

Experimental Insights into the Coupling of Methane Combustion and Steam Reforming in a Catalytic Plate Reactor in Transient Mode

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(Article begins on next page)

1 **Experimental insights into the coupling of methane combustion and steam** 2 **reforming in a catalytic plate reactor in transient mode**

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11 **Abstract**

12 The micro-structured reactor concept is very promising technology to develop a compact reformer for
13 distributed hydrogen generation. In this work, a catalytic plate reactor (CPR) is developed and investigated
14 for coupling of methane combustion (MC) and methane steam reforming (MSR) over Pt/Al₂O₃ coated
15 microchannels in co-current and counter-current modes in transient experiments during start-up. A three
16 dimensional (3D) computational fluid dynamics (CFD) simulation shows uniform velocity and pressure
17 distribution profiles in microchannels. For channel velocity of 5.1 to 57.3 m/s in the combustor, the
18 oxidation of methane is complete and self-sustainable without explosion, blow-off or extinction,
19 nevertheless flashbacks are observed in counter current mode. In the reformer, the maximum methane
20 conversion is 84.9% in the co-current mode slightly higher than that of 80.2% in counter-current mode at
21 residence time of 33 ms, but at the cost of three times higher energy input in the combustor operating at
22 ~1000 °C. Nitric oxide (NO) is not identified in combustion products but nitrous oxide (N₂O) is a function
23 of coupling mode and forms significantly in co-current mode. This research would be helpful to establish
24 the start-up strategy and environmental impact of compact reformers at small scale.

25 *Keywords:*

26 Catalytic plate reactor

27 Methane steam reforming

28 Methane combustion

29 Co-current mode

30 Counter-current mode

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31 1. Introduction

32 Hydrogen is a zero carbon energy carrier for deployment of fuel cell technologies in distributed energy
 33 systems and offers great potential in transition towards a low-carbon economy. In addition to improved
 34 energy efficiency, hydrogen fuel cells can improve air quality with negligible emission of harmful
 35 particulates and nitrogen oxides. Hydrogen can be produced from a variety of feedstocks, such as non-
 36 renewable resources (i.e., natural gas, liquid fuels, coal, and so on) and renewable resources (i.e., biogas,
 37 biomass, solar, wind, hydropower, and so on) using electrolysis and reforming processes.^{1,2} Methane is the
 38 principal component of large distributed renewable (e.g., bio-methane, biogas) and non-renewable (e.g.,
 39 natural gas, shale gas) feedstocks.³ Despite of its significant advantages, the penetration of hydrogen in
 40 existing energy distribution network is very slow⁴ and the lacking of hydrogen infrastructure is a key barrier
 41 for widespread application of fuel cell technologies, representing a typical chicken-and-egg problem.
 42 During the transition period, the distributed generation of hydrogen can be considered as a viable alternative
 43 via electrolysis and reforming technologies.⁵

44 The established reforming processes for low-carbon hydrogen generation are steam reforming,
 45 oxidative steam reforming, partial oxidation and autothermal reforming. Methane steam reforming (MSR)
 46 is a mature technology, dominant at industrial scale supplying 40% of world's hydrogen, with benefits of
 47 higher hydrogen yield and concentration in product stream as compared to other reforming technologies.⁶⁻
 48 ⁹ Conventionally, MSR is a highly endothermic reaction (Eq. 1) producing hydrogen and carbon monoxide.
 49 In the same reaction environment, the exothermic water-gas shift reaction (Eq. 2) transforms carbon
 50 monoxide into hydrogen and carbon dioxide in the presence of steam. MSR is carried out at industrial scale
 51 over Ni-based pellet catalyst packed in multi-tubular reformers operating at high temperature (>800 °C)
 52 and pressure (20 – 40 bar) with steam to carbon (S/C) molar ratio of 2 – 4.¹⁰



55 Heat transfer is critical for the steam reformer's design and performance. Energy is transferred from an
 56 external source¹¹ such as homogeneous or catalytic combustion (Eq. 3). Design of CPR requires the balance
 57 between heat input and heat consumption.¹² Significant research efforts have been devoted to achieving
 58 better temperature control of the reformer and proper handling of heat to enhance energy efficiency.¹³⁻¹⁶ In
 59 a burner-fired industrial reformer, the heat is supplied mostly via radiative and convective transfer from
 60 combustion flames at >1400 °C to the walls of catalyst tubes and via conductive transfer from walls to the
 61 catalyst pellets in the tubes. The homogenous combustion in industrial burner releases significant amount
 62 of harmful pollutants such as carbon monoxide, nitrogen oxides and hydrocarbons. The nitrogen oxides in
 63 hot flue gases are 90 – 95% nitric oxide (NO) and the remainder 5 – 10% are nitrogen dioxide (NO₂) and

64 nitrous oxide (N₂O). The catalytic methane combustion (MC) is pursued for stable heat generation because
 65 a stable gas-phase combustion cannot be sustained below 1000 °C¹⁷ above which thermal NO_x forms^{18, 19}
 66 and is a function of temperature, oxygen concentration and residence time.²⁰ The NO_x and especially N₂O
 67 emissions have not received attentions to date and are less defined in smaller power generation devices as
 68 compared to industrial plants,²¹ especially in transient mode of start-up and shutdown.²² A key issue in the
 69 design and thermal management of catalytic combustor is finding the operating regime for stable
 70 combustion.²³ Based on process requirement, the operating temperature for catalytic methane combustor
 71 can be categorized into low (300 – 700 °C) and high (700 – 1400 °C).²⁴ MSR is highly endothermic
 72 reaction requiring large amount of heat at temperatures up to 1000 °C²⁵ for attractive equilibrium
 73 conversion²⁶, which makes high temperature catalytic combustor as desirable.



75 The scaled down version of the industrial reformer shows poor performance and responds slowly to
 76 throughput variation, mainly because of heat transfer limitations between the flame and the catalyst pellet,
 77 and also due to mass transfer limitations.^{27, 28} Furthermore, flames quench at small scales and catalytic
 78 combustion is needed.²⁹ By improving transport limitations, microreactor technology provides unique
 79 opportunities to realize compact and modular steam reformers.³⁰⁻³³ In a microreactor, the improved heat
 80 and mass transport rates lead to 1 – 3 times higher throughput of hydrogen.³⁴ Radical improvement in
 81 reforming performance can be achieved by replacing the external firing by direct heating or more
 82 augmented methods of heat supply.¹² In this perspective, the catalytic plate reactor (CPR) is a potential
 83 candidate integrating combustor with reformer providing necessary heat mostly via conductive transfer.³⁵
 84 The design of CPR permits higher heat transfer rates due to the short conduction length of thin plate and
 85 also higher mass transfer rates because of short diffusion path in thin catalyst layer,³⁶ thus making it
 86 efficient and compact.³¹ Several modelling studies³⁶⁻⁵⁴ were performed to design and optimize the CPR that
 87 combines the MSR and MC reactions for various applications.

88 Despite significant advantages of CPR, there are certain design and operational challenges that need
 89 further investigation to build confidence for its practical implementation. The primary concern is thermal
 90 imbalance in CPR followed by the formation of hot spots and temperature spikes, thus leading to poor
 91 reactor performance. Moreover, understanding of dynamics and control characteristics are among the
 92 operational challenges of CPR that should be considered at an early design stage. CPR has faster dynamics,
 93 due to its compact size, and any disturbance in temperature can potentially be outstripped rapidly because
 94 of its very low overall heat transfer resistance.⁵⁵ Daily start-up/shutdown is one of the unique requirements
 95 of a compact reformer for distributed hydrogen production. It is challenging and critical for the reformer
 96 operation due to process uncertainty, for example, poor synchronization of heat fluxes can result in

97 appearance of temperature peaks or extinction of combustion.⁵⁶ The development of localized temperature
98 extremes and thermally imbalanced CPR may challenge the reformer dynamic operation prior to reaching
99 stable operating profiles. This is especially true during the start-up phase of operation which must be
100 adapted for a specific reaction.⁵⁷ Design methodologies to properly align the heat production and heat
101 consumption in CPR include the distributed feed design,^{54, 56, 58} a hybrid (segmented and continuous)
102 catalyst coating,^{38, 40, 41, 47, 59-61} a confined layer of phase change material as heat sink,⁶² and bimetallic strips
103 forming a thermally activated valve in combustion channels.⁶³

104 The flow (co-current or counter-current) modes have a direct impact on the temperature profile and
105 thermal behaviour of CPR⁶⁴ and may impact the reactor performance. Few experimental studies have been
106 attempted for thermal coupling of MSR and MC in a CPR. Tonkovich et al.⁶⁵ investigated a microchannel
107 methane steam reformer with integrated methane partial oxidation to produce syngas mixture for
108 subsequent combustion. The reactor achieves methane conversion of >90% on reforming side at 850 °C
109 and forms low amounts of NO_x (< 10 ppm) on combustion side. Venkataraman et al.³¹ reported self-
110 sustained steady state operation of two-pass CPR in co-current mode at 800 – 1000 °C with methane
111 conversion of 95% on the reforming side and >90% on the combustion side. In another study, Irankhah et
112 al.⁶⁶ investigated the performance of methane compact reformer integrated with catalytic methane
113 combustor under various operating conditions. As per author's knowledge, there is a lack of experimental
114 study on thermal coupling of methane combustor and methane steam reformer in CPR in transient mode
115 during start-up. In the present work, a catalytic plate reactor is developed with an integrated reformer and
116 combustor and experiments are performed to couple methane steam reforming and combustion over
117 5wt%Pt/Al₂O₃ coated microchannels on alternate sides of a plate in co-current and counter-current flow
118 modes.

