reforming and partial oxidation reactions. Most of these reactions have been carried out in microchannel reactors. The steam-methane reforming route is particularly attractive for fuel cells. Such a chemical route now accounts for nearly half of hydrogen production. Microreactors have emerged as one of the most promising technologies for hydrogen production. Microchannel reactors can be particularly effective for the highly endothermic steam-methane reforming reaction. Furthermore, the efficiency of the overall process can be improved by closely coupling this reaction with an exothermic catalytic oxidation reaction due to the enhanced transport performance.

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hydrogen production such as increased productivity, processing windows, operational flexibility, and process control. These benefits can effectively eliminate cost and distribution issues that often constrain operation. In addition, the inherent flame quenching properties of microchannel reactors could effectively eliminate safety concerns.31,32

Continuous flow and microreactor technology are now creating new opportunities for the portable production of hydrogen by steam reforming of methane.33,34 The high transport performance possible in microfluidic systems allows the reaction to proceed under more aggressive conditions, thereby offering higher hydrogen yields than can be achieved by existing conventional approaches. However, this chemical process is a complex multiple reaction system, and the overall efficiency depends heavily on the thermally integrated scheme employed for such a microchemical system. Consequently, the yield of hydrogen depends in a complex manner upon the design parameters such as catalysts, physical dimensions, and wall thermal conductivity, and on the process variables such as feed composition, fluid velocity, temperature, and pressure. To improve the yield of hydrogen, there is a need to further explore the effect of these design parameters and process variables on the performance of a thermally integrated microchannel reactor conducting the steam-methane reforming and an exothermic catalytic oxidation reaction simultaneously. The first step in understanding such an effect is usually to determine the operation space for a thermally integrated system in order to improve its operability and stability. The system will operate effectively within the operation space which varies based on the device function and application context. Outside the operation space, the system may fail. It is therefore of great significance to determine the operation space for a thermally integrated methane reforming system in order to provide a theoretical basis for the design and optimization of such systems.

The primary focus of this research is on determining the operation space for a thermally integrated microchannel reactor through identifying conditions for the maximum yield of hydrogen produced by the steam-methane reforming reaction conducted in the reactor. Another dominant design objective is to maximize output power of such microfabricated chemical systems for portable applications such as fuel cells. This is in contrast to the primary concern raised for commercial-scale hydrogen production plants, for which the main focus is on maximizing the energy conversion efficiency of hydrogen production and minimizing its capital and operating costs. This fundamental difference in development objectives leads to drastically different approaches to efficient operation and optimal design of reactors. In developing continuous flow and microreactor technology for hydrogen production through the steam-methane reforming reaction, it is therefore essential to focus on the operating characteristics of thermally integrated microchannel reactors, as well as to evaluate the benefits and disadvantages associated with such a design.

In the current study, steam-methane reforming over rhodium coupled with catalytic oxidation of methane over platinum in a thermally integrated microchannel reactor was investigated numerically. The thermally integrated system was arranged with flow disturbance elements in the channels. Such a design allows the endothermic and exothermic reactions to take place in close proximity, and the reforming and oxidation processes to be intensified with improved momentum, heat, and mass transport performance of the reactor. A two-dimensional computational fluid dynamics model was developed to gain insights into the operating characteristics of the system. Numerical simulations were performed to identify conditions of the steam-methane reforming reaction conducted in thermally integrated microchannel reactors for the maximum hydrogen yield and the highest output power. The effect of design parameters and process variables on the performance of the system was evaluated in detail. The objective of this study is to determine the theoretical limits on hydrogen yield and output power for a thermally integrated methane reforming system under various operating conditions. Emphasis is placed on determining the operation space for the portable hydrogen production system so as to improve its operability and stability. Of particular interest is how flow disturbance elements arranged in the channels affect the performance of transport and the yield of products in the system.

2. RESULTS AND DISCUSSION

2.1. Description of the System. The system considered in the present work is a thermally coupled microchannel reactor with alternating reforming and combustion channels, wherein endothermic and exothermic reactions are conducted simultaneously without mixing the two streams. The heat required for an endothermic reaction is supplied directly through dividing walls from an exothermic reaction occurring on the two opposing sides. The channels within which
the wall material used is 200 W/(m·K). In the present work, the thermal conductivity of the material of the dividing wall is 200 W/(m·K). The structure described for the system is represented as a two-dimensional steady-state model, thereby greatly simplifying the problem. In general, the width of such channels is significantly larger than their height.\textsuperscript{5,6} As a consequence, a two-dimensional representation of the system is reasonable. As the physical geometry of interest is symmetric, only half of each channel and the corresponding dividing wall is modeled.

2.2. Device Characteristics. There are considerable modeling efforts to intensify the process of steam-methane reforming in thermally integrated systems for the production of hydrogen using microreactor technology.\textsuperscript{37,38} However, the mechanism responsible for transfer of heat with such a thermally coupled arrangement is rather complicated, and the operating characteristics of small-scale catalytic devices are poorly understood accordingly. As a result, further research is necessary for these topics.

Typical contour plots of temperature, methane concentration, conversion, and fluid velocity in a parallel flow arrangement are illustrated in Figure 2 for each side of the reactor. The results presented here demonstrate autothermal operation of the system with efficient fuel conversion in both the combustion and reforming processes. Some of the key features of the behavior exhibited by the system are discussed herein. The catalytic oxidation reaction is conducted in the

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Contour plots of temperature, methane concentration, conversion, and fluid velocity for the reactor. The velocity of the combustible fluid inlet flow is 3.0 m/s. The velocity of the process fluid inlet flow is 2.0 m/s. The steam-to-carbon ratio is 3.0, and the equivalence ratio of the combustible mixture at the inlets is 0.8. The thermal conductivity of the material of the dividing wall is 200 W/(m·K).
combustion catalyst washcoat to generate heat by feeding a gas stream comprising the fuel and air. Exothermic heat is transferred from the combustion catalyst washcoat to its adjacent reforming catalyst washcoat across the dividing wall to increase the temperature of the reactants in the reforming channel. The steam-methane reforming reaction is conducted in the reforming catalyst washcoat to produce a synthesis gas product. A hydrogen enriched stream can be produced by flowing synthesis gas produced in such a system through a membrane separator positioned downstream from the reactor. The fuel-air equivalence ratio may change in order to control the amount of heat released by the exothermic reaction conducted in the combustion channel.

