

Design considerations for vapor phase heterogeneous reaction processes in methanol steam reformers

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Abstract

There are significant problems with current methanol steam reformer approaches as applied to vapor phase heterogeneous catalysis. There remains a need for further development in methanol steam reformer processes and systems. The present study aims to provide an improved reactor system and process for the carrying out of vapor phase heterogeneous reactions. The effect of temperature on the methanol mole fraction and effective factor is investigated for a microchannel methanol steam reformer with different shapes of the cross section of the process microchannel. Particular emphasis is placed upon the heat and mass characteristics involved in vapor phase heterogeneous reaction processes in methanol steam reformers. The results indicate that the steam reforming catalyst is adapted to produce a reformat stream from the feed stream, which is delivered to the reforming region at an elevated temperature and pressure. The fuel stream tends to vary in composition and type depending upon the mechanisms used to produce heat. Methanol is a particularly well-suited carbon-containing feedstock for steam reforming reactions. Methanol steam reforming typically takes place at a lower temperature than when other carbon-containing feedstocks are reformed. A methanol steam reforming catalyst is additionally or alternatively not pyrophoric. A benefit of a low temperature shift catalyst is that the reforming catalyst beds do not need to be shielded or otherwise isolated from contact with air to prevent spontaneous oxidation of the catalyst. Improving heat flux from tubular reactor outer environment to inner environment is a critical step to increase reactor efficiency. Smaller diameter catalytic reactors can offer several advantages of improving heat transfer from external heat source to reaction mixture in the tube, enhancing tube life-time by reducing thermal gradients, reducing metal material use, and being applicable for compact steam reformer systems.

Keywords: Heterogeneous catalysis; Vapor phases; Reaction processes; Diffusion coefficients; Heat fluxes; Support structures

1. Introduction

Heterogeneous vapor-phase reactions are used to produce many large volume organic and inorganic chemicals. Examples of vapor-phase processes include oxidation, ammoxidation, and oxychlorination of olefins, alkanes, and inorganic species to yield a variety of chemicals [1, 2]. In commercial processes, these vapor-phase reactions are conducted in fixed-bed or fluidized-bed reactors [3, 4]. Commercial versions of vapor-phase processes typically possess at least one characteristic, namely a dilute reaction stream [1, 2]. The actual volume fraction of the process stream entering the reactor that is converted to products is typically small. The remainder of the stream consists of inert and unconverted reactants [3, 4]. Consequently, process equipment associated with reactor process stream, the recycle stream, and product recovery, and purification streams must be sized to accommodate the combined flow of reacting and nonreacting species. The excess diluent represents a process "inefficiency" that adds to fixed capital and operating costs associated with the processes.

The requirement for excess diluent arises from several process constraints inherent in conventional fixed-bed and fluidized-bed vapor-phase reactor operations [5, 6]. These constraints include the following critical factors: limitations due to inadequate rates of heat transfer to remove heat of reaction from catalyst particles, limitations due to conversion-selectivity trade-offs, and limitations in feed compositions due to flammability and explosion hazards [7, 8]. Vapor-phase heterogeneous oxidations are typically highly exothermic reactions [9, 10]. Reaction rates are limited by the rate at which heat can be removed from the solid catalyst. Rapid reaction rates or poor rates of heat transfer may lead to generation of catalyst hot spots, which reduce product yields and catalyst lifetimes. Frequently, in heterogeneous vapor-phase oxidations, as the extent of reaction increases, the catalyst selectivity to the desired product decreases [11, 12]. Loss in selectivity is often due to side and secondary reactions forming undesirable by-products, for example, carbon dioxide. In economic terms, these trade-offs balance effectiveness of raw materials utilization and, in some cases, the size of recycle streams [9, 10]. Flammable compositions of mixtures containing oxygen and hydrocarbons or other combustibles are demarcated by upper and lower flammability limits [11, 12]. Fixed-bed vapor-phase oxidation processes are typically designed to ensure that the compositions of all process streams lie outside the flammable region to avoid explosion hazards.

These limitations are particularly important in heterogeneous fixed-bed processes. In heterogeneous fluidized-bed processes, heat removal from the catalyst is much improved over fixed-bed designs, and explosion risks are considerably reduced by separating the organic and air feed streams and operating without recycle [13, 14]. Fluidized-bed processes typically run at very high conversion of organic reactant and relatively low conversion of oxygen [15, 16]. However, like their fixed-bed counterparts, they suffer from excess inert in the reactor process stream [17, 18]. Since oxygen efficiency is sacrificed to achieve high conversion of organic reactant, these heterogeneous processes cannot tolerate the relatively high cost of the needed oxygen, and instead use feed air as the oxygen source [19, 20]. A new reactor development that eliminates heat transfer limitations, reduces or eliminates the need for excess inert, and ensures safe operation could provide significant savings in the capital equipment and operating costs associated with chemical manufacture.

There are two classes relating to vapor phase reactions, one related to conventional two-phase reactor systems, and the other related to three-phase reactor systems. The two-phase systems cannot fully address all three issues raised above. In general, two-phase reactor designs solve the problems of flammability and heat removal by dilution of the reaction stream [21, 22]. By utilizing inert components or operating at low conversions with large recycle streams, the composition of the reaction stream can be maintained outside the flammable region [21, 22]. This dilution using inert and unconverted reactants in the recycle stream also serves to mitigate catalyst heating effects by reducing the heat of reaction per unit volume of feed. Heat transfer constraints can also be significantly reduced by utilizing fluidized-bed designs in preference to fixed-bed designs [23, 24]. Smaller catalyst particle size and higher solid-vapor heat transfer coefficients associated with fluidized-bed designs both contribute to the improved performance. However, trade-offs also pertain with respect to fluidized bed designs [23, 24]. Back-mixing, which can lead to reduced catalyst selectivity, often results in lower reaction yields and higher rates of production of undesired reaction products.