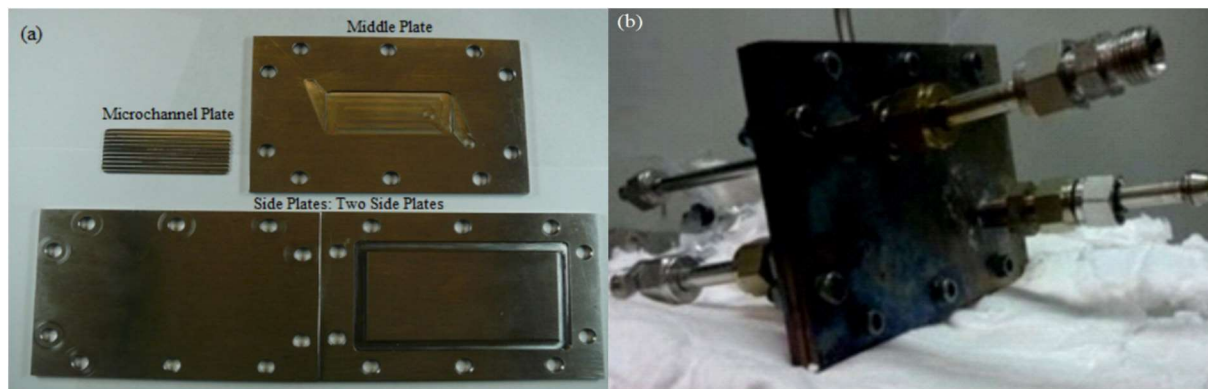
119 **2 Materials and methods**

120 **2.1 Catalytic plate reactor**

121 The CPR is developed to allow combustion and reforming streams to flow in the same direction on
122 alternate side of the middle plate for co-current mode and in opposite direction for counter-current mode.
123 The flow area of CPR is comprised an inlet distributor, 10 rectangular shaped microchannels and an outlet
124 collector (Figure 1), and the design is based on the criteria described in the study by Commenge et al.⁶⁷

125 The CPR is fabricated of 304 stainless steel with assembly of two side-plates and one middle-plate and
126 two microchannel-plates, as shown in Figure 1a. The overall geometrical dimensions of the assembled CPR
127 are 108 mm (length), 75 mm (width) and 15 mm (height), as shown in Figure 1b, where middle-plate is
128 sandwiched in between two side-plates and each side-plate has inlet and outlet tubes. The microchannel
129 plate (50 mm × 20 mm × 1 mm) is fabricated with 10 engraved parallel rectangular shaped microchannels

130 (50 mm × 1 mm × 0.5 mm). In the study by Zanfır et al.,³⁶ a decrease in channel height (0.5 – 2 mm) at
 131 constant flow rate does not introduce significant difference in reactors performance but a slight
 132 improvement in outlet conversion is observed due to reduced external mass transfer coefficient. The two
 133 side-plates have same dimensions and are engraved with rectangular housing for stainless steel reinforced
 134 graphite gaskets to avoid gas leakage. The housing is engraved on both sides of middle-plate for removable
 135 microchannel plates along-with inlet distributor and outlet collector. The collector and distributor are
 136 designed to ensure uniform flow through microchannels, and also serve as feed preheater.



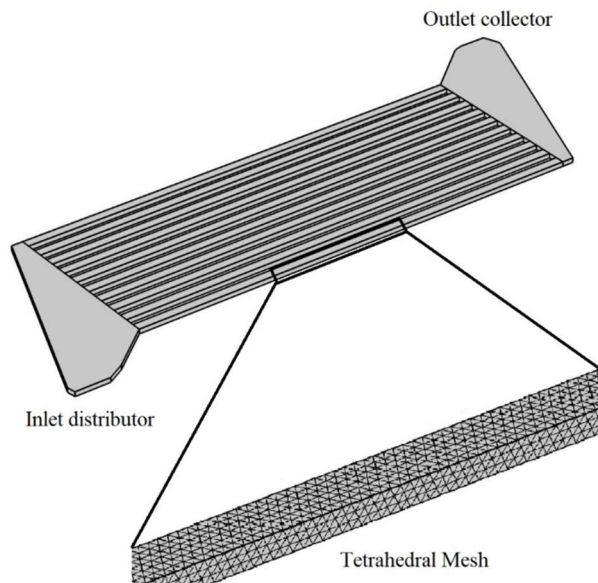
137 Figure 1. Images of catalytic plate reactor: (a) components of CPR, (b) assembled CPR

138 A 3D CFD model is employed in COMSOL Multiphysics to investigate flow uniformity and
 139 distribution, under the range of experimental flow rates, in microchannels (Figure 2) prior to reactor
 140 fabrication. The free and porous media flow interface is applied and governed by the continuity (Eq. 4) and
 141 Navier-Stokes (Eq. 5) equations representing mass and momentum balance, respectively, and solved using
 142 the finite element method.

$$143 \quad \nabla(\rho \cdot u) = 0 \quad (4)$$

$$144 \quad \rho(u \cdot \nabla)u = \nabla \cdot [-pl + \mu(\nabla u + (\nabla u)^T)] \quad (5)$$

145 where ρ is fluid density, u is velocity, p is pressure, and μ is fluid dynamic viscosity. This is applicable to
 146 isothermal and incompressible fluids under the condition of negligible gravitational forces. Nitrogen is
 147 considered as the model fluid flowing at 20 °C and reactor outlet pressure of 1 atm. The free tetrahedral
 148 mesh is selected with a mesh size of 0.2 mm, balanced between computational time and accuracy, to
 149 produce approximately 600,000 elements. The GMRES (generalized minimum residual) iterative linear
 150 solver is applied with left preconditioning. Pre- and post- smoothing are carried out using the Vanka
 151 algorithm and the convergence is achieved when the solution residuals reached 10^{-4} or below with relative
 152 tolerance set to 0.001.



153

154 Figure 2. Microreactor: inlet flow area, distributor, 10 microchannels and outlet flow area.

155 2.2 Catalyst preparation and characterization

156 The commercial Ni-based catalyst for compact reforming^{50, 68} is somewhat limited due to its
 157 susceptibility to deactivation and inability to effectively rapidly remove the heat of combustion, resulting
 158 in high temperatures and materials stability and safety issues, especially when exposed to daily startup
 159 shutdown. The wash coated precious metal catalyst permits a tenfold reduction in reactor size compared to
 160 Ni catalyst pellets. The relatively higher cost of noble metal catalyst is alleviated when considering the
 161 reduced reactor size and existing precious metals recycling processes.⁶⁹

162 The noble metal based catalysts employed for MSR are Rh, Ru, Pt, and Ni,⁷⁰⁻⁷² and for MC are Pd,
 163 Pt, and Rh.^{73, 74} The platinum catalyst is preferred in most cases and selected for this study due to its good
 164 activity toward both reactions. In a study, the effect of Pt catalyst loading (0.03 – 30 wt%) on γ -alumina
 165 was investigated for MC and a maximum methane oxidation rate was observed at 5 wt%.⁷⁵ The 5% Pt/Al₂O₃
 166 catalyst layer is coated over microchannels by following the steps: (i) substrate pre-treatment, (ii) primer
 167 coating, (iii) slurry washcoating, and (iv) incipient wetness impregnation. The primer coating, slurry
 168 properties, and washcoating procedure strongly influence the adherence, uniformity, and the loading of
 169 catalyst layer over the aluminium-free stainless steel microchannels, as investigated in a previous study,⁷⁶
 170 and the optimized conditions for washcoating of γ -Al₂O₃ on the microchannels were selected.

171 In the substrate pre-treatment, the surface of stainless steel microchannels is treated with aqua regia, a
 172 mixture of 1:3 molar ratio of nitric acid (70%, Sigma Aldrich) and hydrochloric acid (37%, Sigma-Aldrich),
 173 increasing surface roughness to help anchoring the primer layer. To remove any contamination, the
 174 microchannel-plates are cleaned with a soap solution followed by sonication in acetone-water solution at

175 33 kHz for 60 min. After washing with deionized water, the microchannel plates are finally dried at 120 °C
176 in stagnant air.

177 In the primer coating step, the microchannels are coated with a thin alumina primer layer to further
178 enhance adherence of the alumina washcoat. A primer solution (2% alumina, 4% polyvinyl alcohol) is
179 prepared using a boehmite sol and polyvinyl alcohol (PVA, Sigma-Aldrich) in water. Boehmite sol is
180 prepared by adding aluminium hydroxide (Disperal P2, 45µm, Sasol) to a 0.4wt% HNO₃ aqueous solution
181 and then aged for 48 h to complete the peptization process. Boehmite sol is mixed with the required amount
182 of PVA and stirred for 2 h. PVA is used as a slurry stabilizer and an additive to control drying and reduce
183 crack formation in the alumina layer. After filling the microchannels with the primer solution, the
184 microplates are dried at room temperature for 3 h and at 120 °C for 8 h, and then finally calcined in stagnant
185 air at 600 °C for 5 h.