The temperature contour plot in Figure 2 indicates that the highly conducting wall enables upstream transport of the heat released by the exothermic reaction toward the two streams near the entrance to the reactor. The two streams are then heated by the dividing wall with such a heat transfer mechanism. The dividing wall is nearly isothermal due to efficient heat transfer caused by its very high thermal conductivity. Most of the fuel is converted before the two fluid streams exit the reactor, as shown from the concentration and conversion contour plots in Figure 2. This will also enhance safety by ensuring that the device is within its specified operating temperature range. It is expected that the effect of inhibition of gas-phase reactions becomes more pronounced in the combustion process with decreasing the physical dimension of the reactor. In this context, excellent thermal uniformity and improved mass transfer rates can be achieved in the reactor. However, small physical dimensions can cause the problem of very large pressure drops and the nonuniform distribution of flow field in the system.

Transverse temperature and methane conversion profiles are illustrated in Figure 3 at various axial distances of the reactor. Near the entrance to the reactor, steep gradients of both temperature and fuel conversion can be found in the transverse direction. Such gradients necessitate a two-dimensional computational fluid dynamics model to represent the structure described for the system. The magnitude of temperature and conversion gradients decreases rapidly in the transverse direction. Specifically, over half the length of the reactor, the temperature profile is relative uniform in the transverse direction, as shown in Figure 3a. Similar behavior can also be found for the fuel conversion profile in the transverse direction near the exit of the reactor, as shown in Figure 3b. Steep gradients exist in the transverse direction for temperature and fuel conversion within the fluid phase, but near-zero gradients of temperature can be found within the solid phase due to the excellent heat transfer performance by the dividing wall made from a highly conductive material.

The steam-to-carbon ratio is usually higher than reaction stoichiometry so as to reduce the formation of carbon or coke. The influence of the steam-to-carbon ratio on the conversion of methane in the reforming channel and the maximum temperature of the dividing wall is investigated, and the results are presented in Figure 4. It is clear that methane conversion increases with increasing the steam-to-carbon ratio.

![Figure 3](image_url)  
(3) Temperature and methane conversion profiles in the transverse section at various axial distances of the reactor. The dashed lines represent various interfaces between two spatial regions occupied by different matter. The parameters used here are the same as those given in Figure 2.

![Figure 4](image_url)  
(4) Effect of the steam-to-carbon ratio on the methane conversion for the reforming reaction as well as the maximum temperature of the dividing wall. All other parameters used here are the same as those given in Figure 2.

However, the rate of the reforming reaction is expected to decrease with increasing the steam-to-carbon ratio because the partial order is 1.0 with respect to methane and 0 with respect to steam. Under the conditions studied here, however, the factor determining the performance of the reactor is the amount of methane in the feed, when the amount of heat available from the combustion channel is kept constant. As the steam-to-carbon ratio increases, the amount of methane in the feed decreases. As a consequence, the maximum temperature of the dividing wall increases, which leads to an increase in the conversion of methane in the reforming channel.

2.3. Effect of Flow Disturbance Elements. The engineering science issue around heterogeneous catalytic flow systems is that they are notoriously mass transfer limited, whether in turbulent flow or laminar flow, because of the formation of boundary layers near the catalytic surface, making...
the transfer of both heat and mass limited by slow diffusive and conductive mechanisms. One potential solution to this problem is the disruption of boundary layers by producing wakes, particularly transient vortex shedding due to the flow around obstacles, suitably placed. Wakes introduce convection, but also crucially periodic wakes that disrupt the formation of boundary layers. Periodic vortex shedding, with a period shorter than the time scale for the establishment of the boundary layer,\(^{32}\) will result in the dominance of transient convection as the mass transfer mechanism, accelerating the limiting step, potentially resulting in a kinetics limited regime for the heterogeneous catalysis. This is important as the whole role of catalyst design is to increase the activity of the catalyst chosen for a heterogeneous catalytic flow system, which is wasted if the overall transformation is mass transfer limited. In this research, the above hypothesis is tested by the introduction into the design of a thermally integrated methane steam reformer of two adjacent protuberances, with varying geometries, and studied by a computational fluid dynamics model with the heterogeneous reaction tracked, so as to assess the effectiveness of wake disruption of boundary layers for the increase in predicted reactive flux. The first step in designing and optimizing the structure of protuberances is usually to understand the effect of such flow disturbance elements on reactor performance, so as to assess their effectiveness from the point of view of fluid mechanics.

Protuberances are employed for the reactor to fulfill design requirements in terms of both stability and reliability for the system. By utilizing such a design method, transport performance can be significantly improved for the reactor, as shown from the fluid velocity contour plot in Figure 2. Specifically, the rectangular-shaped protuberances arranged in the channels can cause hydrodynamic instability of fluid flow by forming local flow field disturbances. The cold reforming reaction stream encompasses catalyst surfaces, accompanied by the absorption of energy in the form of heat from the hot combustion reaction stream flowing in its adjacent channel. In this context, the protuberances arranged in the channels can achieve better transport performance within the system, but there is no significant increase in pressure drop. Such flow disturbance elements designed for the reactor may also have a beneficial effect on the stability of flame in the combustion channel. This unique geometry also increases the contact area between different phases, in addition to improving reactor performance by increasing transport rates within the system.