Three-phase reactors offer significantly better heat transfer than is obtainable using two-phase reactors [25, 26]. Higher rates of heat removal are achieved by contacting the catalyst directly with a liquid solvent. Three-phase reactors come in several forms: fixed beds, either trickle-bed or bubble-bed reactors, depending on whether the vapor phase is continuous or not; ebullated bed reactors, the three-phase equivalent to a fluidized-bed reactor; and slurry reactors in which the catalyst and vapor phases are dispersed in the liquid phase, either with or without forced convection [27, 28]. The predominant application of three-phase reactors has been to liquid-phase hydrogenations, although some liquid-phase

oxidations have also been proposed [25, 26]. In three-phase systems, the distinction between vapor-phase and liquid-phase heterogeneous catalysis is not entirely obvious since both phases coexist with the solid catalyst [27, 28]. It is possible, however, to distinguish between vapor-phase and liquid-phase catalytic processes in these three-phase systems, based on the mass transfer mechanisms and the resultant reaction rates [29, 30]. If the vapor-phase reactants must diffuse through the liquid to reach the active catalyst sites, the overall reaction rates will be much slower than if mass transfer proceeds through the vapor phase [31, 32]. Thus, liquid-phase processes are characterized by much lower space velocities and slower reaction rates than vapor-phase processes.

The three-phase, liquid-phase oxidation processes remove the heat transfer limitations, and in many cases, provide yields and selectivity superior to commercially practiced technology [33, 34]. They have failed to achieve commercial significance because, as liquid-phase processes, they do not generate commercially acceptable rates of reaction [35, 36]. Reaction rates comparable to vapor-phase processes have been achieved recently in three-phase reactors by using non-wetted support material [37, 38]. On such supports, the solvent does not capillary condense in the pores of the support, and the reactants have direct access to the active catalyst sites by vapor-phase transport without the additional mass transfer resistances associated with absorption and diffusion in the liquid phase [39, 40]. The three-phase reactor processes provide better heat transfer than conventional vapor-phase processes due to the higher heat capacity of the liquid phase [41, 42]. They also provide for in situ product recovery in the liquid phase [43, 44]. However, there are two significant problems with current three-phase reactor approaches as applied to vapor phase heterogeneous catalysis.

The first problem is inherent in trickle-bed designs utilizing hydrophobic catalyst supports in vapor-phase oxidation processes [45, 46]. The catalyst support must be hydrophobic to ensure vapor-phase reaction rates. It must also be intimately contacted with liquid to remove the heat and recover reaction products. For example, in trickle-bed reactors, the support catalysts are bonded to ceramic packing [47, 48]. A solvent flows through the column with the gas and contacts the catalyst and removes the oxidation product and the heat of reaction. However, if the support is hydrophobic, liquid flow will tend to be characterized by liquid rivulets with large portions of the catalyst bed remaining dry. Consequently, heat and mass transfer rates will be low, resulting in catalyst overheating and inefficient product recovery. The second serious limitation of this approach is that such trickle-bed processes are co-continuous in the liquid and vapor phases [49, 50]. Consequently, there is significant risk of explosion if operating within the flammability limits. To eliminate explosion hazards, such processes, use excess reactant or inert species to dilute the reactive species and minimize the risk of explosion [51, 52]. There remains, therefore, a need for further development in three-phase reactor processes and systems. Such development will desirably overcome the two significant problems referred to above with respect to vapor-phase heterogeneous catalysis.

The present study aims to provide an improved reactor system and process for the carrying out of vapor phase heterogeneous reactions. The present study relates to plurality of small diameter, high aspect ratio, multi-pass tubular catalytic steam reforming reactors loaded with rolled catalyst inserts positioned in a non-vertical parallel configuration thermally coupled with a heat source such as oxidation reactors. This unique arrangement allows rolled catalyst inserts to be self-supported on the reactor wall, efficient heat transfer from the reactor wall to the reactor interior, improved gas mixing within reactor interior while achieving lower pressure drop than known particulate catalysts. In reactors being provided with a bed of highly active steam reforming catalyst, the temperature at the catalyst surface in the upper portion of the bed is, thereby, considerably lower than the temperature of the oxidation gas traversing it and deposition of solids takes place typically in the uppermost layers of the catalyst bed. Deposition of solids is, therefore, concentrated substantially to a thin layer in the uppermost portion of the catalyst bed and causes restriction of gas passage in this layer leading to heterogeneous flow distribution in subjacent

layers of the bed and eventually to detrimental channeling through the catalyst bed. The effect of temperature on the methanol mole fraction and effective factor is investigated for a microchannel methanol steam reformer with different shapes of the cross section of the process microchannel. Particular emphasis is placed upon the heat and mass characteristics involved in vapor phase heterogeneous reaction processes in methanol steam reformers.

2. Methods

The microchannel reactor comprises a plurality of process microchannels containing the catalyst, transferring heat from the process microchannels to a heat exchanger, and removing the product from the microchannel reactor. The heat exchanger comprises a plurality of heat exchange channels adjacent to the process microchannels. The heat exchange channels are microchannels. The unstructured mesh of the microchannel reactor is illustrated schematically in Figure 1 in which the reactor comprises a plurality of process microchannels transferring heat from the process microchannels to a heat exchanger. The term microchannel refers to a channel having at least one internal dimension of height or width of up to about 2.0 millimeters. The microchannel has a diameter of 0.7 millimeters and length of 50.0 millimeters. The other dimension of height or width may be of any dimension. Fluid flows through the microchannel along the length of the microchannel. The process microchannel has an entrance and an exit and at least one heat exchange zone adjacent to the process microchannel. The heat exchange zone comprises a plurality of heat exchange channels, and the heat exchange channels extend lengthwise at right angles relative to the lengthwise direction of the process microchannel. The length of the heat exchange zone is less than the length of the process microchannel. The width of the process microchannel at or near the process microchannel exit is greater than the width of the process microchannel at or near the process microchannel entrance.