186 In the washcoating step, the slurry (14 wt% γ -Al₂O₃, 2 wt% PVA, 3 wt% colloidal alumina) is
187 washcoated over the primer coated microchannels. Colloidal alumina AL20 (20 wt% aluminium hydroxide
188 oxide, NYCOL) is used as inorganic binder. A 30 wt% aqueous γ -Al₂O₃ (Fluka) slurry is milled in ball mill
189 (Pulverisette 6, Fritsch, Germany) and the pH is adjusted to 3.0 by adding nitric acid. After adding the
190 required amounts of PVA and colloidal alumina, the slurry is stirred for 2 h and left for 24 h at ambient
191 conditions. A coating of alumina washcoat is applied by filling the primer-coated microchannels with
192 alumina-slurry. Then the microchannels are dried at room temperature for 3 h and at 120 °C for 8 h, and
193 then calcined in stagnant air at 600 °C for 5 h. The washcoat layer outside the channel is removed and the
194 washcoating process is repeated until the desired weight is obtained.

195 In the incipient wetness impregnation step, the Pt (5 wt%) catalyst is impregnated onto the alumina
196 washcoated microchannels. The aqueous solution of tetra-ammine platinum (II) nitrate ([Pt(NH₃)₄](NO₃)₂,
197 99.995% trace metal basis, Sigma-Aldrich) is added dropwise with a micro-pipette on alumina washcoat
198 in the microchannels. The catalytic microchannel plates are dried at 120 °C for 10 h followed by calcination
199 in stagnant air at 300 °C for 2 h.

200 The topology of uncoated, acid treated and washcoated microchannels is examined using scanning
201 electron microscopy (SEM FEI Quanta Inspect LV 30 KV). The adherence of catalyst layer to
202 microchannels is very important for successful application of the microreactor. The adherence of catalyst
203 layer is evaluated using ultra-sonication. The washcoated microplates are dipped in acetone and water
204 solution (50:50 vol%) in a glass beaker and sonicated at 33 kHz and 130 W for 30 min in the S3M 2200
205 device by Sonica. Then the microchannel plates are dried at 110 °C for 30 min and the procedure is repeated.
206 The percent weight loss (ΔW) is the normalized weight difference of microplates before (W_b) and after
207 (W_a) the ultrasonic treatment, as described by the following equation.

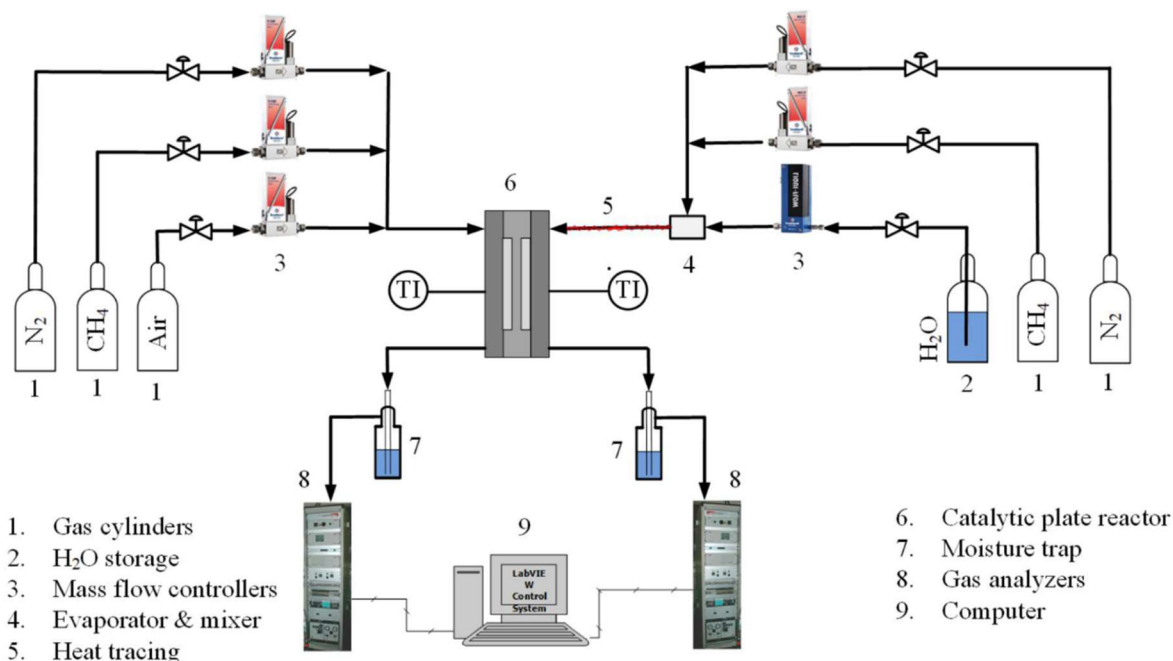
$$\Delta W(\%) = \frac{(W_b - W_a)}{W_b} \times 100 \quad (6)$$

2.3 Experimental setup

A schematic diagram of the experimental setup is depicted in Figure 3. It is comprised a feeding system, a catalytic plate reactor, and an analysis system. The gases (i.e., methane, air and nitrogen) are supplied from high pressure cylinders using Brooks mass flow controllers, then premixed at desired flow rates and fed to the CPR operating at atmospheric pressure. The flow rate of deionized water from a N₂-pressurized water vessel is controlled by a Bronkhorst mass flow controller. The feed water is evaporated and mixed with methane at 120 °C in a specially designed evaporator-mixer. The reformer feed tube is wrapped with electric trace heating and maintained at temperature >120 °C to avoid water condensation. The combustor feed tube is not heated externally by electric trace heating.

The CPR is placed in a horizontal split tube furnace (Carbolite, 500 mm heating length) with a PID temperature regulator. To minimize heat losses, the CPR is insulated with vermiculite (3M Italia S.p.A) and aerogel (Aspen Aerogels). The feed tubes (24 cm each) inside the furnace serve as preheaters before entering the CPR. It is important to confine the combustion reaction in the combustion channels, and for this purpose, the inlet and outlet tube of the combustion section are filled with alumina balls to suppress the propagation of flames. It is difficult to insert a thermocouple in the reaction channels; therefore, two K-type thermocouples are mounted at the outer surfaces of CPR to measure the combustion (T_{COMB}) and reforming (T_{REF}) surface temperature. To record the furnace temperature (T_{FURN}), a third K-type thermocouple is positioned in the wrapped insulation at a distance of 5 cm from the CPR inside the furnace.

The effluent product streams from the reformer and the combustor are passed through water condensers before feeding to online gas analysers. The dry reformed gas is analysed by a non-dispersive infrared absorption analyser (NDIR Uras 14 for CH₄/CO/CO₂, ABB Company) and a thermal conductivity analyser (Caldos 17 for H₂, ABB Company). The composition of the combustion outlet stream is measured by a paramagnetic analyser (MAGNOS 106 for oxygen) and a non-dispersive infrared analyser (URAS 14 for CO/CO₂/NO/N₂O/CH₄, ABB Company).



233

234 Figure 3. Schematic of experimental setup for coupling of MSR and MC in catalytic plate reactor.

235 The main challenge for methane combustor is to raise its temperature to ignition point, which can be
 236 achieved by resistive heating or using a self-igniting fuel-catalyst system. This methodology is also
 237 applicable to a CPR stack comprising of multiple plates. Zhang et al,⁷⁷ used an electrically resistive heated
 238 catalyst to ignite MC while coupling with MSR in the alternate channels of the CPR. To initiate CPR
 239 heating at room temperature, hydrogen is a promising candidate that can be ignited over Pt catalyst but
 240 results in non-uniform temperature profile and poses an explosion risk.⁷⁸ On the other hand, part of the
 241 methane reforming feed can be used in combustor but requires a high temperature to initiate the oxidation
 242 reaction.⁶⁶ In the present study, an electric furnace is used for heating the reactor to the desired reaction
 243 temperature. Initially heat from electric furnace is used to initiate methane combustion and after that the
 244 methane-air flow in combustor is varied to regulate the reactor temperature.

245 Prior to coupling experiments, preliminary experiments are carried out in CPR to evaluate the activity
 246 of 5% Pt/Al₂O₃ towards MC and MSR reactions. The reactor is placed without insulation in the electric
 247 furnace to provide heat necessary for the reaction. The feed stream is passed through one side and nitrogen
 248 (100 mL/min) on the other side of the reactor. Nitrogen flow of 100 mL/min is passed through the reactor
 249 during cooling to avoid catalyst damage.