The design with flow disturbance elements allows reforming and combustion reactions to be increased in rate by enhancing transport within the system, as discussed above. To further illustrate how such flow disturbance elements can increase the effectiveness of the performance of transport within the system, a comparison of temperature and methane concentration fields is made between reactors with and without flow disturbance elements. Typical contour plots of temperature and methane concentration are illustrated in Figure 5 in the absence of flow disturbance elements. Autothermal operation is also feasible for reactors without flow disturbance elements. However, there exists a noticeable difference in temperature and methane concentration fields between the two types of reactors as shown in Figures 2 and 5, which verifies the effectiveness of the flow disturbance elements arranged in the channels. This indicates that the protuberances arranged in the channels will be of benefit to the performance of heat and mass transport within the system. In addition, higher temperatures and conversion can be achieved for reactors with flow disturbance elements as shown in Figure 2 due to notably increased rates of transport within the system. Furthermore, the ignition delay time is shortened in the gas phase. Overall, flow disturbance elements are of great importance to the improvement of the performance of transport within the system. In the presence of flow disturbance elements, the enhanced mass transport within the system is attributable, in part, to the increased contact area between different phases. Flow disturbance elements have also certain regulatory function of flow field distribution along the length of the reactor, as illustrated in Figure 2.

The primary bottleneck in the development of a heterogeneous catalytic flow system is caused by the diffusive transport within its boundary layer. Rectangular-shaped protuberances are introduced into the design of a thermally integrated microchannel reactor to disrupt the boundary layer and thereby to increase the effectiveness of the performance of heat and mass transport within the system. To examine how such flow disturbance elements can enhance transport performance, the effectiveness of wake disruption of boundary layers for the increase in heat and mass transfer rates is assessed herein. Typical contour plots of the fluid velocity in the transverse direction of the reforming channel are illustrated in Figure 6 for the reactor in a parallel flow arrangement. Rectangular-shaped protuberances can serve as a vortex generator to enhance heat and mass transfer within the

![Figure 5](attachment:image5.png)  
**Figure 5.** Contour plots of temperature and methane concentration for the reactor in the absence of flow disturbance elements. The parameters used here are the same as those given in Figure 2.

![Figure 6](attachment:image6.png)  
**Figure 6.** Contour plots of the fluid velocity in the transverse direction of the reforming channel. The parameters used here are the same as those given in Figure 2.
system. External flow over a stationary rectangular-shaped protuberance exhibits periodic vortex shedding, with a period shorter than the time scale for the establishment of the boundary layer, eventually leading to the dominance of transient convection as the heat and mass transport mechanisms. The transport of heat and mass in the reforming channel is enhanced by utilizing the vortex shedding mechanism from rectangular-shaped protuberances subjected to the wake disruption of boundary layers in the transverse direction, potentially resulting in a kinetics limited regime for the reforming process. It can be expected that the effectiveness of the improvement in heat and mass transport is related closely to vortex dynamics, which depends to a great degree on complex vortex shedding patterns and their interplay with the boundary layers. As a result, the flow disturbance elements arranged in the system may be effective in reducing the resistance to the transport of heat and mass within the boundary layer.

2.4. Effect of Fluid Velocity. One of the main objectives of the thermally coupled system is to utilize energy released by the catalytic oxidation reaction to maximize the yield of hydrogen from the steam-methane reforming reaction performed in the reactor, that is, the total amount of hydrogen obtained in the reforming process. To make the system more efficient, the effect of fluid velocity is evaluated herein, and critical velocities are also determined for the process fluid inlet flow.

The temperature profiles in the streamwise direction are depicted in Figure 7 for various velocities of the process fluid inlet flow.

![Figure 7. Temperature profiles in the streamwise direction along the centerline of the combustion channel, the reforming channel, and the dividing wall at various velocities of the process fluid inlet flow. All parameters used here are the same as those given in Figure 2, except the velocity of the process fluid inlet flow.](image)

Inlet flow. Under low fluid velocity conditions, a small amount of energy released by the exothermic catalytic oxidation reaction is removed from the combustion channel by the endothermic steam reforming reaction in its adjacent channel, making the device temperature very high. Because the traditional catalysts used for the two chemical reaction processes are not stable at high temperatures, the heat released from the thermally coupled device needs to be removed at a rate sufficient to keep local temperatures low enough to avoid catalyst deactivation. As the device generates heat during operation, the reactor requires careful thermal management to ensure that it is within the specified range of operating temperatures. Specifically, high temperatures are the primary issue that requires careful thermal management, and the device should be operated below the maximum allowable operating temperature.

On the other hand, under high fluid velocity conditions, a large amount of energy released by the exothermic catalytic oxidation reaction is removed from the combustion channel, making the device temperature very low, as shown in Figure 8. This will lead to slower preheating of the fluid in the combustion channel to the ignition temperature, which in turn shifts the catalytic oxidation reaction downstream. As the combustion chamber is in direct thermal contact to the reforming chamber for the endothermic reaction, extinction could occur on the exothermic side and the microdevice may fail when the velocity of the fluid in the reforming channel is very high. The term “extinction” refers to a process by which the catalytic oxidation reaction is terminated in the combustion chamber of the reactor. Consequently, particular attention must be paid to the actual flow rate of the reforming reaction stream in order to achieve self-sustained operation for the system.

2.5. Critical Fluid Velocity. It has been found that high fluid velocities in the reforming channel could serve a double purpose of producing high flow rates of hydrogen for use in fuel cells, while simultaneously reducing the temperature of a thermally integrated microchannel reactor to satisfy the requirement of stability of the catalysts and materials used by such a device. The maximum fluid velocity in the reforming channel allowed for self-sustained operation of a thermally coupled system is hereafter termed as “maximum critical fluid velocity”. Similarly, the minimum fluid velocity in the reforming channel allowed to meet the requirement of stability of the catalysts and materials used by a thermally coupled system is hereafter termed as “minimum critical fluid velocity”. To provide clear guidance as to what materials can be used for the reactor, critical velocities of the process fluid inlet flow are shown in Figure 8 for a countercurrent flow exchange system and a parallel flow exchange system at various thermal conductivities of the dividing wall. Each of the shaded regions in Figure 8 represents the operation window determined within the limits of stability of combustion as well as the limits of stability of the catalysts and materials used within the context of practical applications.

