INNORIGINAL
Originating innovation
Innoriginal International Journal of Sciences

Vol 4, Issue 2, 2017 ISSN 2349-7041

Original Article

STEAM REFORMING OF METHANE IN CATALYTIC MICROREACTORS FOR HYDROGEN PRODUCTION

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ABSTRACT

The steam reforming of methane in catalytic microreactors was modeled using a two-dimensional computational fluid dynamics (CFD) model with detailed chemistry and transport. The reactor consists of alternating channels carrying out reforming and combustion on opposite sides of a wall. It was shown that at high fuel conversions, the choice of hydrocarbon combustible fuel is immaterial when suitable compositions are used so that the energy input is kept the same. Additionally, direct comparison of nickel and rhodium suggested that the choice of reforming catalyst is critical. Furthermore, speed up of heat transfer through miniaturization is insufficient for process intensification; catalyst-intensification is also needed to avoid hot spots and enable compact devices for portable and distributed power generation. Finally, some alternative strategies for improving reformers running on nickel were discussed and explored.

Keywords: Steam reforming; Catalytic combustion; Catalytic Microreactor; Hydrogen production; Process intensification; Computational fluid dynamics

INTRODUCTION

Intensifying fuel processors for hydrogen production is a rather pressing topic due to the increasing demand for cleaner and more economical processes [1]. Such processes may find several applications, ranging from portable electronic devices to onboard power production in vehicles as well as distributed energy and gas-to-liquid systems at local scale in urban or rural areas and offshore. Contrary to the industrial scale, where process economics dictate design, process intensification is challenging due to the need, among others, to match process conditions of a downscaled processor [2].

Methane steam reforming is still the principal industrial method for hydrogen production [3]. It has been studied in microreactors theoretically and experimentally [4]. Recent work has confirmed that steam reforming of methane on rhodium at sub-millimeter characteristic length scale and millisecond contact times is feasible and therefore, hydrogen production can be intensified by hundred to thousand times [5]. Stefanidis and Vlachos [6] performed the simulations for catalytic plate reactors, where steam reforming of methane on rhodium and propane combustion on platinum take place in alternate channels. The role of operating conditions and design parameters were analyzed. Different operating lines were mapped out, and an operation strategy for variable power output was presented.

In this study, the role of the combustible fuel and the reforming catalyst was explored. Regarding combustion, methane and propane fuels were compared. Methane is an obvious combustible fuel due to its availability in natural gas and the process simplification stemming from using a single fuel. On the other hand, propane exhibits enhanced stability, and natural gas is a mixture of small hydrocarbons. In integrated systems, one may envision burning leftover hydrogen from a fuel cell. Furthermore, reforming of ethanol coupled with combustion of ethanol may also become attractive in some applications. Since the combustible fuel will most probably be a mixture of fuels, it is important to understand how the operating strategies may vary with the choice of combustible fuel.

Regarding steam reforming, rhodium and nickel were compared. Nickel is the industrial catalyst for hydrocarbon steam reforming because it is a robust, active catalyst and relatively tolerant to poisons. However, coking, although lower on nickel than on other transition metals of the fourth period, is a major issue industrially and requires high inlet steam-to-carbon ratios. Noble metals are highly active and less prone to coking, allowing operation at lower steam-to-carbon ratios, which increase hydrogen yield. However, these are very expensive and sensitive to poisoning catalysts. Industrially, steam reforming on nickel is heat transfer controlled. In this study, it was explored whether steam reforming on nickel is feasible by intensifying the process through miniaturizing.

MODEL

Reactor model

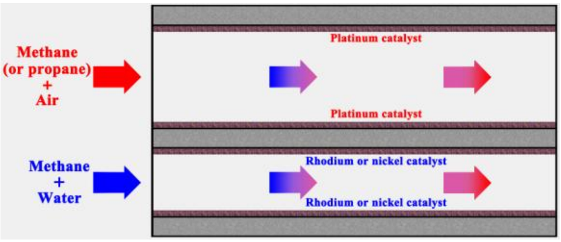

Fig. 1: Schematic diagram of the simulated multifunctional microreactor.

Figure 1 shows the schematic diagram of the simulated multifunctional microreactor. The reactor combines a catalytic combustion channel and a steam reforming channel. The two channels are separated by a solid wall, being catalytically coated on the two sides, which acts as a heat exchanger between the two processes. This is a relatively simple reactor concept, which offers the advantage of compactness, the possibility of scaling out the process by stacking up together many plates and the flexibility of using different configurations as well as different catalysts in the two channels. In this work, propane or methane combustion on platinum takes place on one side of the wall. Methane steam reforming along with water-gas shift on rhodium or nickel take place on the other side of the wall. The reverse methanation reaction is also accounted for.