250 In each coupling experiment, the start-up of the reactor is performed in two phases: i) a furnace-heating
 251 phase and ii) a furnace-off phase. In the furnace-heating phase, heat is provided from the electric furnace
 252 to initiate MC and increase the reactor temperature at a ramp rate of 10 °C/min. Prior to start heating, the
 253 reactor is purged with N₂ at a flow rate of 100 mL/min for 30 minutes. Then methane and air streams are

254 premixed and replace the nitrogen stream. Meanwhile on the reforming side, nitrogen flow is switched to
 255 a constant methane-steam mixture flow when T_{ref} reaches 400 °C. One important factor to consider during
 256 start-up is the susceptible formation of carbon deposits on the catalyst surface in the reformer.⁷⁹ Therefore
 257 to avoid coke formation, MSR is performed at a steam to carbon molar ratio (S/C) of 4 that is very close to
 258 the typical industrial reforming value of 3.3, much higher than the minimum ratio of 1.7.³⁶ In the second
 259 furnace-off phase, T_{COMB} was monitored, and methane-air flow rate was varied manually to control the
 260 amount of energy on the combustion side to regulate the reactor temperature. The reactor temperature is
 261 raised to a maximum of 1100 °C for a short duration without detection of any visible physical deterioration.
 262 For safety and to avoid catalyst deterioration, the reactor is purged with nitrogen (100 mL/min) during
 263 cooling. The methane conversion (X_{CH_4}) and CO selectivity (S_{CO}) are defined as follows:

$$264 \quad X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100 \quad (7)$$

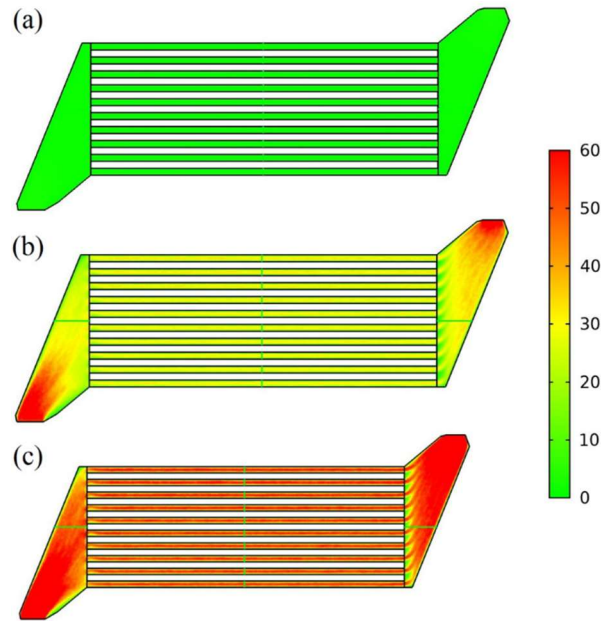
$$265 \quad S_{CO} = \frac{F_{CO,out}}{F_{CH_4,in} - F_{CH_4,out}} \times 100 \quad (8)$$

266 where $F_{CH_4,in}$, $F_{CH_4,out}$ are the inlet and outlet molar flow rates of methane and $F_{CO,out}$ is the outlet molar
 267 flow of carbon monoxide.

268 3. Results and discussion

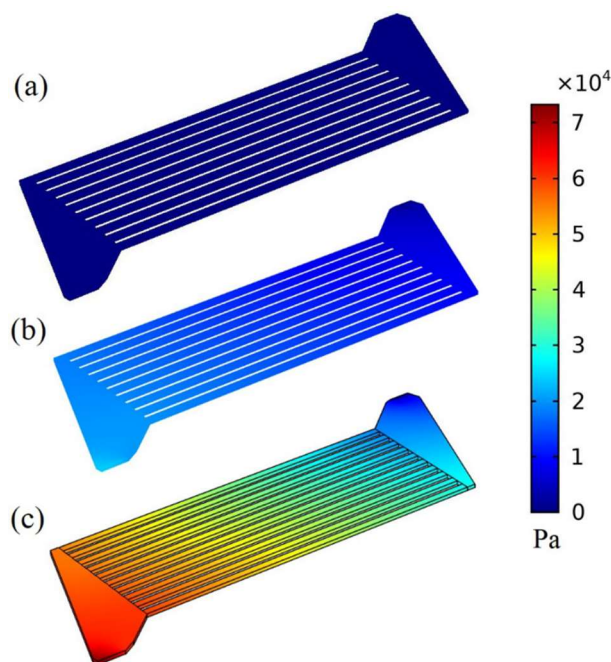
269 3.1 CFD Modelling

270 The catalytic plate reformer needs careful design to avoid flow maldistribution, a typical pathology,
 271 for uniform reaction conditions in each channel and higher reforming efficiency in the reformer.⁸⁰ Any
 272 flow maldistribution can lead to burning more methane in one or more channels, misalignment of reaction
 273 zones, hot spot formation, overheating, and significantly lower reformer performance.^{81, 82} A two-
 274 dimensional (2D) view of the velocity profile in the flow area of the CPR is shown in Figure 4 (a – c) for
 275 an average channel inlet velocity at 1.4 m/s, 32.2 m/s and 57.3 m/s, respectively. More data in terms of
 276 channel inlet velocity and velocity profiles are shown in Table S3 and Figure S1. The highest velocities
 277 occur at the inlet and outlet of the flow distributors. The difference between the highest and the lowest
 278 velocities in the microchannels is never higher than 7.1% of the average value. The difference between the
 279 minimum and maximum velocities in microchannels increases linearly with the average velocity, as shown
 280 in Figure S2. In spite of these variances, uniform velocity profiles are obtained across the microfluidic
 281 channels to enable high performance reactions.



282
 283 Figure 4. 2D velocity profile in flow area of CPR at average channel inlet velocity of (a) 1.4 m/s, (b) 32.2
 284 m/s and (c) 57.3 m/s.

285 An additional approach to assess the flow is by investigating the pressure drop. The pressure profile in
 286 the flow area of CPR is shown in Figure 5 for channel inlet velocity from 1.4 to 57.3 m/s; the pressure is
 287 uniformly distributed across all the microchannels (see also Figure S3). The pressure drop contributes to
 288 parasitic losses and is important for practical application. The pressure drop across the micro channels is
 289 increased from 81 to 57397 Pa as the flow increases from 0.4 to 15.7 L/min, as shown in Table S4.
 290 Therefore, the maximum velocity is an important parameter to be controlled to remain within acceptable
 291 pressure drops. Unfortunately, there is a lack of experimental data to validate the pressure drop estimated
 292 from fluid flow model.

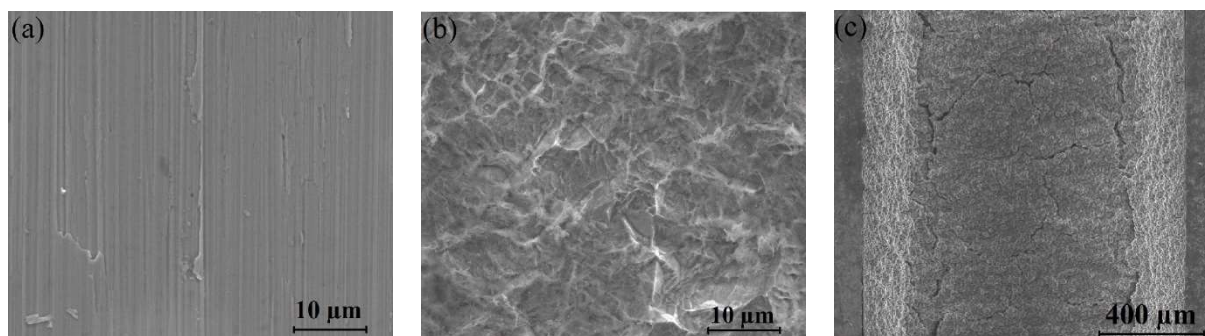


293
 294 Figure 5. 3D pressure profile in the flow area of the CPR at a channel inlet velocity of (a) 1.4 m/s, (b) 32.2
 295 m/s and (c) 57.3 m/s.

296 3.2 Catalyst Characterization

297 The surface roughness of stainless steel microchannels is analysed using SEM before and after the acid
 298 treatment, as shown in Figure 6 (a – b), respectively. The result shows an enhanced surface roughness after
 299 acid treatment (Figure 6b) which could amplify the adherence of the washcoat layer in the microchannels.
 300 The thickness of the primer layer is estimated as 1.46 μm considering the apparent coating density of 1.5
 301 g/cm^3 and the primer layer weight gain.

302 The SEM image (Figure 6c) shows the morphology and homogeneity of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst layer coated
 303 on the walls of microchannels. The catalyst layer is homogeneous and uniformly distributed throughout the
 304 channel with strong washcoat-wall interaction. The catalyst layer shows a rough, porous, and uniform
 305 morphology. Minor cracks are observed in the catalyst layer which may be due to the stresses developed
 306 by shrinkage and gas formed during drying and calcination. The average catalyst layer thickness in the
 307 microchannels varies from 121 μm (10.2 mg/cm^2) to 147 μm (12.4 mg/cm^2). The higher catalyst loading
 308 offers performance advantages in dynamic mode of heat exchange-microreactor⁸³ but is quite a challenging
 309 to coat a thick catalyst layer on a metallic microchannel with good adherence.⁸⁴



310 Figure 6. SEM images of topology of microchannels of (a) uncoated, (b) acid treated microchannel, and
 311 (c) catalyst coated.