The reactor will operate effectively when the velocity of the process fluid inlet flow is lower than the critical point determined by extinction as shown in Figure 8. The critical fluid velocity varies based on the wall thermal conductivity used. When the velocity of the process fluid inlet flow is higher than such a critical point, autothermal operation cannot be sustained, and the reactor will no longer function. Higher thermal conductivities of the dividing wall will lead to improved heat recirculation within the system, making possible higher velocities of the process fluid inlet flow, irrespective of the flow arrangement designed for the reactor, as shown in Figure 8. There is a decrease in both critical fluid velocities when the system is operated in a parallel flow arrangement, especially for highly insulating materials. For highly conductive materials, interestingly, the difference in critical fluid velocity between the two flow arrangements becomes less pronounced.

Low velocities of the process fluid inlet flow will lead to high temperatures of the dividing wall and of the catalysts used. In contrast, high velocities of the process fluid inlet flow may result in loss of stability of the system. The shaded regions in Figure 8 allow stable operation of the device in terms of the stability of both combustion and materials. The upper
boundary of the reacting flow represents the high inlet fluid velocity limit determined by loss of stability due to extinction. In contrast, the lower boundary of the reacting flow represents the low inlet fluid velocity limit determined by loss of stability of materials, and it is assumed that a reasonable threshold temperature of 1500 K is the limit of materials stability. Between the two boundaries of these inlet fluid velocities, stable operation is allowed for the system. However, stable operation is not available outside of the inlet fluid velocity envelope. The countercurrent flow configuration has a slight advantage over the parallel flow configuration in terms of the criterion used for assessing the stability of the system due to extinction, as shown in Figure 8. However, the parallel flow configuration offers a wider choice of wall materials for practical applications.

The output power generated from the system is one of the most important performance metrics, as the main objective of the device is to maximize the yield of hydrogen as much as possible.\textsuperscript{5,18} The value of output power is determined from the lower heating value of hydrogen, at a temperature of 298.15 K available in the literature.\textsuperscript{45,46} To obtain the output power generated from the system, the width of the reactor is assumed to be 10.0 mm in the third dimension. The output power generated from the reactor with various wall thermal conductivities is shown in Figure 9 for a countercurrent and a parallel flow arrangement. Each of the shaded regions in Figure 9 represents the operation window determined within the limits of stability of combustion as well as the limits of stability of the catalysts and materials used. The upper boundary of each shaded region represents the maximum critical velocity of the process fluid inlet flow, determined by loss of stability of combustion due to extinction. The maximum output power line represents the maximum yield of hydrogen produced in the system. However, such an operating line is within the regime of incomplete conversion for the reforming reaction. Any further increase in the velocity of the process fluid inlet flow beyond the maximum output power line will extinguish both reactions. The maximum output power line presented in Figure 9 has similar feature compared with the critical velocity of the process fluid inlet flow shown in Figure 8, leading to the same preference regarding the choice of flow arrangement.

The primary focus here is on the critical fluid velocity in terms of the stability of both combustion and materials. However, careful attention should also be paid to other physical and mechanical properties, such as mechanical strength, stiffness, and threshold temperatures of the structure of a continuous flow microreactor system designed for the production of hydrogen.

2.6. Effect of Wall Thermal Conductivity. Hot spots may be formed within the dividing wall under low wall-thermal-conductivity conditions.\textsuperscript{47,48} In hot spots, the temperature is locally very high, and its gradient is steep in the streamwise direction. Clearly, such a situation is undesirable. It is therefore of considerable interest to evaluate the effect of the thermal properties of the dividing wall on the behavior of the system in order to optimize the design required to implement the reforming process.

To clarify the effect of the thermal conductivity of the dividing wall, the results obtained for the maximum temperature are presented in Figure 10 for various velocities of the process fluid inlet flow, while the velocity of the combustible fluid inlet flow is kept constant. The maximum temperature of the dividing wall depends strongly on its thermal conductivity. It is clear that the thermal conductivity of the dividing wall is a key factor determining the thermal performance of the system. The maximum temperature of the dividing wall decreases with increasing wall thermal conductivity. A high velocity of the process fluid inlet flow will cause an increase in the amount of

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**Figure 8.** Effect of the thermal conductivity of the dividing wall on the critical velocity of the process fluid inlet flow for the reactor operated in a countercurrent flow arrangement and in a parallel flow arrangement. The shaded region represents the operation window determined within the limits of stability of combustion as well as the limits of stability of the catalysts and materials used for the reactor. The parameters used are given as follows. The velocity of the combustible fluid inlet flow is 3.0 m/s. The steam-to-carbon ratio is 3.0, and the equivalence ratio of the combustible mixture at the inlets is 0.8.

**Figure 9.** Effect of the thermal conductivity of the dividing wall on the output power from the reactor operated in a countercurrent flow arrangement and in a parallel flow arrangement. The shaded region represents the operation window determined within the limits of stability of combustion as well as the limits of stability of the catalysts and materials used for the reactor. All parameters used here are the same as those given in Figure 8.
The parameters used are given as follows. The velocity of the fluid inlet is 0.8 m/s. The steam-to-carbon ratio is 3.0, and the equivalence ratio of the combustible mixture at the inlets is determined by the maximum critical velocity of the process range. Any results presented herein at temperatures above 1273 K are adjusted by extrapolation. The change of washcoat efficiency is assumed for a downstream processing device. A two-parameter continuation algorithm is implemented to trace three main metrics of reactor performance: hydrogen yield, the methane conversion for the reforming reaction, and the maximum temperature of the dividing wall. The influence of the velocity of the combustible fluid inlet flow on the output power generated from the reactor as well as the maximum temperature of the dividing wall is shown in Figure 12. The output power that can potentially be generated from the system is one of the most important metrics of reactor performance. This performance metric is therefore used as an indicator of the total amount of hydrogen produced from the system by the steam-methane reforming reaction per unit time. This parameter is especially valuable for portable power applications such as fuel cells. The theoretical limits of maximum and minimum allowable output power are also given in Figure 12 as a function of the velocity of the combustible fluid inlet flow.