Only the co-current flow configuration is studied since it has been found to provide hot-spot minimization and better reaction zone overlap [7]. The reactor dimensions and the nominal operating conditions are as follows. Reactor length: 50.0 mm, wall thickness: 0.2 mm, wall thermal conductivity: 80.0 W/m·K. Steam reforming channel, gap size: 0.4 mm, inlet temperature: 400 K, catalyst to geometric surface area: 1.0, steam-to-carbon ratio: 2. Combustion channel, gap size: 0.6 mm, inlet temperature: 300 K, catalyst to geometric surface area: 1.7.

Mathematical model

The value of Knudsen number is estimated, and it is found that the Navier-Stokes equations are still applicable to the present work. The assumptions made are as follows: the ideal gas law is assumed; a laminar flow is employed in each channel; the radiative heat transfer is considered because it plays an important role in operation, whereas the gas radiative emission and absorption are ignored. A two-dimensional computational fluid dynamics (CFD) model with detailed chemistry and transport is used. Since the heat conduction within the walls strongly affects stability, the two-dimensional steady-state energy equation in the solid phase is considered.

Kinetic model

For the catalytic combustion of methane-air mixtures over platinum, the detailed heterogeneous reaction scheme of Deutschmann *et al.* [8] is employed. The scheme consists of 24 elementary reactions with 9 gaseous and 11 surface species. For the steam reforming of methane over rhodium, the detailed heterogeneous reaction scheme of Karakaya *et al.* [9] is employed, involving 48 elementary reactions with 6 gaseous and 12 surface species. For the steam reforming of methane over nickel, the recently updated detailed heterogeneous reaction scheme of Delgado *et al.* [10] is employed, based on the detailed heterogeneous reaction scheme of Maier *et al.* [11]. This newly updated scheme consists of 52 elementary reactions with 6 gaseous and 14 surface species, and has been successfully demonstrated by comparing experimentally derived selectivity and conversion with predictions. Gaseous and surface thermodynamic data are included in the provided schemes. Mixture-average diffusion coefficients are used in conjunction with the CHEMKIN transport database. Homogeneous and heterogeneous reaction rates are evaluated with CHEMKIN and Surface-CHEMKIN, respectively.

Computation scheme

The species thermal conductivity and viscosity are computed using the kinetic theory of gases, whereas the species specific heat is computed using a piecewise polynomial fit of temperature. Within the solid walls, an isotropic thermal conductivity is specified. Fluid transport properties, such as the fluid thermal conductivity, specific heat, and viscosity, are computed by a mass-fraction-weighted average of species properties, depending on the local mixture temperature and composition. At the channel inlets, the species mass fraction, axial velocities and temperatures profiles are uniform. No-slip boundary condition is applied for both velocity components at each fluid-solid interface. At the channel outlet, the transverse velocity is set to zero and zero-Neumann conditions are used for all other gas phase variables. To minimize the computational intensity, symmetry boundary condition is applied at the symmetry planes, indicating a zero normal velocity and zero normal gradients of all variables. Continuity in heat flux and temperature is applied at each fluid-solid interface. Computations are very intensive, and the convergence of CFD simulations is judged based on the residuals of all governing equations to be less than 10^{-6}.

ROLE OF COMBUSTIBLE FUEL

In general, higher hydrocarbons have a lower activation energy compared to methane; they ignite at lower temperatures, are more resilient to heat losses, and offer a wider operating regime. In this study, propane and methane catalytic combustion in the stable regime in terms of different operating lines away from the extinction or blowout stability limits was compared. The inlet methane-air equivalence ratio is 0.91. The inlet propane-air equivalence ratio is 0.85. Using these inlet compositions, the heat release upon complete combustion is the same for the two combustible fuels at equal combustible mixture inlet velocities. Methane steam reforming on rhodium takes place in the reforming channel. Below, a propane/air mixture at an equivalence ratio of 0.85 is used as the combustible stream.

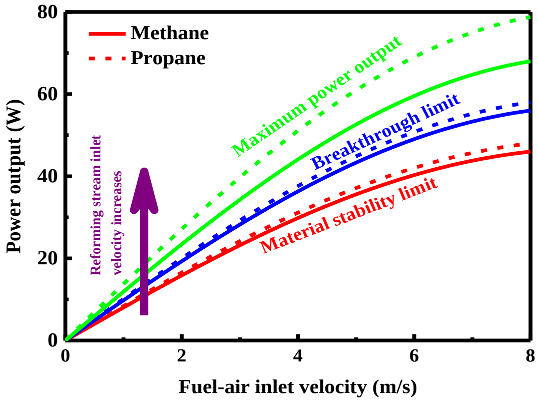

Fig. 2: Power output from the reactor in terms of hydrogen production.