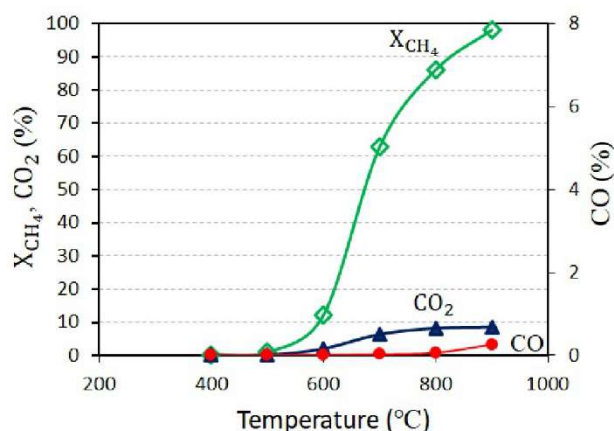
312 The mechanical stability of catalytic washcoat lined over stainless steel microchannels is critical to
 313 avoid catalyst loss during operation. Quantification of the catalyst layer's adherence can be done by ultra-
 314 sonication, simulated environment, thermal shock, drop test, abrasive test, pull-off method and scratch
 315 methods.⁸⁵ For comparison with previous work,⁷⁶ the adherence of washcoat is evaluated by most
 316 commonly used ultra-sonication method and no peeling off of the catalyst layer was observed. The weight
 317 loss of two microplates is evaluated as 9.5% and 10.3% with an average value of 9.9% in good agreement
 318 with the prior work.⁷⁶ Weight loss of less than 12% represents good adherence that is necessary for
 319 successful application of catalyst coated microreactor.

320 3.3 Single reaction in the catalytic plate reactor (CPR)

321 3.3.1 Catalytic methane combustion (MC)

322 MC is evaluated by varying the reactor temperature with premixed methane-air mixture (5 vol % CH₄
 323 in air, equivalence ratio = 2) flowing over 5wt% Pt/Al₂O₃ coated microchannels at a constant residence
 324 time of 41.1 ms. The equivalence ratio (λ) is defined as the ratio of actual air-fuel ratio to the stoichiometric
 325 air-fuel ratio for a given mixture. Lean methane-air mixtures are favourable to achieve high conversion and
 326 thermal efficiencies as compared to a stoichiometric mixture.^{86, 87} As shown in Figure 7, methane
 327 conversion starts at 0.3% at 400 °C, and increases to 98.1% at 900 °C. The temperatures (T_{10} , T_{50} , T_{90}) at
 328 which methane conversion reaches 10%, 50% and 90% are 589 °C, 669 °C and 845.5 °C, respectively. In
 329 a study for lean methane-air mixture ($\lambda = 2$),⁸⁸ methane conversion of 95.7% was obtained at 450 °C over
 330 3.8wt% Pt/Al₂O₃ coated microchannels with a residence time of 14.4 s in a stainless steel microreactor.
 331 The exhaust fraction of CO₂ and CO was increased to 8.6% and 0.3%, respectively, at 900 °C. The notable
 332 CO formation above 800 °C might be due to the contribution of slow homogeneous combustion⁸⁹ which is
 333 unavoidable above 600 °C²⁵ or steam and dry methane reforming reactions during combustion.⁹⁰ The
 334 results may suggest the presence of both catalytic and homogeneous MC in the reactor, where the purely
 335 homogeneous gas-phase MC cannot be sustained in channels gap below a critical dimension of 2.8 mm for

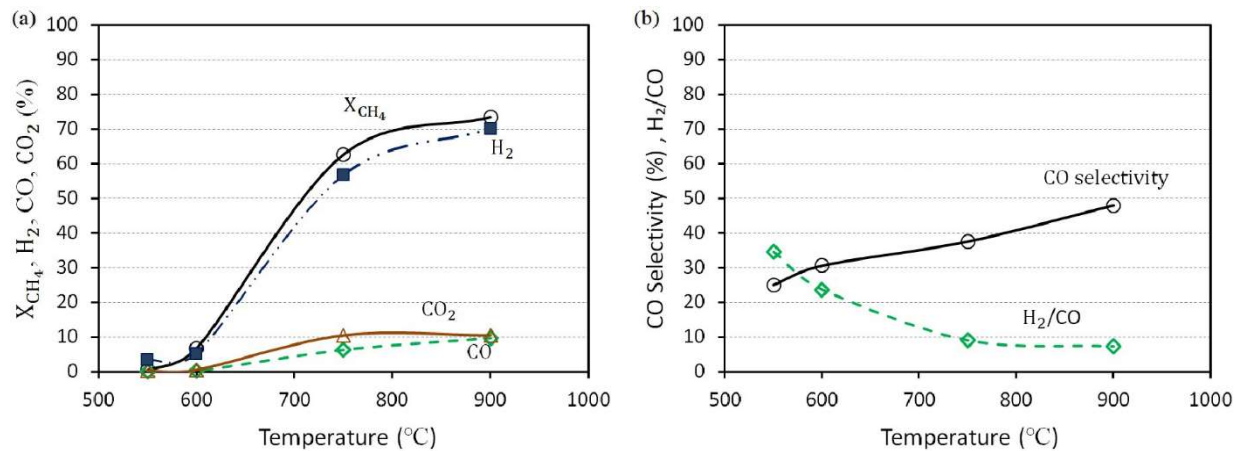
336 premixed lean methane-air mixtures.⁹¹ The coexistence of homogenous combustion in a catalytic
 337 combustor makes catalytic combustion more complex, which leads to complex coupling the two.⁹²
 338 However, the catalyst still maintained its utility in limiting the formation of CO through its oxidation into
 339 CO₂.



340
 341 Figure 7. Methane conversion and product (CO and CO₂) composition as a function of temperature.

342 3.3.2 Methane steam reforming

343 Steady state MSR is carried out by varying reactor temperature over 5wt% Pt/Al₂O₃ coated
 344 microchannel at constant space velocity (WHSV = 36 NL/h/g_{cat}) with S/C ratio of 4.0. As shown in Figure
 345 8a, methane conversion is increased with temperature as it reaches 73.4% at 900 °C and hydrogen
 346 concentration follows the same pattern with a value of 70% at 900 °C. Similar to CO concentration (Figure
 347 8a), CO selectivity (Figure 8b) also increases from 25% to 47.9% with a rise in temperature. As a measure
 348 of the selectivity to hydrogen, the H₂/CO molar ratio shows an opposite trend to methane conversion and
 349 drops from 34.5 to 7.2, similar values were also observed in the previous studies,^{70, 71} probably due to
 350 increased contribution of MSR over the water-gas shift reaction at higher temperatures. At lower
 351 temperatures, the high H₂/CO ratio is because of the lower methane conversion and the significant
 352 contribution of the water-gas shift reaction.



353 Figure 8. Steady state MSR performance as a function of temperature (a) methane conversion and product
 354 gas (H_2 , CO , CO_2) composition and (b) CO selectivity and H_2/CO ratio.

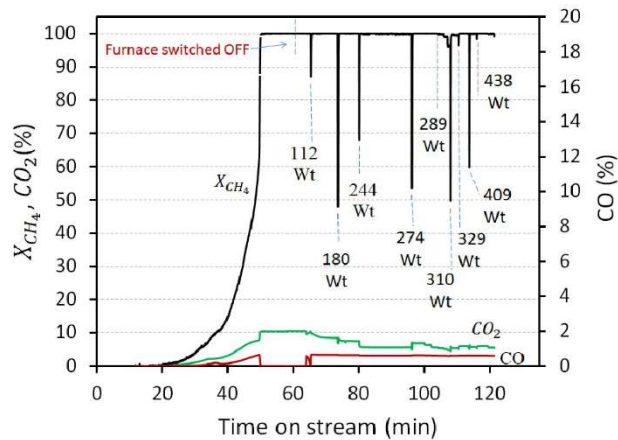
355 3.4 Coupled reactions in the catalytic plate reactor (CPR)

356 For coupling experiments in co-current and counter-current modes, the reformer is operated at constant
 357 methane flow of 45 mL/min and S/C of 4:1 (WHSV of 110 NL/hr/g_{cat}, channel inlet velocity of 1.5 m/s,
 358 and residence time of 33 ms). After high methane conversion in the combustor is reached, the electric
 359 furnace is turned off and the heat generated is used to maintain T_{COMB} at ~ 1000 °C by regulating the
 360 methane-air flow (7 vol% CH_4 , stoichiometric ratio $\lambda = 1.40$). The autoignition temperature of gas-phase
 361 MC is minimum at 7 vol% methane in air and is 600 °C⁹³. The heat generated in the form of thermal energy
 362 (W_t) is calculated based on the lower heating value of methane (LHV_{CH_4}). The combustor feed channel inlet
 363 velocity of 5.3 – 60.9 m/s (residence time of 9.5 – 0.8 ms) is much higher than the typical channel inlet
 364 velocity of 1 m/s in a micro-combustor.²³ For co-current and counter-current operation, the combustor
 365 channel inlet velocity as a function of time on stream is provided in Supplementary Information (Figure
 366 S4). Freshly coated catalytic microchannel plates were used for each experiment and no deterioration of
 367 catalyst layer was observed after each experiments. The expansion and contraction during start-up and
 368 shutdown and associated attrition are alleviated by having the noble metal catalyst washcoated on metallic
 369 structures.⁹⁴

370 The internal and external mass transfer limitations are evaluated for MSR at the maximum conversion
 371 in the co-current and counter-current modes. The absence of external mass transfer limitation in MSR
 372 reaction is confirmed using the Carberry criterion⁹⁵ (co-current mode: $0.007 < 0.05$, counter-current mode:
 373 $0.006 < 0.05$), see Supporting Information. The reactants diffuse from the alumina washcoat surface
 374 through the pores to the Pt catalyst active sites. The lack of significant diffusion limitation in the catalyst
 375 washcoat is established using the Weisz-Prater criterion⁹⁶ (co-current: $0.91 < 1.0$, counter-current: $0.85 <$
 376 1.0).