For a given velocity of the combustible fluid inlet flow, the output power increases first and then decreases with increasing the velocity of the process fluid inlet flow, as shown in Figure 12a. The cause of decrease in output power is due to the loss of the heat transferred in the reactor from the combustion side to the reforming side, but a decrease in the maximum temperature of the dividing wall as shown in Figures 7 and 10. The shaded region in Figure 10 represents the operation window obtained for wall thermal conductivity of 200 W/(m·K), determined within the limits of stability of combustion and of the catalysts and materials used. Clearly, the choice of catalysts, materials, and the velocity of the process fluid inlet flow is restricted to a particular, narrow operation window, as depicted in Figure 10. In most cases, only fast reacting flows are allowed for the reforming reaction stream, and the system would need to be designed with highly conductive materials for the dividing wall. The reactor should also be carefully designed to ensure that the velocity of the process fluid inlet flow is lower than its critical value, as discussed earlier. However, such an operation window will depend on the catalysts used as well as the velocity of the combustible fluid inlet flow to a certain extent.

2.7. Effect of Reforming Catalyst. In industry, the steam-methane reforming reaction is conducted in the presence of a nickel–alumina catalyst under high-temperature and high-pressure conditions. The influence of reforming catalyst on methane conversion and the maximum temperature of the dividing wall is shown in Figure 11 for different velocities of the process fluid inlet flow. Specifically, a comparison of the two performance parameters of the reactor is carried out between a rhodium-based catalyst and a nickel-based catalyst. The steam-methane reforming reaction over nickel is modeled using the kinetic mechanism proposed by Maier et al. Each of the kinetic mechanisms has its applicable temperature range. Any results presented herein at temperatures above 1273 K are adjusted by extrapolation. The change of washcoat properties caused by such a nickel-based catalyst may have an influence on system performance but is not considered in the present work, that is, the same washcoat structure is modeled herein for the two reforming catalysts.

The horizontal dashed line in Figure 11 represents the threshold temperature as defined early, that is, the limit of materials stability. The shaded region represents the available range of methane conversion in the case of nickel at temperatures below the limit specified. When the system is operated at low velocities of the process fluid inlet flow, the conversion of the fuel and the maximum temperature of the dividing wall are both high, as shown in Figure 11. In addition, the two parameters decrease with increasing the velocity of the process fluid inlet flow. Clearly, rhodium has performance advantages relative to nickel in this regard. Such advantages are derived from improved catalytic activity, resulting in increased conversion for the reforming reaction. In the presence of a nickel-based catalyst, the realization of the reforming process with a high conversion will require lower velocities of the process fluid inlet flow or higher velocities of the combustible fluid inlet flow. Unfortunately, the stability of the materials used will be a critical issue in the design of the system. Overall, the use of a reforming catalyst with high catalytic activity provides the potential for conducting the steam-methane reforming reaction, making possible an efficient hydrogen production device.

2.8. Hydrogen Yield and Output Power. To further assess the performance of the system, the attainable operation space for the reactor is discussed based on the power generated from the hydrogen produced by the steam-methane reforming reaction. Full efficiency is assumed for a downstream processing device. A two-parameter continuation algorithm is implemented to trace three main metrics of reactor performance: hydrogen yield, the methane conversion for the reforming reaction, and the maximum temperature of the dividing wall.

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The influence of the velocity of the combustible fluid inlet flow on the output power generated from the reactor as well as the maximum temperature of the dividing wall is shown in Figure 12. The output power that can potentially be generated from the system is one of the most important metrics of reactor performance. This performance metric is therefore used as an indicator of the total amount of hydrogen produced from the system by the steam-methane reforming reaction per unit time. This parameter is especially valuable for portable power applications such as fuel cells. The theoretical limits of maximum and minimum allowable output power are also given in Figure 12 as a function of the velocity of the combustible fluid inlet flow.
be desirable to operate the system along the nearly complete conversion line or the maximum output power line.

The ratio of the velocity of the process fluid inlet flow to that of the combustible fluid inlet flow is shown in Figure 13 for the system operated along the materials stability line, nearly complete conversion line, and maximum output power line. The operation space for the reactor is relatively large under low fluid velocity conditions, but shrinks significantly under high fluid velocity conditions. There is a considerable range in the velocity of the fluid inlet flow within which conversion is nearly complete for the reforming reaction and temperatures are moderate in the reactor. In such a range, there is a good thermal balance between the endothermic and exothermic reactions conducted in the reactor, thus reducing the gradient of temperature within the system.

The horizontal arrow in Figure 13 denotes the ratio obtained from a theoretical energy balance for the system in the case of complete conversion of the fuel used for the exothermic and endothermic reactions. The theoretical, global energy balance for the system in a steady state dictates that the net heat liberated by the reactor is absorbed as sensible heat by the process fluid and the combustible fluid. The overall balance of energy in the system can be expressed as

$$\gamma_{\text{fuel,inlet}} \Delta h(\text{combustion}) + \gamma_{\text{fuel,inlet}} \Delta h(\text{reforming})$$

$$+ \frac{m_{\text{fuel}}}{m_{\text{fuel,inlet}}} (T_{\text{outlet}} - T_{\text{inlet}})(\text{combustion})$$

$$+ \frac{m_{\text{fuel}}}{m_{\text{fuel,inlet}}} (T_{\text{outlet}} - T_{\text{inlet}})(\text{reforming}) = 0$$

In the above equation, the enthalpy change of the exothermic and endothermic reactions at constant pressure is computed at a reference temperatures of 300 and 400 K, respectively. The results based on the above theoretical, global energy balance formula indicate that the ratio of the velocity of the process fluid inlet flow to that of the combustible fluid inlet flow is 0.58 when the system is operated at the maximum velocity of the combustible fluid inlet flow given in Figure 13. Overall, the above formula provides a convenient tool for initial assessment of such a ratio.