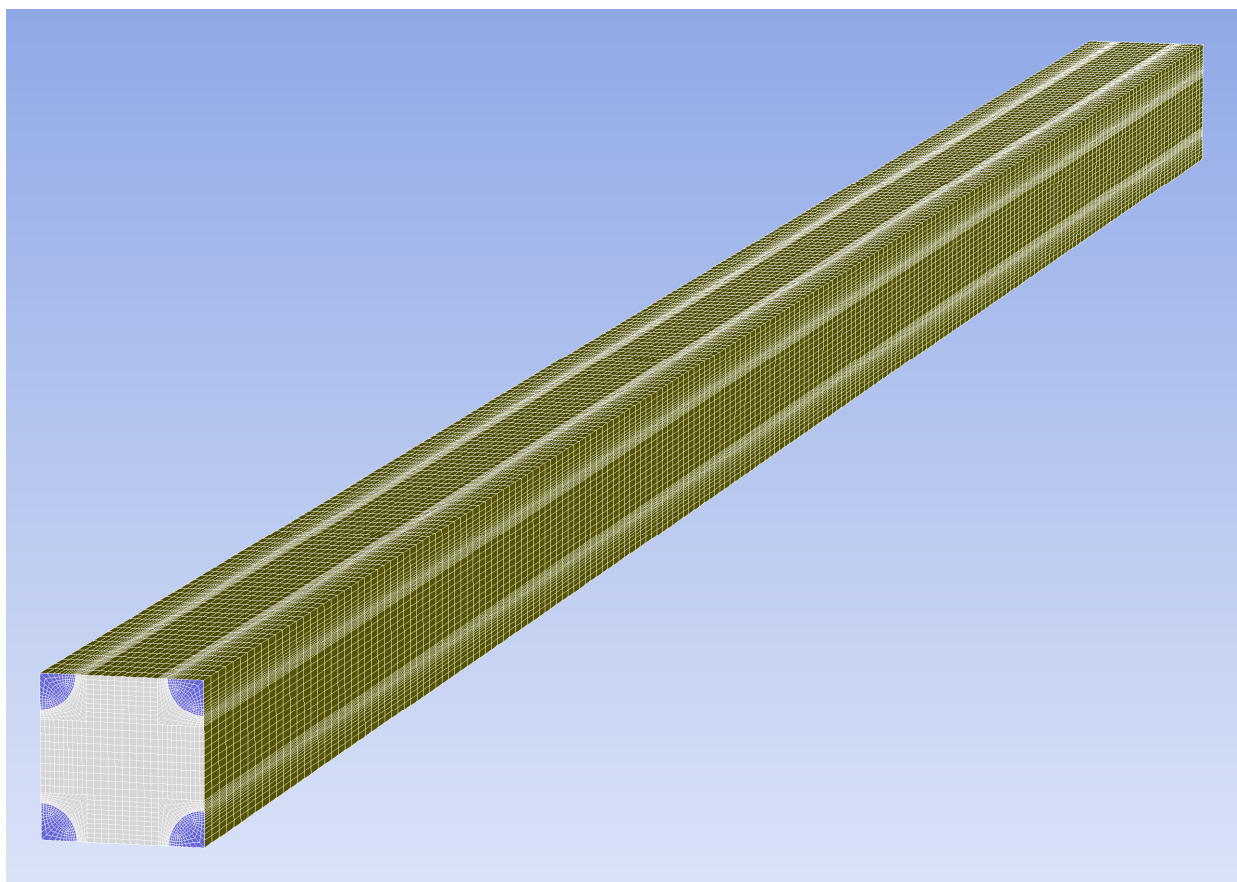


Figure 1. Schematic illustration of the unstructured mesh of the reactor that comprises a plurality of process microchannels transferring heat from the process microchannels to a heat exchanger.

The computational domain of the microchannel reactor is illustrated schematically in Figure 2 in which the microchannel reactor comprises a plurality of process microchannels transferring heat from the process microchannels to a heat exchanger. Although the microchannel has a cross section that is circle, it is to be understood that the microchannel may have a cross section having any shape, for example, a square, circle, semi-circle, and trapezoid. The shape and size of the cross section of the microchannel may vary over its length. For example, the height or width may taper from a relatively large dimension to a relatively small dimension, or vice versa, over the length of the microchannel. The term adjacent channels when referring to the position of one channel relative to the position of another channel means directly adjacent such that a wall separates the two channels. This wall may vary in thickness. However, adjacent channels are not separated by an intervening channel that would interfere with heat transfer between the channels. In some cases, one channel may be adjacent to another channel over only part of the dimension of another channel. For example, a process microchannel may be longer than and extend beyond one or more adjacent heat exchange channels. The term fluid refers to a gas, a liquid, or a gas or a liquid containing dispersed solids or liquid droplets. The term contact time refers to the volume of the reaction zone within the microchannel reactor divided by the volumetric feed flow rate of the reactant composition at room temperature and a pressure of one atmosphere [53, 54]. The term residence time refers to the internal volume of a space occupied by a fluid flowing through the space divided by the average volumetric flowrate for the fluid flowing through the space at the temperature and pressure being used [55, 56]. The term reaction zone refers to the space within the process microchannels wherein the reactants contact the catalyst. The catalyst bed may be segregated into separate reaction zones in the process microchannels in the direction of flow through the process microchannels. In each reaction zone the length of one or more adjacent heat exchange zones may vary in their dimensions.

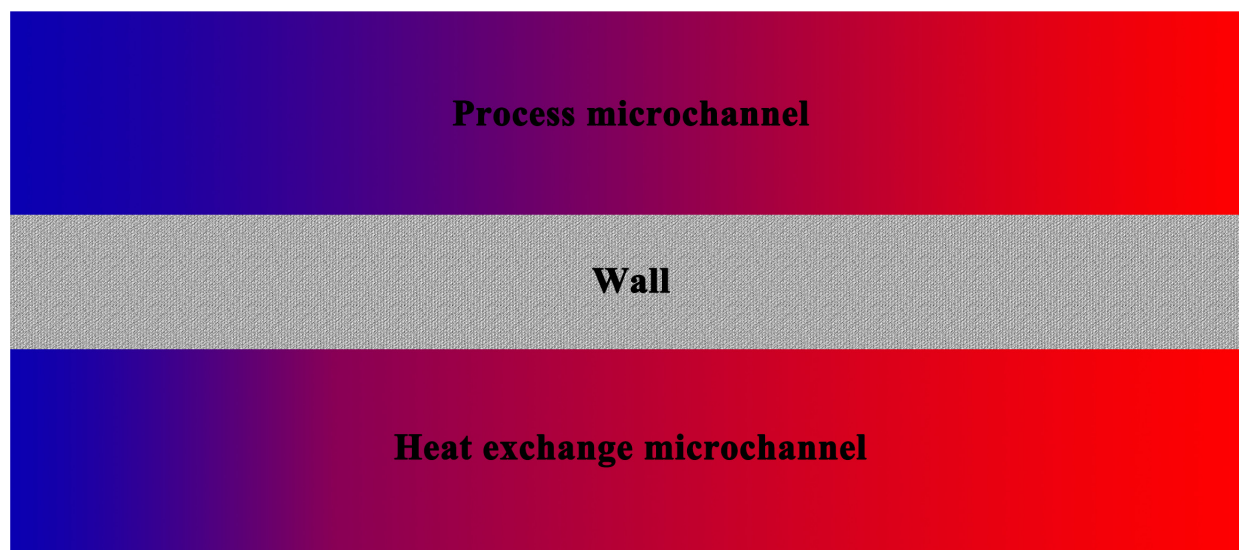


Figure 2. Schematic illustration of the computational domain of the microchannel methanol steam reformer reactor that comprises a plurality of process microchannels transferring heat from the process microchannels to a heat exchanger.