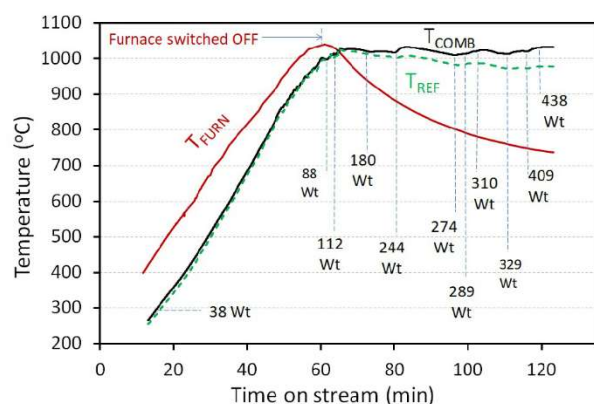
377 3.4.1 Co-current coupling

378 In co-current mode, the feed streams flow in the same direction in the combustor and reformer on
 379 alternate sides of the middle plate. In the combustor, the methane conversion increases with time, as shown
 380 in Figure 9. The temperatures (T_{10} , T_{50} , T_{90}) of the combustion surface at which MC reaches conversion of
 381 10, 50, and 90% are 631, 861, and 884 °C, respectively. Complete methane conversion is achieved at T_{comb}
 382 of 901 °C and TOS of 50.2 min. In an experimental study, Ismagilov et al.,⁹⁷ observed the ignition
 383 temperature of 1037 °C for MC over Pt/Al₂O₃ catalytic foam while coupling with MSR in a catalytic heat
 384 exchange-tubular reactor. The concentrations of CO₂ and CO increase with methane conversion and reach
 385 values of 10.6 vol% and 0.65 vol% (6460 ppm), respectively, at 901 °C. Both catalytic reactions as well as
 386 homogeneous gas-phase reactions may contribute to CO formation. As the reactor temperature increases,
 387 gradient in temperature between the catalyst surface and bulk gas in the microchannels may form, which
 388 may initiate gas-phase combustion in the boundary layer. With further rise in temperature, reactions may
 389 start in the bulk phase and their rate can significant.¹⁸ For MC, homogenous gas-phase reactions start
 390 contributing at >700 °C.²⁴ In transient and steady state operations, gas-phase reactions result in reduced
 391 CH₄ emissions and increased CO emissions.²³ After complete methane conversion, CO declines sharply
 392 down to 25 ppm that confirms the contribution of catalytic reaction in MC. After a stabilizing period of
 393 about 14 min, the CO concentration jumps up to 586 ppm and the CO₂ concentration declines down to 9.6
 394 vol% at 64 min when the thermal energy input was increased to 112 W_t. At this point gas-phase temperature
 395 in the microchannel might have reached a value where homogeneous reaction starts contributing more. A
 396 downward spike in methane conversion is also observed with a quick recovery at each flow variation due
 397 to time needed for the system to re-equilibrate.



398
 399 Figure 9. Methane conversion and concentration profiles in the combustion side in co-current operation as
 400 a function of time on stream.

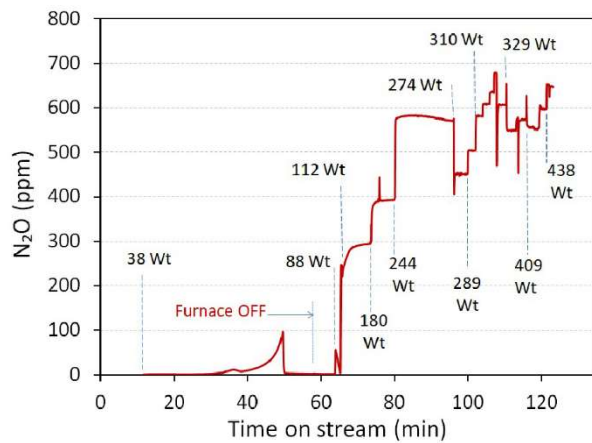
401 After stabilization of the MC reaction, confirmed by product gas composition online analysis, the
 402 furnace is switched off at T_{FURN} of 1021 °C and heat from the combustor sustains both the oxidation
 403 reaction⁹⁰ and steam reforming reaction. The principal method of heat transfer is wall-to-wall/in-wall
 404 thermal conduction. However, the heat transfer by radiation become significant as the wall temperature
 405 exceeds 800 °C.¹⁸ In the absence of sharp temperature peaks in Figure 10, T_{COMB} profile indicates that the
 406 MC is stabilized and confined inside the catalytic microchannels. After turning off the electric furnace,
 407 T_{FURN} is drops continuously and T_{REF} and T_{COMB} differ somewhat. As the furnace temperature drops below
 408 the reactor temperatures, the thermal energy input is increased exponentially (Figure S5) to compensate for
 409 the heat losses to maintain T_{COMB} . For example, when set at 438 Wt, $\Delta T_1 = T_{COMB} - T_{FURN} = 295.7$ °C
 410 and $\Delta T_2 = T_{COMB} - T_{REF} = 54.1$ °C at the end of experiment.



411
 412 Figure 10. Temperature profile of co-current mode in CPR.

413 NO is not detected in the combustor outlet thus excluding thermal NO formation known as the
 414 Zeldovich mechanism.⁹⁸ The use of a lean methane-air mixture also excludes fuel rich (prompt NO) and
 415 fuel bound NO mechanisms. Another route for NO formation is by oxidation of N_2O intermediate to NO
 416 through the N_2O mechanism during lean MC when the combustion temperature is below 1200 °C.⁹⁹⁻¹⁰¹ By
 417 this mechanism, N_2O formation is initiated by recombination of molecular nitrogen with atomic oxygen by
 418 a three-body recombination reaction ($O + N_2 + M \rightarrow N_2O + M$), where M is any collision partner,
 419 followed by oxidation of N_2O to NO.¹⁰² The formation of N_2O is confirmed at T_{COMB} of 490 °C, as shown
 420 in Figure 11. N_2O formation becomes important at gas phase temperature of > 550 °C, well within the
 421 range of catalytic combustion.⁹⁰ Formation of significant quantities of N_2O can occur by catalytic
 422 reactions.^{18, 103} The appearance of N_2O only in the product stream suggests that the residence or the
 423 temperature is not high enough for the decomposition of N_2O to NO. With increase in energy input, the
 424 N_2O level rises sharply till 580 ppm then it is incremental to > 650 ppm, which is much higher than the

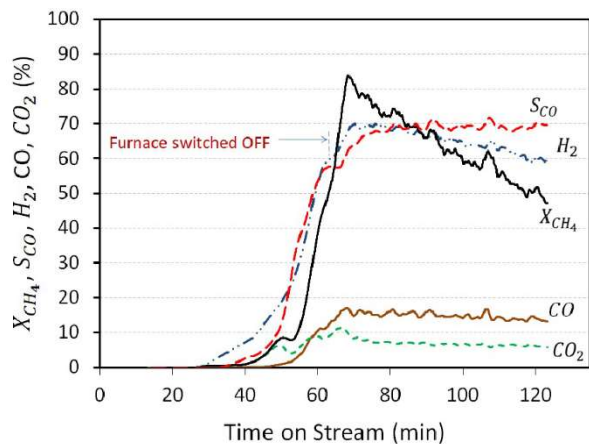
425 N₂O concentration of <5 ppm found in most combustion devices. The main exception to this is fluidized
 426 bed which burns coal forming flue gas with N₂O ~50 ppm.¹⁰⁴



427
 428 Figure 11. The concentration of N₂O (ppm) for co-current mode in catalytic plate reactor.