Figure 12. Effect of the velocity of the combustible fluid inlet flow on (a) the output power from the reactor as well as (b) the maximum temperature of the dividing wall. The nearly complete conversion line represents 90% conversion of the fuel used for the reforming reaction. The parameters used are given as follows. The steam-to-carbon ratio is 3.0, and the equivalence ratio of the combustible mixture at the inlets is 0.8. The thermal conductivity of the material of the dividing wall is 200 W/(m·K).

Figure 13. Ratio of the velocity of the process fluid inlet flow to that of the combustible fluid inlet flow for the reactor operated along the materials stability line, nearly complete conversion line, and maximum output power line, respectively. The ratio obtained from a theoretical energy balance for the system is 0.58 at the maximum velocity of the combustible fluid inlet flow studied herein, as indicated by the horizontal arrow. The parameters used here are the same as those given in Figure 12.
3. CONCLUSIONS

Numerical simulations were performed for a portable hydrogen production system to gain insights into its operating characteristics and to provide an effective method for design. The system was designed in a thermally integrated manner, and its channels were arranged with rectangular-shaped protuberances. The effectiveness of wake disruption of boundary layers for the increase in transport performance was assessed. The effect of design parameters and process variables on various performance metrics was evaluated. Some of the key features of the behavior exhibited by the thermally integrated system were presented. The operating window in terms of various design parameters and process variables was determined.

The results indicated that continuous flow and microreactor technology have great potential for the development of portable hydrogen production systems. Autothermal operation of the thermally integrated system is feasible provided that its geometry structure, design parameters, and process variables are well designed. The flow disturbance elements arranged in the channels are of great benefit to the performance of the system. Such a design is effective in reducing the resistance to transport within the boundary layer, thereby enhancing transport within the system. There exists a trade-off between fuel utilization and output power. Output power should be evaluated in the context of a constraint imposed by a minimum acceptable yield of hydrogen. The high temperatures generated by catalytic combustion of methane make it feasible to operate the system effectively. Careful thermal management is always necessary for small-scale, thermally integrated reacting systems to preserve operational safety and device integrity. In particular, it is critical to ensure an effective thermal balance between the exothermic and endothermic reactions conducted in adjacent channels to avoid both reactor extinction and severe temperature excursions. Adjustment of fluid velocities affords an effective way of balancing the thermally coupled exothermic and endothermic reactions and of mitigating the formation of hot spots. Efficient and stable operation of a thermally integrated reacting system is favored by materials with high thermal conductivities. The catalytic activity of reforming catalysts must be high enough to achieve the desired level of fuel conversion with a lower temperature peak.

4. COMPUTATIONAL METHODS

Computational fluid dynamics has become an important tool for the analysis of chemically reacting flows to provide a fundamental understanding of the coupling between physical and chemical processes, especially at the micro-scale. The definition of computational fluid dynamics has expanded from its original emphasis on fluid dynamics to include heat and mass transport and detailed chemical reactions. The continued growth of computational power will make it possible to solve more and more complex problems associated with chemically reacting flows. Microchannel reactor modeling is usually performed using such a methodology because computational fluid dynamics can serve as a means for treating reacting flows by solving the spatial distribution of the temperature, concentration, and velocity fields. In thermally coupled microchemical systems, reacting flows offer many difficult challenges and require specialized models to describe the coupling between chemical reactions and transport processes as well as between endothermic and exothermic reactions. In this study, a computational fluid dynamics model is developed to guide reactor design and analysis. The model includes all hydrodynamic effects, mass transfer, heat transfer, and surface and gas-phase reaction mechanisms.

4.1. Modeling of the System. To understand the fundamental characteristics of a thermally integrated microchannel reactor, a simple system will be of significance for design and optimization, with which valuable insights could be gained. Thermal radiation is negligible in the gas phase. Homogeneous reactions are negligible in the reforming channel due to their insignificant contributions even at very high temperatures. Furthermore, a laminar reacting flow is considered for the system, given that the reactants flow in the channels to produce a Reynolds number, based on the height of the channels and the velocities of the fluid inlet flow, up to about 280. The governing equations of fluid dynamics are described in detail in standard textbooks on transport phenomena for such a chemical reacting system. The commercial computational fluid dynamics code ANSYS Fluent is applied to simulate the system and subsequently to obtain steady-state solutions of the problem.

The steady-state balance of mass can be expressed for each fluid phase as

$$\frac{\partial (\rho u)}{\partial x} + \frac{\partial (\rho v)}{\partial y} = 0$$

(2)

The balance of momentum can be written for each fluid phase as

$$\frac{\partial (\rho uu)}{\partial x} + \frac{\partial (\rho uv)}{\partial y} - \frac{\partial \rho}{\partial x} - \frac{\partial}{\partial x} \left[ \mu \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right] = 0$$

(3)

$$\frac{\partial (\rho vw)}{\partial x} + \frac{\partial (\rho vw)}{\partial y} - \frac{\partial \rho}{\partial x} - \frac{\partial}{\partial x} \left[ \mu \left( \frac{\partial v}{\partial y} + \frac{\partial u}{\partial x} \right) \right] = 0$$

(4)

The balance of energy is given for each fluid phase by

$$\frac{\partial (\rho h)}{\partial x} + \frac{\partial (\rho h)}{\partial y} + \frac{\partial}{\partial x} \left( \sum_{k=1}^{K} \frac{Y_k}{\rho} \frac{h_k}{h} \frac{\partial T}{\partial x} \right) - \frac{\rho}{\partial y} \left( \sum_{k=1}^{K} \frac{Y_k}{\rho} \frac{h_k}{h} \frac{\partial T}{\partial y} \right) = 0$$

(5)

The balance of mass for each gaseous species takes the following form

$$\frac{\partial (\rho u Y_k)}{\partial x} + \frac{\partial (\rho v Y_k)}{\partial y} + \frac{\partial}{\partial x} (\rho Y_k \frac{u}{u}) + \frac{\partial}{\partial y} (\rho Y_k \frac{v}{v}) = 0$$