The present study performs research on a highly precise simulation of diffusion of a gas in a porous material which is performed in a short time. In pores of a porous material, while gas particles collide with pore walls and collide with particles of at least one different type of gas, the gas diffuses. In the gas diffusion, the collision with the pore walls and the collision between the gas particles are combined with each other, and a gas diffusion simulation is performed by Boltzmann equation. Hence, the gas diffusion simulation takes a long time. In the calculation of the Knudsen diffusion coefficient by collision between gas particles and the pore walls, the pores of the porous material are each assumed to have a uniform

cylindrical linear shape. However, this assumption is different from actual pores, and therefore, the precision of the gas diffusion simulation using this Knudsen diffusion coefficient is inferior. When a diffusion equation represented by the sum of an interdiffusion term and a Knudsen diffusion term based on the mean square displacement of first gas particles in spaces surrounded by wall surfaces is used, a gas diffusion simulation can be highly precisely performed in a short time. A gas diffusion simulation method is used to simulate diffusion of a gas in a porous material having many pores. The method includes: calculating, in the pores, a Knudsen diffusion coefficient based on the mean square displacement of first gas particles in spaces surrounded by wall surfaces and a Knudsen diffusion term using the Knudsen diffusion coefficient, calculating an interdiffusion term using an interdiffusion coefficient between the first and second gas particles different therefrom, and performing simulation of the gas diffusion of the first gas particles by using a diffusion equation of the first gas particles represented by the sum of the Knudsen diffusion term and the interdiffusion term.

Since the Knudsen diffusion coefficient based on the mean square displacement of the first gas particles in the spaces surrounded by the wall surfaces is obtained, a highly precise gas diffusion simulation based on an actual porous material can be performed. In addition, since the diffusion equation of the first gas particles represented by the sum of the Knudsen diffusion term and the interdiffusion term is used, the gas diffusion simulation can be performed in a short time. The spaces surrounded by the wall surfaces may be defined by positional information of the wall surfaces of the pores. Accordingly, the diffusion of the gas in the spaces surround by actual wall surfaces can be highly precisely simulated. The positional information of the wall surfaces of the pores may be identified by shape information of the wall portions of the porous material surrounding the peripheries of the pores. Accordingly, the gas diffusion simulation based on the shapes of the wall portions to be simulated can be highly precisely simulated. The wall surfaces of the pores may be formed at least from surfaces of liquid water in the pores. Accordingly, a highly precise gas diffusion simulation in consideration of the liquid water in the pores can be simulated. The positional information of the wall surfaces of the pores may be identified by the shape information of the wall portions of the porous material surrounding the peripheries of the pores and a saturation degree of the liquid water occupied in the pores. Accordingly, since the positional information of the wall surfaces can be obtained without performing experiments or the like, the gas diffusion simulation can be performed in a short time.

In the porous material, wall portions and many pores are provided. The wall portions are formed, for example, from an organic material, such as a resin and carbon, an inorganic material, such as glass, and a mixture thereof. The pores are spaces, the peripheries of which are surrounded by the wall portions, and are defined by all surfaces of the wall portions surrounding the peripheries of the pores. In the pores, spaces in which gas particles are movable are provided. For example, in the case of a fuel cell, as the gas particles, hydrogen, oxygen, nitrogen, and the like may be mentioned by way of example. According to Stefan-Maxwell law, by expanding Fick's first law which indicates that diffusion of a certain component gas is influenced only by the concentration gradient of the component, the diffusion of the gas is not only influenced by the concentration gradient of the component but also by the physical quantity of another component [57, 58]. In addition, the interdiffusion coefficient of a two-component bulk can be obtained by the Chapman-Enskog equation [59, 60]. In this simulation, the diffusion spaces are defined by the positional information of the defining wall surfaces of the pores of an actual porous material. Accordingly, a highly precise gas diffusion simulation in accordance with actual pores can be performed. The Knudsen diffusion coefficient in the diffusion spaces defined by this positional information is determined. Hence, the parameter of the Knudsen diffusion coefficient in accordance with the shape of the porous material is not necessarily obtained by experiments, and hence, the time required for the gas diffusion simulation can be significantly reduced.

3. Results and discussion

The effect of temperature on the methanol mole fraction is illustrated in Figure 3 along the fluid centerline of the process microchannel of the microchannel reactor. In the context of a steam reformer that is producing a fuel stream for a fuel cell stack containing a plurality of fuel cells, many fuel cells are subject to damage if exposed to certain components, such as carbon monoxide and carbon dioxide above certain threshold concentrations. For at least many conventional proton-exchange membrane fuel cells, the concentration of carbon monoxide should be less than 8 parts per million. Preferably, the system limits the concentration of carbon monoxide to less than 5 parts per million, and even more preferably, to less than 0.8 parts per million. The concentration of carbon dioxide may be greater than that of carbon monoxide. For example, concentrations of less than 20 percent carbon dioxide may be acceptable. Especially preferred concentrations are less than 60 parts per million. In some cases, the methanol reforming catalysts are not active at temperatures below 200 °C. In some cases, the methanol steam reforming catalyst includes a sulfur-absorbent material. The steam reforming catalyst is adapted to produce a reformat stream from the feed stream, which is delivered to the reforming region at an elevated temperature and pressure. The reforming region contains a reforming catalyst bed to which the feed stream is delivered and in which the reformat stream is produced.