429 In co-current flow, the temperature is the highest near the channel inlet of the methane combustor and
 430 the kinetics of reforming is also very fast. Due to early conversion in channels⁴⁶ and overlapping of reaction
 431 zones in co-current mode, the heat generated by MC is subsequently used by the endothermic steam
 432 reforming reaction on alternate side of the middle plate. Overlap of reaction zones helps to reduce hot spots
 433 and temperature spikes.¹⁰⁵ Co-current flow mode is favourable in preventing the runaway of highly
 434 exothermic reactions where cooling is provided by steam reforming. The combustion generates surplus
 435 heat which is consumed by the highly endothermic steam reforming reaction moving in the same direction
 436 on alternate side due to overlapping of both reaction zones. This overlapping of reaction zones helps to
 437 reduce hot spots in the reactor.¹⁰⁵

438 The methane conversion, CO selectivity and H₂ fraction increase with reactor temperature during the
 439 furnace heating phase, as shown in Figure 12. The highest CH₄ conversion (84.9%) H₂ fraction of 68.1%
 440 occur at T_{REF} of 1022 °C when the temperature difference between T_{FURN} , T_{COMB} and T_{REF} is at minimal.
 441 The corresponding CO selectivity is 61.3% and continues to rise and stabilizes at ~ 70% when the
 442 combustion surface temperature is maintained at ~1000 °C. As per the study of Zafir et al.,³⁶ the catalyst
 443 layer thickness has a pronounced effect on the thermal behaviour and outlet conversions and the drop in
 444 reforming performance at higher catalyst loading is more pronounced compared to catalytic combustion.
 445 The drop in CH₄ conversion can be attributed to heat losses resulting from the colder environment once the
 446 furnace is turned off. This comes with concomitant decrease in hydrogen concentration and a more gradual
 447 decrease in CO. Good performance of the reactor requires fast heat exchange between the two sides and
 448 low heat dissipation to the surroundings. The high heat loss results in significant loss of efficiency.⁵¹

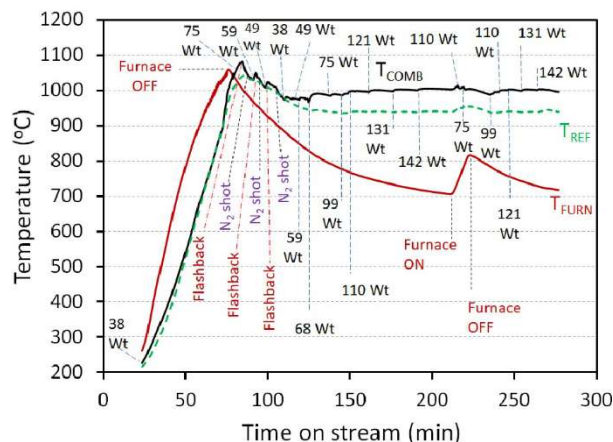


449
 450 Figure 12. CH₄ conversion, CO selectivity and percent profiles (H₂, CO and CO₂) of MSR for co-current
 451 flow mode with methane flow rate of 45 mL/min and S/C molar ratio of 4.0.

452 Another experiment was performed with fixed flows to combustor and reformer in the CPR to further
 453 investigate the effect of heat loss on MSR during co-current operation. After complete methane combustion
 454 was achieved, the furnace was turned ON and OFF, to estimate the heat necessary to overcome external
 455 heat losses and maintain the reactor temperature. The results are provided in the Supporting Information
 456 (Figure S6 – S9). The methane conversion with the furnace on was stabilized at $35 \pm 4\%$ but dropped under
 457 heat loss. A similar influence of heat loss on the reformer performance was observed during coupling of
 458 MSR and MC in a previous study,⁵¹ where the methane conversion in the steam reformer dropped from
 459 80% under adiabatic conditions to 10% under laboratory heat loss conditions. As mentioned in the study
 460 of Mettler et al.,⁴⁸ methane fuelled smaller microreactor stacks are unstable because of heat losses.
 461 Moreover Mettler et al.,⁵¹ also investigated the influence of number of catalytic plates in stack reactor on
 462 the coupling of exothermic and endothermic reactions for syngas production. The results suggest that the
 463 heat losses strongly influence the combustion reaction and the energy transfer from combustion to
 464 reforming side declines and decrease the performance of the reformer. The negative influence of heat losses
 465 can be minimized by increasing the number of catalytic plates in stack reactor. Under laboratory heat loss
 466 conditions, the moderately conductive walls of stainless-steel catalytic plate reactor are unstable due to lack
 467 of effective insulation. As suggested by Mettler et al.,⁴⁸ the stability of plate reactor can be enhanced by
 468 increasing the number of catalytic plates, enhancing the net power input, modifying the dimension and wall
 469 material, increasing catalyst loading, and changing combustion fuel. As per theoretical study by Zanfiri
 470 Gavriilidis,⁵³ co-current is more thermally balanced and shows lower conversion for MSR as compared to
 471 counter-current operation.

472 3.4.2 Counter-current coupling

473 For counter-current mode, the temperature profiles of CPR are shown in Figure 13. The temperatures
 474 (T_{10} , T_{50} , and T_{90}) to reach 10, 50, and 90% methane conversion in the combustor are 754, 920, and 934
 475 °C, respectively. Complete conversion for methane is observed at $T_{COMB} = 943$ °C, $T_{FURN} = 1038$ °C and
 476 $T_{REF} = 924$ °C.



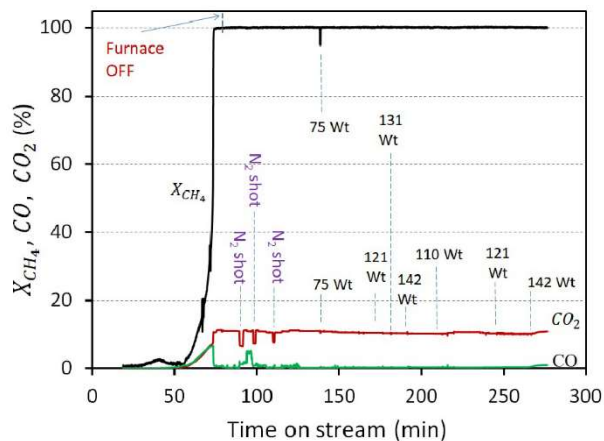
477
 478 Figure 13. Temperature profile in counter current flow operation.

479 The MC reaction becomes thermally unstable due to either flashback, in which the reaction front
 480 propagates upstream, blow-off, in which reaction front propagates downstream, or extinction⁸⁷. After
 481 switching-off the furnace at T_{FURN} of 1059 °C, three flashbacks are observed in the combustor when the
 482 flame velocity exceeds the methane-air mixture inlet velocity.¹⁰⁶ The flashbacks appear after three
 483 excessive temperature peaks with a sharp decline in T_{COMB} profile and the flame moves from the catalytic
 484 channels to the feed tube just after the alumina ball packed flame arrestor. These high temperature peaks
 485 are a main obstacle in the implementation of counter-current operation mode.¹⁰⁷ The delocalization of
 486 reactions zones leads to extra heat generation that drives the combustion temperature to be unnecessarily
 487 high resulting in flashback. After each flashback, the combustor is purged with nitrogen (50 mL/min) and
 488 the combustor feed stream is introduced again. No blow-off or extinction is observed in the methane
 489 combustor under the investigated conditions.

490 According to Mundhawa et al.,⁴¹ the combustion reaction completes in the first 20 – 30% of the channel
 491 length of the plate reactor. As the combustion reaction is much faster than the reforming reaction, heat
 492 generation overcomes the heat consumption and sudden rise in temperature is observed especially as the
 493 reaction zone do not overlap. Another possible reason for flashback in counter-current mode is the light-
 494 off phenomena through convective feedback of heat, something that is prevented in the concurrent mode.¹⁰⁷
 495 To overcome sharp temperature rise in counter-current mode, a distributed feed design at multiple locations
 496 can be implemented at the cost of complex reactor design.^{54, 105} The flashbacks of counter-current mode

497 can be avoided successfully by adjusting the flow rate, see in additional coupling experiments in Supporting
 498 Information (Figure S11 –S14).

499 The thermal energy input to the combustion section is about three times lower for counter-current
 500 operation due to preheating as compared to co-current operation, specifically evaluated at a furnace
 501 temperature of 730 °C. The counter-current operation benefits from heat recovery from the hot products to
 502 preheat the cold reformer feed–stream. However, this results in large temperature gradients in the reactor,³⁶
 503 leading to hot spot formation. Large temperature transients and thermal gradients may also be generated
 504 during the startup.¹⁰⁸ Hot spots lead to higher thermal stress in the reactor in counter-current mode
 505 compared to the co-current mode.¹⁰⁹

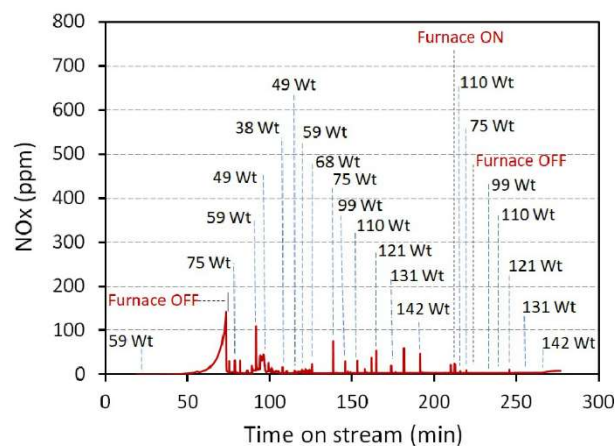


506
 507 Figure 14. CH₄ conversion and percent of products of the combustion stream in counter-current operation
 508 as a function of time on stream.