(6)

The diffusion velocity of gaseous species $k$ is defined by
\[
\bar{V}_s = -D_{k,s} W \left[ \ln \left( \frac{Y_i W}{W_i} \right) \right] + \left( \frac{D_k^s W}{\rho Y_i W} \right) V(\ln T)
\]

Density is defined for the mixture as

\[
p = \frac{\rho RT}{W}
\]

The total number of active surface sites is conserved as described by

\[
\theta_m^\text{eff} = 0, \quad m = K_g + 1, \ldots, K_s + K_i
\]

The balance of energy for the solid phase by

\[
\frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda \frac{\partial T}{\partial y} \right) = 0
\]

The balance of mass at each interface between phases is given for each gaseous species by

\[
\eta \alpha W_i \frac{\delta_{i,\text{eff}}}{i} + (\rho Y_i V_i)_{\text{interface}} = 0, \quad k = 1, \ldots, K_g
\]

This surface species coverage equation is solved for each interface between phases.

The washcoat structure is modeled as porous media wherein chemical reactions occur. As internal pore diffusional effects can be significant, the effectiveness factor is used to account for

\[
\eta = \frac{\delta_{i,\text{eff}}}{i} = \tanh(\Phi)
\]

where the Thiele modulus can be expressed as

\[
\Phi = \left( \frac{\eta_i}{C_{D_i,\text{eff}}} \right)^{0.5}
\]

Large values of the Thiele modulus represent slow diffusion with fast reactions, whereas small values of the Thiele modulus represent fast diffusion with slow reactions. The Thiele modulus and the effectiveness factor can be determined with the user-defined species such as methane.

The exposed catalyst area per unit of volume can be formulated as

\[
\gamma = \frac{\alpha}{\rho}
\]

Both the bulk and Knudsen diffusion are assumed to contribute to the mass transfer rate in the washcoat. The effective diffusivity for species \(i\) in the washcoat can be expressed as follows

\[
D_{i,\text{eff}}^{-1} = \frac{D_p}{k_p} (D_{i,\text{Knudsen}}^{-1} + D_{i,\text{molecular}}^{-1})
\]

where the Knudsen diffusivity is defined for species \(i\) as

\[
D_{i,\text{Knudsen}} = \frac{d_{\text{pore}}}{3} \left( \frac{8RT}{\pi W_i} \right)^{0.5}
\]

The effective thermal conductivity of the catalyst washcoats can be formulated as

\[
\lambda_{\text{eff}} = \epsilon_p \rho c_p + (1 - \epsilon_p) \lambda_i
\]

Continuity in heat flux and temperature is applied at each interface between phases. The balance of energy at each interface between phases can be expressed as

\[
\dot{q}_{\text{radiation}} + \sum_{k=1}^{K_s} (\delta_{i,\text{eff}} W_k)_{\text{interface}} + \lambda \left( \frac{\partial T}{\partial y} \right)_{\text{interface}} = 0
\]

The view factor for solid-ambient, \(F_{s-\text{wall}}\), is introduced into the equation to account for radiative loss of heat, which is assumed to be at unity. In addition, the external heat loss coefficient, \(h_i\), is assumed to be 20 W/(m²·K).

### 4.2. Chemical Kinetic Model

The conservation equations described above are solved for the model with specified reaction kinetics. Detailed reaction mechanisms, coupled with computational fluid dynamics, are often necessary for describing complex reacting flows. In the present work, a full set of surface reactions involved in the steam-methane reforming process is considered.

The reforming process is modeled using the kinetic mechanism proposed by Karakaya et al. The kinetic mechanism is thermodynamically consistent only in a temperature range from 273 to 1273 K. This limitation will become very critical when temperatures are very high in the system. Many possible reaction processes in the reactor being modeled are included in the kinetic mechanism. For example, steam and dry reforming reactions, partial and total oxidation reactions, the water–gas shift reaction, and the reverse methanation reaction are all accounted for.

An important consideration in the catalytic oxidation process is the thermal and chemical coupling between the surface and gas-phase reactions involved. In general, surface reactions occurring at the interfaces between phases and gas-phase reactions occurring in the fluid phase must be both accounted for. Surface and gas-phase reaction processes are modeled simultaneously. The surface reaction process is modeled using the kinetic mechanism developed by Deutschmann et al. The gas-phase reaction process is modeled using the kinetic mechanism GRI-Mech 3.0, which is widely used in the field of combustion modeling.

Detailed reaction mechanisms are included in the model. Most of the reaction mechanisms used in the model involve hundreds of elementary reaction steps, and thus these steps are not included herein for the sake of simplicity. However, full details of the surface reaction mechanisms used in the model are freely available for download on the website: https://www.detchem.com/home. Full details of the gas-phase reaction mechanism, GRI-Mech 3.0, used in the model are freely available for download on the website: http://www.me.berkeley.edu/gri-mech/.
In the present work, gas-phase and surface reaction rates are handled by the CHEMKIN \textsuperscript{74} and Surface-CHEMKIN \textsuperscript{75} codes, respectively. Variable transport properties are determined by the CHEMKIN transport database. \textsuperscript{76}

### 4.3. Numerical Approach

A nonuniform grid is used with more nodes accumulated near the protuberances. Computations are conducted using grids with various node densities to determine the optimum node density and spacing that would give the desired accuracy and minimize computation time. The typical grid used consists of 20,000 nodes in total, and the grid independence of the solution is verified. A uniform, flat velocity profile is used at the inlets to the channels. Zero Neumann boundary conditions are applied for both temperature and fluid velocity at the outlets of the channels. The second-order upwind scheme is used for discretization, and the SIMPLE algorithm is used for pressure–velocity coupling in steady flows. The residuals of the conservation equations are used to check the convergence of the solution. The convergence criterion used is $10^{-6}$ for all conservation equations. Note that the most significant drawbacks of the model developed herein are its limitation in terms of Reynolds number and of geometrical complexity.