Figure 2 shows the power output from the reactor in terms of hydrogen production. The power output is computed based on the lower heating value of hydrogen at the ambient temperature. This graph is in essence a two-parameter continuation diagram where both combustible and reforming stream inlet velocities vary. The reforming stream inlet velocity is gradually increased from the bottom to the top of the graph for each combustible stream inlet velocity. The solid lines with filled symbols represent operating lines with propane as the combustible fuel, and the dashed lines with open symbols those with methane as the combustible fuel. Irrespective of the combustible fuel, three operating lines exist. (A) The material stability line at low reforming inlet velocities. This represents a maximum allowable temperature limit for the wall materials, which is set to 1500 K [12]. (B) The breakthrough line, which delimits the complete conversion regime in the reforming channel; underneath it, conversion is nearly complete and temperatures are high; above it, conversion is incomplete and temperatures are lower. (C) The maximum power output line in the incomplete conversion regime, which corresponds to the maximum hydrogen yield, and is determined from the inlet flow rate and the methane conversion [13]. Depending on the overall process flow sheet, operation along the maximum power output line or the breakthrough line may be desirable. In the complete fuel conversion regime, the material stability lines for the two fuels practically coincide; the same is true for the breakthrough lines. This is because for the residence times considered, the high reactor temperatures allow for complete combustion of either fuels and complete conversion of methane in the reforming channel.

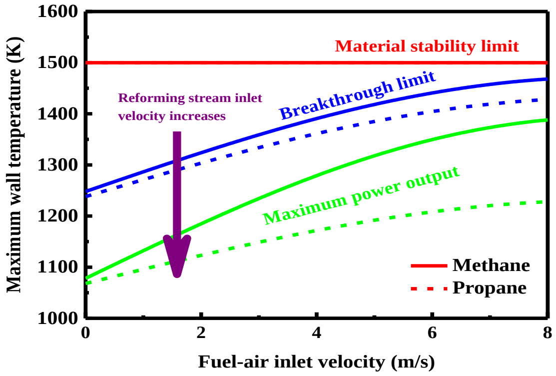

Fig. 3: Maximum wall temperature as a function of combustible stream inlet velocity along different operating lines.

Figure 3 shows the maximum wall temperature as a function of combustible stream inlet velocity along different operating lines. The combustible fuel plays an important role when the reactor is operated along the maximum power output line. Past a certain combustible stream inlet velocity, the maximum power output lines for the two fuels progressively diverge. In the incomplete conversion regime, temperatures are lower, and methane, which has higher activation energy for adsorption than propane, becomes sensitive to temperature at low residence times. Methane breakthrough in the combustion channel occurs at lower reforming inlet velocities, compared to the ones at propane breakthrough. Therefore, the maximum power output in the case of methane decreases. At the maximum combustible stream inlet velocity considered, the maximum power output with propane is higher than that with methane at lower temperature. At this point, the three operating lines in the case of methane are close to one another and practically determine the approximate upper bound of the combustible stream inlet velocity and the theoretical maximum power that can be obtained with this fuel. On the contrary, in the case of propane, there is a wide power output window at the maximum combustible stream inlet velocity, i.e., further increase in the combustible stream inlet velocity along the maximum power output line is feasible. The use of higher hydrocarbons as combustible fuels in multifunctional reactors extends the inlet velocity operating regime and the theoretical maximum power that can be obtained. Similar behavior is expected with other fast burning fuels, such as hydrogen and carbon monoxide.

ROLE OF REFORMING CATALYST

Industrially, steam reforming on nickel is a relatively bulky process with a typical time scale in the order of seconds [14]. The steam reforming of methane on rhodium at the micro-scale is feasible at millisecond contact times due to intrinsic fast chemistry and fast mass/heat transfer [15]. Herein, the steam reforming of methane on rhodium is compared to nickel in order to explore whether miniaturization alone (fast transport) is sufficient for process intensification using nickel.