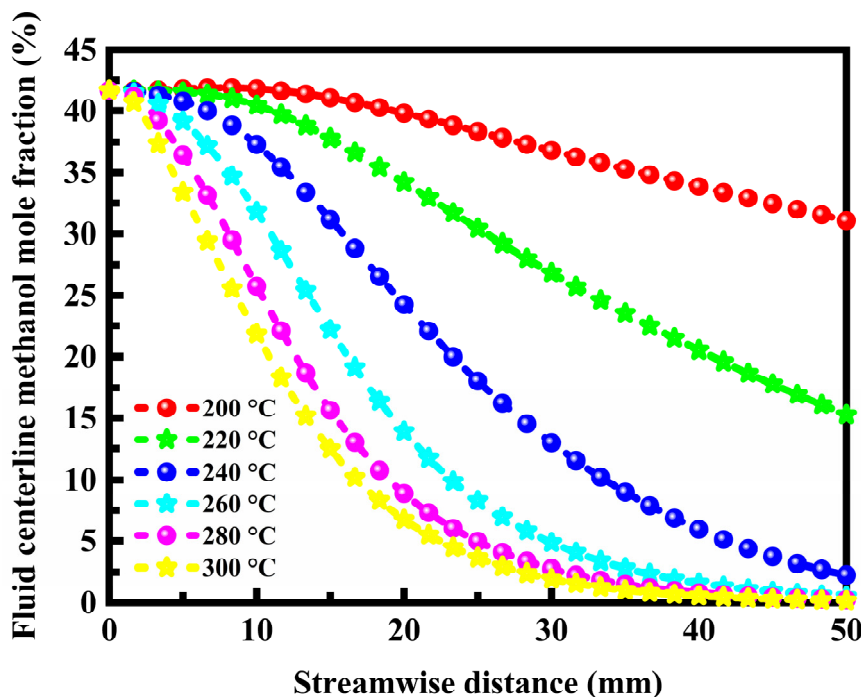


Figure 3. Effect of temperature on the methanol mole fraction along the fluid centerline of the process microchannel of the microchannel methanol steam reformer reactor.

The effect of temperature on the methanol mole fraction on the catalyst surface is illustrated in Figure 4 along the length of the process microchannel of the microchannel methanol steam reformer reactor. Steam reforming reactions are typically performed at temperatures in the range of 200 °C and 300 °C, and at pressures in the range of 50 psi and 800 psi. Therefore, a steam reformer typically includes, or is in thermal communication with, a heating assembly. The heating assembly may be located within the steam reformer, external the steam reformer, or both. The heating assembly may utilize any suitable heating mechanism or device to heat the steam reformer to a selected operating temperature. For example, the heating assembly may include a resistance heater, a burner or other oxidation unit that produces a heated exhaust stream, and heat exchange with a heated fluid stream. The heating assembly includes a fuel stream, which will tend to vary in composition and type depending upon the mechanisms used to produce heat. For example, when the heating assembly is a burner or otherwise creates heat by oxidation,

the stream will include a stream of a combustible fuel, such as an alcohol or hydrocarbon, and a combustible gas, such as hydrogen gas. When the heating assembly includes an electric resistance heater, then the stream will include an electrical connection to an electrical power source. In some cases, the feed stream may be delivered to the steam reformer at an elevated temperature, and accordingly may provide at least a portion of the required heat. When a burner or other oxidation chamber is used, a fuel stream is consumed and a heated exhaust stream is produced. The feed stream is vaporized prior to undergoing the reforming reaction, and the heating assembly may be adapted to heat and vaporize any liquid components of the feed stream.

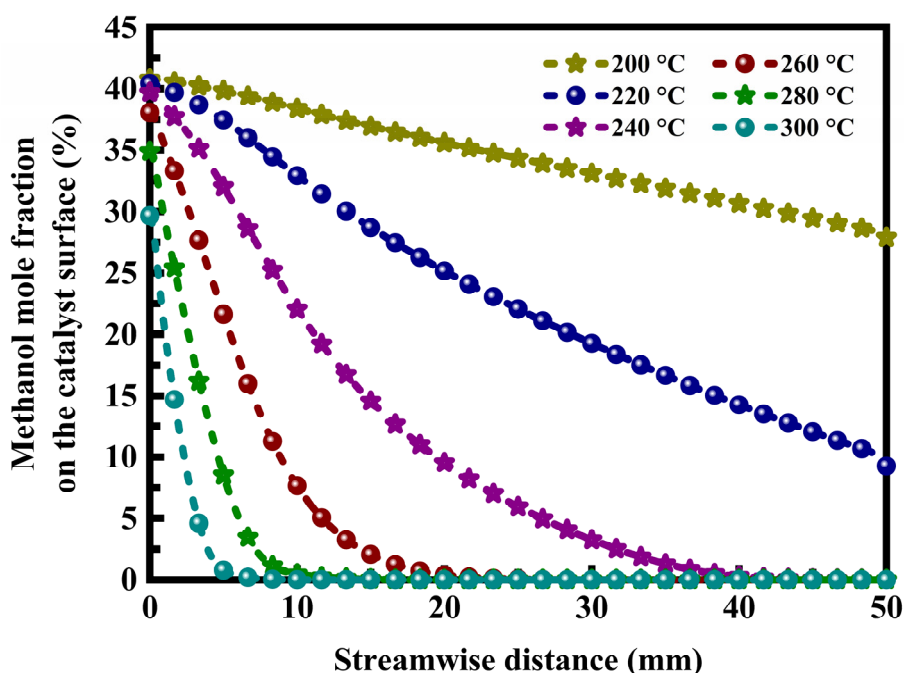


Figure 4. Effect of temperature on the methanol mole fraction on the catalyst surface along the length of the process microchannel of the microchannel methanol steam reformer reactor.

The effect of temperature on the ratio of the methanol mole fraction along the fluid centerline to that on the catalyst surface is illustrated in Figure 5 along the length of the process microchannel of the microchannel reactor. As discussed above, steam reformers produce a reformat stream from water and a carbon-containing feedstock. Examples of suitable carbon-containing feedstocks include alcohols and hydrocarbons. Nonexclusive examples of suitable alcohols include methanol, ethanol, and polyols, such as ethylene glycol and propylene glycol. Methanol is a particularly well-suited carbon-containing feedstock for steam reforming reactions. Methanol steam reforming typically takes place at a lower temperature than when other carbon-containing feedstocks are reformed. For example, methanol steam reformers typically have reforming regions that are heated to temperatures of approximately 200-300 °C. Methanol steam reformers typically receive a feed stream having approximately a 1:1 molar ratio of methanol to water or approximately 64 percent methanol by weight, but this feed ratio may be varied and still produce sufficient amounts of hydrogen gas. In the present study, the methanol steam reformer receives a feed stream having approximately a 1:1.14 molar ratio of methanol to water. The feed stream may be delivered to the steam reformer via any suitable mechanism, such as by a suitable feed stream delivery system. The delivery system includes any suitable mechanism, device, or combination thereof that delivers the feed stream to the steam reformer. In the case of a methanol steam reformer, where the feed stream contains water and methanol, these components may be mixed together and delivered as a single stream. Alternatively, these components may be separately delivered to the reforming region. Traditionally, low temperature shift catalysts are used as methanol steam reforming catalysts. These catalysts were designed to catalytically facilitate the conversion of water and carbon monoxide to

hydrogen and carbon dioxide at temperatures less than 280 °C, such as in the range of 200-280 °C. These catalysts typically are copper-based compositions, such as stabilized compositions of copper and zinc. More particularly, low temperature shift catalysts typically include copper oxide and zinc oxide supported on alumina.