### 4.4. Validation of the Model

To demonstrate that the implemented model is a reasonable representation of the system being modeled, validation is carried out by comparing the results obtained from the model with the experimental data available in the literature. \textsuperscript{77,78}

To validate the combustion model, the measurement data available in the literature \textsuperscript{77} are utilized. Numerical simulations are conducted under exactly the same conditions as the combustion system designed in the literature. \textsuperscript{77} The length, width, and height of the combustion channel used in the system are 250.0, 100.0, and 7.0 mm, respectively. Because of the high width-to-height ratio, the combustion channel can be modeled as a two-dimensional system. The material of the walls used in the combustion channel is silicon carbide. Platinum is used as a catalyst in the combustion process, as reported in the literature. \textsuperscript{77} In comparison with the experimental data, the centerline concentration profiles of hydroxyl radicals in the streamwise direction are shown in Figure 14a. Results are presented in the figure for three cases, which are denoted as (a–c). The temperature, fluid velocity, and equivalence ratio at the inlet to the combustion channel are given as follows: case (a): 750 K, 1.0 m/s, and 0.37; case (b): 729 K, 2.0 m/s, and 0.37; case (c): 754 K, 1.0 m/s, and 0.31. The centerline concentration profiles of hydroxyl radicals predicted by the model are shifted longitudinally to match the peak positions of hydroxyl radicals measured by planar laser-induced fluorescence. The relative longitudinal position is the position of hydroxyl radicals relative to the homogeneous ignition in the gas phase in the longitudinal direction. The results produced by the model are close to the measurement data available in the literature. \textsuperscript{77} There is a rapid increase in the concentration of hydroxyl radicals along the length of the combustion channel, which is an important indicator of the initialization of homogeneous ignition in the gas phase. As the results obtained from the model coincide with the experimental data, it may be taken as evidence that the model behaves correctly with respect to the combustion system.

To validate the reforming model, the experimental data available in the literature \textsuperscript{78} are utilized. The catalysts contained therein are rhodium and nickel, and the study is focused primarily on the catalytic performance of a steam-methane reforming process. \textsuperscript{78} The length, width, and height of the reforming channel are 30.0, 18.0, and 0.5 mm, respectively. Because of the very high width-to-height ratio, the reforming channel can also be modeled as a two-dimensional system. The results obtained for rhodium are used to validate the reforming scheme described above. The temperature at the inlet of the reforming channel is 900 K, and the steam-to-carbon ratio is 3.0. The material of the walls used in the reforming channel is -alumina. The -alumina is coated with \(\alpha\)-alumina and \(\gamma\)-alumina in sequence. Computational fluid dynamics simulations are conducted with the model under exactly the same conditions as the reforming system designed in the literature to determine whether or not the model is reasonable and correct. In comparison with the experimental data, the selectivity to carbon dioxide and the conversion of methane during the steam-methane reforming process in the presence of a rhodium catalyst are shown in Figure 14b. The results obtained from the model coincide with the experimental data. Validation of the model has been conducted against the measurement data available in the literature \textsuperscript{77,78} to check the accuracy and credibility of the model. Overall, the implemented model can be assumed to be a valid representation of the system being modeled.

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NOTATIONS

- $C_i$: concentration of species $i$ at an interface between phases, eq 13
- $D_i$: thermal diffusivity, eq 7
- $D_{i\text{eff}}$: effective diffusivity, eq 13
- $D_{\text{eff}}$: diffusivity, eq 1
- $F_i$: view factor, eq 19
- $\Delta H$: enthalpy of a reaction at constant pressure, eq 1
- $K_p$: number of gaseous species, eq 9
- $K_s$: number of surface species, eq 9
- $R_i$: ideal gas constant, eq 8
- $T$: temperature, eq 1
- $V_i$: diffusion velocity, eq 6
- $W$: molecular weight, eq 6
- $\bar{w}$: average molecular weight, eq 7
- $y$: mass fraction, eq 1
- $\bar{v}_p$: specific average heat capacity at constant pressure, eq 1
- $d_{\text{pore}}$: mean pore diameter, eq 16
- $h_i$: enthalpy, eq 1
- $h_i'$: external heat loss coefficient, eq 19
- $m$: total number of species in a mixture, eq 9
- $m$: mass flow rate, eq 1
- $p$: pressure, eq 3
- $q_i$: heat flux, eq 18
- $s_i$: surface reaction rate, eq 9
- $s_{i\text{eff}}$: effective surface reaction rate, eq 12
- $u_i$: fluid velocity in the streamwise direction, eq 2
- $v_i$: fluid velocity in the transverse direction, eq 7
- $x_i$: streamwise component, eq 5
- $y$: transverse component, eq 3
- $\infty$: surroundings, eq 19

Greek Letters

- $\Gamma$: surface site density, eq 9
- $\Phi$: Thiele modulus, eq 12
- $\alpha$: active catalyst area per unit volume, eq 11
- $\gamma$: exposed catalyst area per unit of volume, eq 13
- $\delta$: thickness of a washcoat, eq 13
- $\epsilon$: emissivity of the wall surface, eq 19
- $\epsilon_p$: porosity, eq 15
- $\eta$: effectiveness factor, eq 11
- $\lambda$: thermal conductivity, eq 5
- $\lambda_{i\text{eff}}$: effective thermal conductivity, eq 17
- $\mu$: dynamic viscosity, eq 3
- $\rho$: density of fluid phase, eq 2
- $\sigma$: Stefan–Boltzmann constant, eq 19
- $\theta$: surface coverage, eq 15
- $\tau_p$: tortuosity factor, eq 15
- $\omega$: gas-phase reaction rate, eq 6

Subscripts

- $g$: gas, eq 5
- $i$: species index, eq 12
- $k$: gaseous species index, eq 5
- $m$: surface species index, eq 9
- $s$: solid, eq 10

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