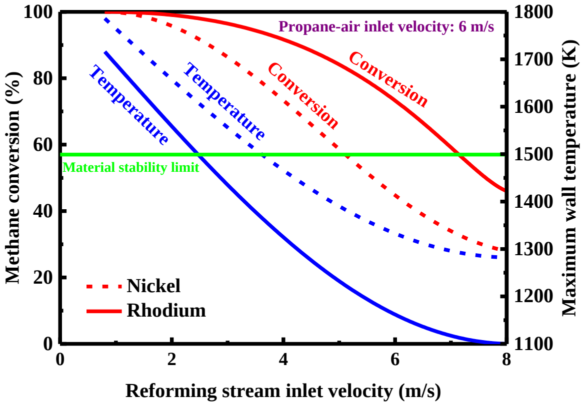

Fig. 4: Methane conversion in the reforming channel and maximum wall temperature as a function of reforming stream inlet velocity at a constant propane-air inlet velocity in the combustion channel.

Figure 4 shows the methane conversion in the reforming channel and maximum wall temperature as a function of reforming stream inlet velocity at a constant propane-air inlet velocity in the combustion channel. Nominal catalyst loading is used in both channels. This is expressed through the surface area factor (SAF), which is the ratio of the 'effective' catalyst surface area to the geometric one. The nominal surface area factor for the combustion channel is set to 1.7; the nominal surface area factor for the reforming channel is set to 1.0. These values, which multiply the reaction rates, account for the uncertainties of the actual catalyst surface that is available for reaction as well as possible internal mass transfer limitations, catalyst sintering and deactivation. For noble metals deposited on anodized alumina wafers, the surface area factor can be as high as 100 [16]. Consequently, the values used here are rather conservative estimates. In general, higher surface area factor values make the process faster and allow for operation at higher flow rates, which entails higher power output and increased stability [17]. At low reforming stream inlet velocities, conversions and temperatures are high; both gradually decrease with increasing reforming stream inlet velocity. The horizontal line at 1500 K denotes the material stability limit. The grey shaded and the hatched zones show the attainable methane conversion range at temperatures below the material stability limit for rhodium and nickel, respectively. It is clear that using rhodium, complete conversion can be obtained over a certain inlet velocity range at temperatures below the material stability limit. On the other hand, on nickel the methane conversion is only 60% at the material stability limit. Much higher reactor temperatures are required to achieve complete fuel conversion with nominal nickel loading by using lower reforming stream flow rates or increasing combustible stream flow rates. Mechanical stability will be though an important issue.

The results indicate that reactor miniaturization alone is insufficient to render the traditionally limited heat transfer reforming process on nickel workable for portable and distributed power devices. Under nominal conditions, nickel is too slow to cope with the rate of heat release and temperatures get too high. This is because the intrinsic reforming chemistry on nickel is rate limiting. Reactor intensification is not enough; a fast reforming catalyst is also necessary. Rhodium achieves precisely this.

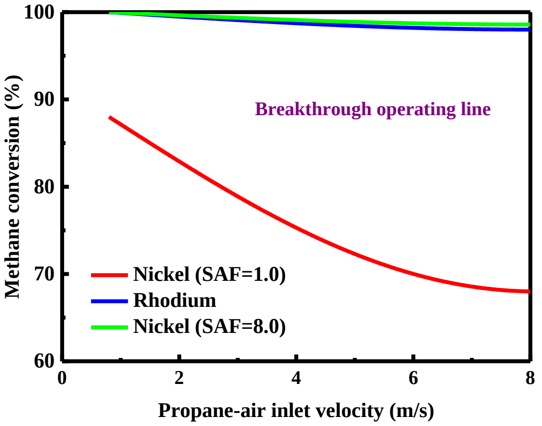

Fig. 5: Methane conversion as a function of combustible stream inlet velocity along the breakthrough line for rhodium at nominal catalyst loading and for nickel at different catalyst loadings.

Figure 5 shows the methane conversion as a function of combustible stream inlet velocity along the breakthrough line for rhodium at nominal catalyst loading and for nickel at different catalyst loadings. With nominal nickel loading, complete methane conversion is impossible. Figure 6 shows the maximum wall temperature as a function of combustible stream inlet velocity along the breakthrough line for rhodium at nominal catalyst loading and for nickel at different catalyst loadings. With nominal nickel loading, maximum temperatures exceed the material stability limit at higher velocities due to low methane conversion. Figure 7 shows the power output as a function of combustible stream inlet velocity along the breakthrough line for rhodium at nominal catalyst loading and for nickel at different catalyst loadings. With nominal nickel loading, power outputs are lower due to low methane conversion. On the other hand, when the nickel loading increases, almost identical reactor performance to that with rhodium is obtained. This is in agreement with the finding of Turchetti *et al.* [18] showing that the nickel chemistry is roughly an order of magnitude slower than that of rhodium under certain operating conditions. Minimizing internal mass transfer limitations, reducing nanoparticle size, and increasing nickel loading are possible routes to increasing the surface area factor of nickel catalysts. While the surface area factor as high as 80 is feasible in reactors, at least at lower reactor temperatures, an obvious question is of course catalyst stability, i.e., how one can minimize sintering and evaporation at high temperatures to ensure high surface area factor for nickel and avoid coking. Due to these issues, it remains to be seen experimentally if reformers running on nickel are possible.