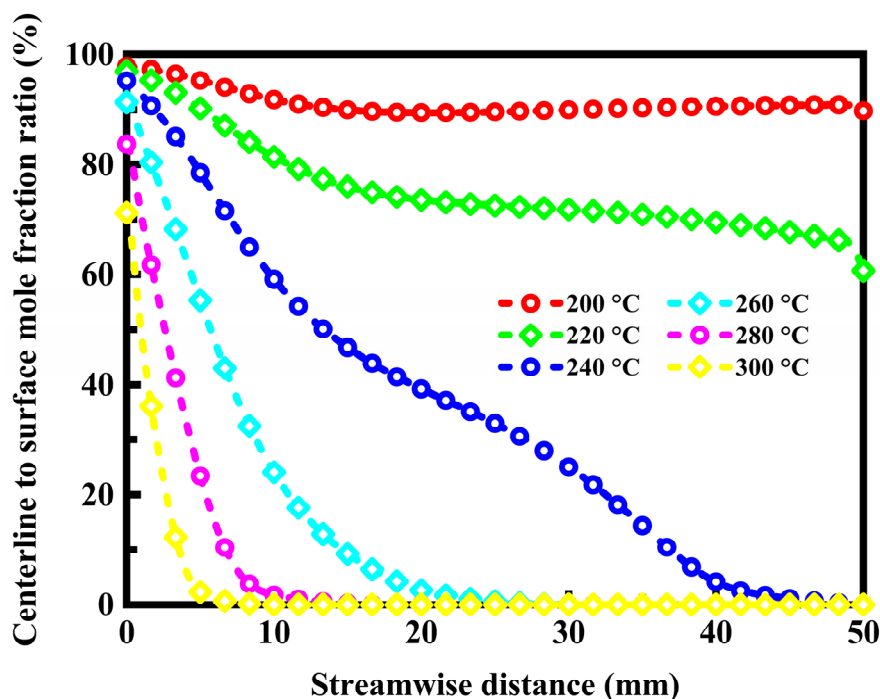


Figure 5. Effect of temperature on the ratio of the methanol mole fraction along the fluid centerline to that on the catalyst surface along the length of the process microchannel of the microchannel reactor.

The effect of temperature on the effective factor of the microchannel reactor is illustrated in Figure 6 with different shapes of the cross section of the process microchannel. Although effective for relatively short periods of use, low temperature shift catalysts also introduce several difficulties to practical long-term use of these catalysts as methanol steam reforming catalysts in commercial products. For example, the copper-zinc low temperature shift catalysts described above are pyrophoric, which means that these catalysts will spontaneously combust in the presence of air. The heat produced by this spontaneous oxidation of the catalyst may damage the catalyst and other portions of the reformer, as well as being a safety hazard. Therefore, steam reformers using a low temperature shift catalyst as a reforming catalyst generally include sufficient seals, guards or related mechanisms to minimize or prevent air from contacting the catalyst. Another disadvantage of the low temperature shift catalysts, as used as methanol steam reforming catalysts, is that the copper oxide component of the catalyst is easily reduced to elemental copper and then sintered at the temperatures in which methanol steam reforming is conducted. The speed at which the low temperature shift catalyst is reduced and then sintered increases as the temperature at which the low temperature shift catalyst is used as a methanol steam reforming catalyst. For example, the low temperature shift catalysts tend to be sintered and deactivated within approximately 200 hours or less when used at temperatures at or above 300 °C. This active life decreases even further when used at more preferred methanol steam reforming temperatures of at least 300 °C. The sintered catalyst is deactivated and therefore decreases the ability of the steam reformer to produce hydrogen gas from the feed stream. The present study is directed to methanol steam reforming catalysts that do not exhibit one or both of the above-described disadvantages of copper-zinc low temperature shift catalysts while still providing a comparable, or even greater, conversion of the feed stream into hydrogen gas. The methanol steam reforming catalyst also should not be reduced from an oxidized state and deactivated during use as a steam reforming catalyst in the temperature range of 200-300 °C. As such, the steam reforming catalyst will have a much longer useful life than low temperature shift catalysts when used as

a methanol steam reforming catalyst. A methanol steam reforming catalyst is additionally or alternatively not pyrophoric. A benefit of such a catalyst is that the reforming catalyst beds do not need to be shielded or otherwise isolated from contact with air to prevent spontaneous oxidation of the catalyst, as is typically required for low temperature shift catalysts. Therefore, the reforming catalyst beds may be air permeable or otherwise exposed to air.

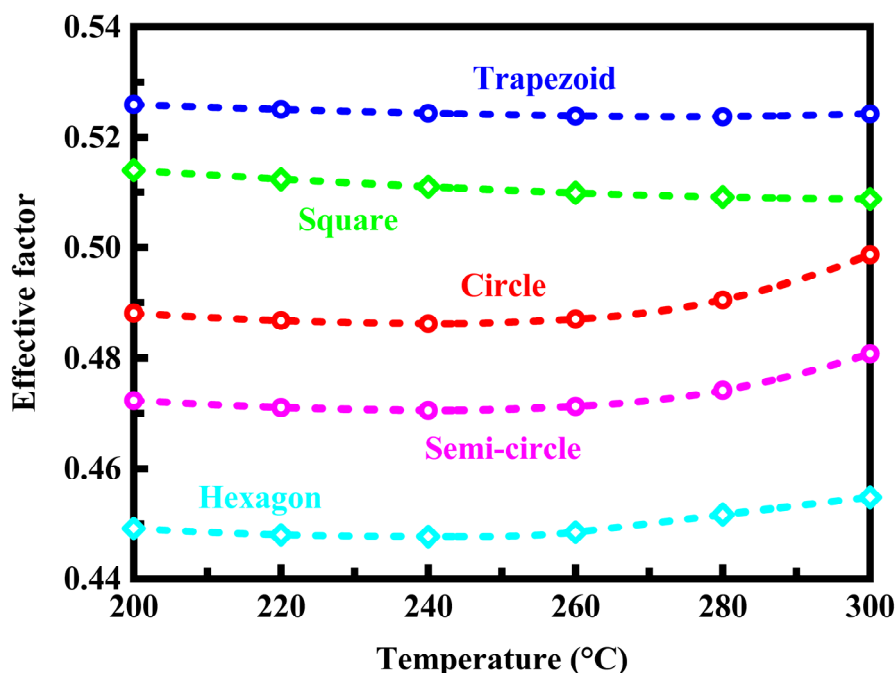


Figure 6. Effect of temperature on the effective factor of the microchannel methanol steam reformer reactor with different shapes of the cross section of the process microchannel.

The methanol mole fraction contour maps are illustrated in Figure 7 for the microchannel reactor that comprises a plurality of process and heat exchange microchannels. The acceptable maximum concentrations presented herein are illustrative examples, and concentrations other than those presented herein may be used and are within the scope of the present study. For example, particular users or manufacturers may require minimum or maximum concentration levels or ranges that are different than those identified herein. Similarly, when steam reformers are used with a fuel cell stack that is more tolerant of these impurities, then the product hydrogen stream may contain larger amounts of these gases [61, 62]. Similarly, when the steam reformers are used to produce product hydrogen streams that are used for applications other than as a fuel stream for a fuel cell stack, it may be desirable to remove other components from the product hydrogen stream and it may not be necessary to utilize a separation process [63, 64]. For example, when the product hydrogen stream is intended for use in a proton-exchange membrane fuel cell stack or other device that will be damaged if the stream contains more than determined concentrations of carbon monoxide or carbon dioxide, it may be desirable to include a methanation catalyst [65, 66]. Polishing regions may also include a steam reforming catalyst to convert any unreacted feedstock into hydrogen gas [67, 68]. Since the steam reforming process is highly endothermic, external heating sources are required. Burners installed within the furnace housing combust natural gas or some other fuel to support endothermic reactions within catalyst filled tubes. Heat released from oxidation reactions is transferred by radiation and convection to tubular reactor outer wall, then by conduction from the outer wall to the inner wall, and then by conduction and convection to the reaction mixture in the tubular reactor interior. A portion of the heat absorbed by the tubular reactor is utilized to bring natural gas and steam feeds from their feed temperature to reaction temperature in a range of from about 200 °C to about 300 °C to achieve desired methanol conversion. Improving heat flux from tubular reactor outer environment to inner environment is a critical step to increase reactor efficiency. The

catalytic endothermic reforming reactions occur on the catalyst particle exterior surface, as well as within the pores accessible to the reactants. The heat absorbed by the tubular reactor, conducts through the tube wall into the interior to support endothermic reactions. Both convective and conductive heat transfer mechanisms are in play inside the reactor tube. The lower thermal conductivity of catalyst particles affects heat available for endothermic reactions in the reactor interior. The upper limits on gas velocity to minimize pressure drop and prevent catalyst particle fluidization affect the heat transfer rate from the tube wall to the catalyst particles, on whose surface the endothermic catalytic reactions occur and where heat is needed. The tube wall temperature typically ranges from about 200 °C to about 300 °C. Such higher temperatures cause considerable expansion of tubes. Since the catalyst particles have a lower coefficient of thermal expansion, the potential exists for considerable slumping of the catalyst particles upon reactor heat up. This may cause suboptimal reactor performance due to inadequate heat transfer, higher pressure-drop, and increased diffusional resistances. The potential also exists for catalyst attrition due to crushing forces when the tube contracts. Attempts can be made to address these problems by providing support structures to hold the catalyst particles in position or dividing the catalyst bed within the tube into multiple beds with support structures in between, however these add complexities and can lead to undesirable higher pressure drop.

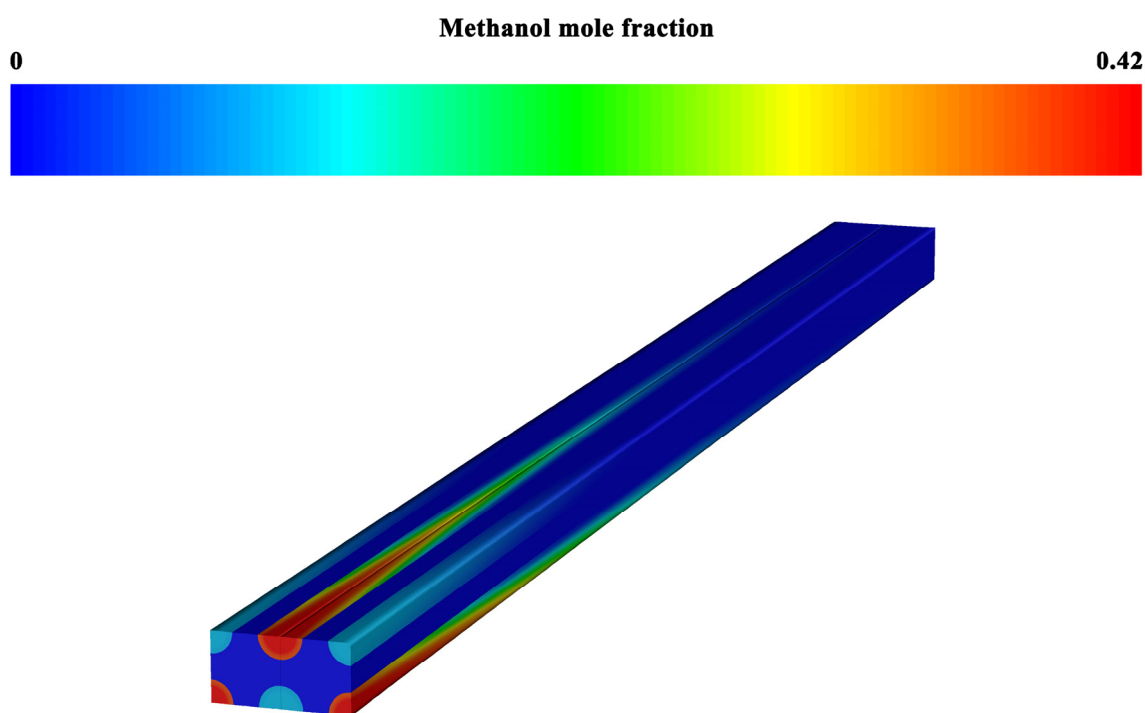


Figure 7. Methanol mole fraction contour maps in the microchannel methanol steam reformer reactor that comprises a plurality of process and heat exchange microchannels.