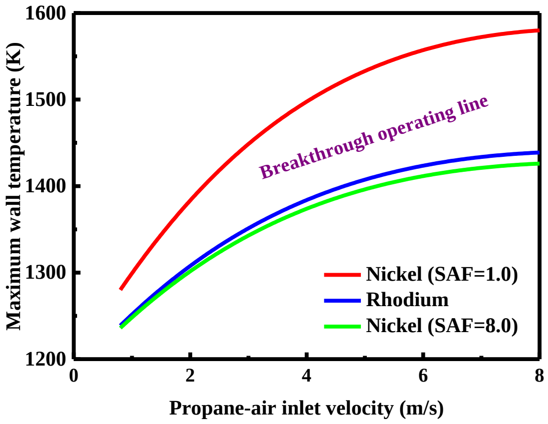

Fig. 6: Maximum wall temperature as a function of combustible stream inlet velocity along the breakthrough line for rhodium at nominal catalyst loading and for nickel at different catalyst loadings.

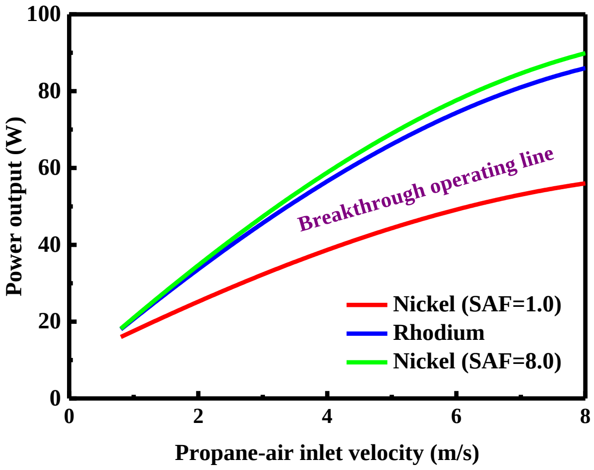

Fig. 7: Power output as a function of combustible stream inlet velocity along the breakthrough line for rhodium at nominal catalyst loading and for nickel at different catalyst loadings.

Some alternative strategies for improving reformers running on nickel are summarized as follows (data not shown). Operating with a higher reforming flow rate or a lower combustible flow rate can reduce the maximum wall temperature. In this case, a longer reactor can give similar performance with rhodium. In order to decrease the maximum wall temperature, the gap size of combustion channel could be increased to make the process more transport limited and slow down the rate of heat release; however, the breakthrough of propane may occur. A decrease of the combustion catalyst loading reduces the maximum wall temperature but methane reforming conversion is only moderate. A longer reactor combined with a reduced combustion surface area factor may give complete fuel conversion at reduced wall temperatures. Overall, a longer reactor, use of a lower combustible flow rate, increasing the corresponding one of the reforming catalyst, and reducing the activity or loading of the combustion catalyst could give results comparable to rhodium with possibly about an order of magnitude less compact systems.

CONCLUSION

The steam reforming of methane in catalytic microreactors have been numerically studied using methane and propane as the combustible fuel as well as rhodium and nickel as the reforming catalyst. The main points can be summarized as follows. Use of propane as combustible fuel extends the inlet velocity operating regime as well as the maximum power and hydrogen yield that can be obtained. In the lower hydrogen yield regime, the fuel conversion is complete and no apparent differences between combustible fuels are found if the equivalence ratios are such that the same energy input is supplied. The process intensification through reactor miniaturization is not sufficient for portable and distributed reforming processing. Fast reforming catalysts are required to remove the heat released through combustion. Otherwise, system temperatures are too high for practical operation. While temperature reduction is, in principle, possible through combustible flow rate reduction or fuel dilution, extinction of catalytic combustion may be unavoidable; longer residence times will be necessary for high fuel conversions. Overall, the catalyst and process intensification must be symbiotic. The steam reforming of methane and propane on nickel at the micro-scale with millisecond contact times is in principle feasible at increased catalyst loadings. Suitable strategies can result in high efficiency with at least an order of magnitude increase in reactor size using nickel as the reforming catalyst. Nickel poisoning and thermal stability may be an issue for practical realization of a nickel based steam reforming process.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 51506048).

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