The hydrogen mole fraction contour maps are illustrated in Figure 8 for the microchannel reactor that comprises a plurality of process and heat exchange microchannels. An interfacial layer containing one or more active metals or alloys can be deposited on the engineered shape to provide catalytic functionality. An intermediate interfacial layer may be deposited between the metal substrate and the catalyst containing interfacial layer to enhance structural integrity of thus formed outer catalyst containing interfacial layer. An important factor that commonly used to describe reactor reforming capacity of a tubular reactor is the heat transfer rate. Surface heat flux is referred to as the rate of heat energy transfer through the reactor walls for a given tube surface area, while the volumetric heat flux is referred to the rate of heat energy transfer through the reactor walls for a given tube interior volume. Smaller diameter catalytic reactors can offer several advantages, for example improving heat transfer from external heat source to reaction mixture in the tube, enhancing tube life-time by reducing thermal

gradients, reducing metal material use, and being applicable for compact steam reformer systems. To achieve similar production capacity as steam methanol reformer plants, small diameter tubular reactors require a plurality of tubing components in series and much higher space velocity. It is challenging for direct catalyst coating on tubing wall to achieve high methanol conversion due to limitation of catalytic surface area and coating delamination at high operating temperature and large temperature gradient across tube wall. The catalyst inserts, structured monoliths can be configured with a single layer metal sheet stamped with a plurality of peaks and grooves. Peaks on metal sheets serve as geometry support to prevent structure deformation and create multiples of open channels for reactant gas flow, while grooves on metal sheets provide open windows for gas communications between each layer of the monoliths. The present design allows for the efficient use of metal foil comprising plurality of designed patterns on its surface, rolled into a multi-layer spiral shaped like a compact foil cylinder and catalyzed to serve as a catalyst insert in a high aspect ratio reactor. The designed patterns establish open gas channels between each of the rolled layers. This unique geometry accelerates gas mixing and the large surface area of metal foil provides a high catalytic active surface area.

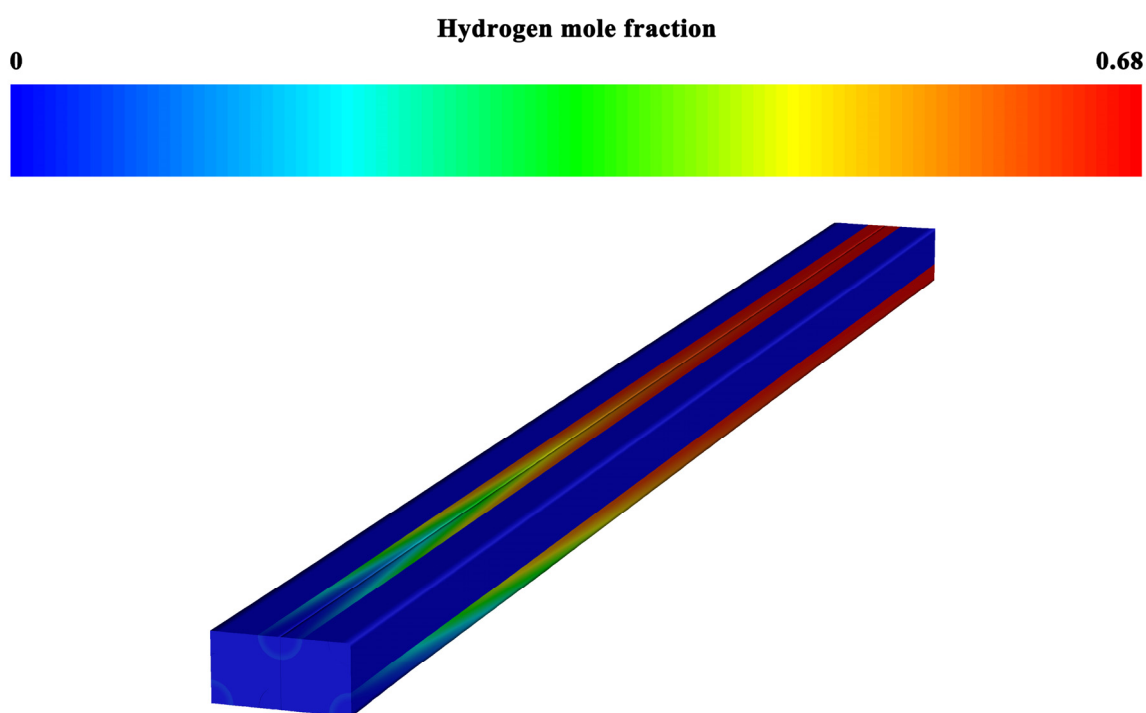


Figure 8. Hydrogen mole fraction contour maps in the microchannel methanol steam reformer reactor that comprises a plurality of process and heat exchange microchannels.

4. Conclusions

The present study aims to provide an improved methanol steam reformer reactor system and process for the carrying out of vapor phase heterogeneous reactions. The effect of temperature on the methanol mole fraction and effective factor is investigated for a microchannel methanol steam reformer with different shapes of the cross section of the process microchannel. Particular emphasis is placed upon the heat and mass characteristics involved in vapor phase heterogeneous reaction processes in methanol steam reformers. The major conclusions are summarized as follows:

- The steam reforming catalyst is adapted to produce a reformat stream from the feed stream, which is delivered to the reforming region at an elevated temperature and pressure.
- The fuel stream tends to vary in composition and type depending upon the mechanisms used to produce heat.
- Methanol is a particularly well-suited carbon-containing feedstock for steam reforming reactions.

Methanol steam reforming typically takes place at a lower temperature than when other carbon-containing feedstocks are reformed.

- A methanol steam reforming catalyst is additionally or alternatively not pyrophoric. A benefit of a low temperature shift catalyst is that the reforming catalyst beds do not need to be shielded or otherwise isolated from contact with air to prevent spontaneous oxidation of the catalyst.
- Improving heat flux from tubular reactor outer environment to inner environment is a critical step to increase reactor efficiency.
- Smaller diameter catalytic reactors can offer several advantages of improving heat transfer from external heat source to reaction mixture in the tube, enhancing tube life-time by reducing thermal gradients, reducing metal material use, and being applicable for compact steam reformer systems.

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