509 For counter-current mode, the methane conversion and profiles of CO and CO₂ vs. TOS are shown in
 510 Figure 14. During the three flashbacks, the methane conversion remains at 100% whereas the CO₂
 511 concentration drops due to purge-shots of N₂ in feed, and the CO concentration varies non-monotonically.
 512 Like the co-current operation, the energy input to the combustion increases when the furnace temperature
 513 drops. To confirm this phenomenon, the furnace is turned on to increase the temperature surrounding the
 514 CPR which results in drop in energy input from 142 to 110 W_t. This energy input is increased exponentially
 515 (Figure S10) again when the furnace is turned off and the furnace temperature declines to the same value
 516 with the same energy input to the combustion section. T_{FURN} is dropped continuously after the turning off
 517 electric furnace that results in bigger difference T_{REF} and T_{COMB} . At the end of the experiment, the
 518 temperature difference $T_{FURN} - T_{COMB}$ increases to 278.7 °C and energy input to the combustor rises to
 519 142 W_t.

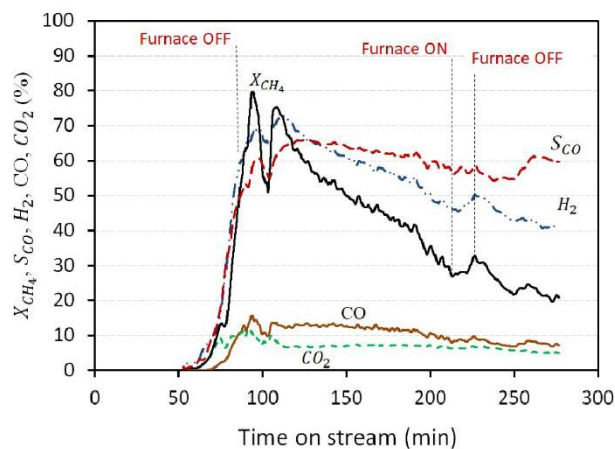
520 The concentration of carbon dioxide correlates with methane conversion and reaches a value of 10.7
 521 vol% at 943 °C with complete methane conversion at 73.7 min of TOS, as seen in Figure 14. A similar
 522 trend is observed for the CO concentration with a maximum value of 6.5 vol%. After complete methane

523 conversion, CO declines sharply down to 2456 ppm. This confirms the catalytic combustion of methane in
 524 the catalytic plate reactor. A downward spike in methane conversion was observed at the same time which
 525 suggests a decline in methane conversion at every flow rate change during the experiment but with a quick
 526 recovery in conversion. Like co-current mode, NO is also not detected in the combustor outlet stream. The
 527 formation of N₂O is confirmed at T_{COMB} of 384 °C, as shown in Figure 15. During ignition, the N₂O
 528 concentration increases up to 142.8 ppm with a subsequent sudden drop that remains < 9 ppm except during
 529 flashbacks and instantaneous spikes at flow variation points representing changes in energy input.



530
 531 Figure 15. Concentration of N₂O (ppm) for counter-current mode in the catalytic plate reactor.

532 For MSR in counter-current mode, the highest value of CH₄ conversion of 80.2% occurs at $T_{REF} =$
 533 1027 °C along with CO selectivity and H₂ fraction of 60.4% and 70.2%, respectively (Figure 16). After
 534 switching furnace off, the CH₄ conversion in the reforming side drops due to heat losses. To confirm the
 535 influence of the surrounding temperature on heat losses and reactor performance, T_{FURN} was increased
 536 from 704.9 °C to 810 °C by switching it on/off. As a result, the heat input to the combustion section
 537 decreased and the CH₄ conversion increased. As the difference between the furnace and CPR temperatures
 538 increased, reactor performance dropped in all cases due to external heat losses. CH₄ catalytic combustion
 539 reaction was self-sustained for all conditions investigated while the CH₄ conversion in the reforming
 540 section dropped after switching the furnace off. Ineffective insulations are the primary cause of heat losses
 541 and the small throughput of the system is not capable of keeping up. In reality, ineffective insulations were
 542 needed to initiate methane catalytic oxidation reaction by providing heat from the furnace. CPR was made
 543 of moderately conductive stainless steel wall which is also unstable under laboratory heat loss conditions.^{48,}
 544 ⁵¹ The increase in the number of plates in the form of a stack can help to improve stability. As in the study
 545 of Mettler et al.,⁴⁸ plate reactor stack consisting of 9 alternating steam reforming and combustion plates
 546 provides a middle ground in terms of stability.



547
 548 Figure 16. CH₄ conversion, CO selectivity and fraction of CO, CO₂ and H₂ in MSR for counter-current
 549 flow mode with methane flow rate of 45 mL/min and S/C molar ratio of 4.0.

550 4. Conclusions

551 With the resurged interest in distributed hydrogen production, design of small, portable, more energy
 552 efficient reformers becomes important. Due to their small size, flames typically used for heating large scale
 553 reformers are impractical and catalytic combustion is the preferred heat generation approach. A catalytic
 554 plate reactor was designed and developed to study coupling of methane combustion and methane steam
 555 reforming over 5wt%Pt/Al₂O₃ coated microchannels and understand the start-up behaviour. The reactor
 556 setup was assessed using CFD simulations, which showed uniform velocity and pressure distribution along
 557 the microfluidic channels. The catalyst layer shows homogeneous distribution and excellent adherence.
 558 The combustor and reformer were successfully coupled experimentally in co-current and counter-current
 559 modes, and issues posed by the CPR during startup were identified. Regarding methane conversion, the
 560 transient performance of methane steam reformer is slightly better in co-current mode than counter-current
 561 mode at the cost of three fold higher energy consumption in the combustor operating at ~1000 °C. In the
 562 catalytic methane combustor, complete conversion was achieved over a wide channel velocity range (5.1
 563 – 57.3 m/s) without NO formation, but with N₂O identified in the combustor outlet. The concentration of
 564 N₂O is much lower in the counter-current mode, probably due to higher energy input in the latter. Three
 565 flashbacks were encountered in counter-current mode indicating thermal imbalance as a result of
 566 delocalization and minimal coupling of reaction zones. Mitigation strategies regarding safety were
 567 discussed. This study contributes to the understanding of coupling methane combustion and reforming in
 568 a single plate reactor in transient mode during start-up. Future work will focus on the development and
 569 experimental evaluation of CPR of multiple plates coated with active catalyst suitable for each reaction.

570 Supporting Information

571 S1. Additional details of calculation. Table S1. Operating conditions of catalytic methane combustion for
572 co-current flow mode. Table S2. Operating conditions of catalytic methane combustion for counter-current
573 flow mode. Table S3. Average inlet velocity in the center of channels in CPR. Figure S1 (a – I). The velocity
574 profile in microchannels of catalytic plate reactor at channel inlet velocity from 1.4 to 57.3 m/s. Figure S2:
575 Difference between minimum and maximum velocities (m/s) versus average channel inlet velocity. Figure
576 S3 (a – I). The pressure profile in microchannels of catalytic plate reactor at channel inlet velocity from 1.4
577 to 57.3 m/s. Table S4. Pressure drop across microchannels in catalytic plate reactor. Figure S4: Channel
578 inlet velocity as a function of time on stream (TOS) for coupling of MSR and MC. Figure S5: Energy input
579 as a function of $\Delta T_1 = T_{COMB} - T_{FURN}$ for co-current operation. S2. Second co-current coupling experiment
580 – Furnace heat management. Figure S6: Temperature profile of co-current mode in CPR managed by
581 furnace heat. Figure S7: CH₄ conversion, CO selectivity and percent profiles (H₂, CO and CO₂) of MSR
582 for co-current furnace heat managed with a methane flow (45 mL/min) and S/C of 5.0 (172 NL/h/g_{cat}).
583 Figure S8: Methane conversion and concentration profiles in the combustion side in co-current operation
584 as a function of time on stream (furnace heat managed). Figure S9: The concentration of N₂O (ppm) for
585 co-current mode in CPR (furnace heat managed). Figure S10: Energy input as a function of $\Delta T_2 = T_{COMB} -$
586 T_{FURN} for counter-current operation. S3. Second counter-current coupling experiment. Figure S11. The
587 temperature profile for second counter current coupling experiment. Figure S12. CH₄ conversion and
588 concentration profiles of on combustion side for counter-current operation as a function of time on stream.
589 Figure S13. The concentration of N₂O (ppm) for counter-current mode in catalytic plate reactor. Figure
590 S14. CH₄ conversion, CO selectivity and concentration profiles (CO, CO₂ and H₂) of methane steam
591 reforming for counter-current flow mode with methane flow rate of 45 mL/min and S/C molar ratio of 4.0.

592 **Conflicts of Interest**

593 There is no conflict of interest to declare.

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599 **References**

- 600 1. Staffell, I.; Scamman, D.; Velazquez Abad, A.; Balcombe, P.; Dodds, P. E.; Ekins, P.; Shah, N.;
601 Ward, K. R., The role of hydrogen and fuel cells in the global energy system. *Energy & Environmental*
602 *Science* **2019**, 12, (2), 463-491.
- 603 2. Züttel, A.; Borgschulte, A.; Schlapbach, L., *Hydrogen as a Future Energy Carrier*. Wiley-VCH
604 Verlag GmbH & Co. KGaA: Weinheim, 2008.
- 605 3. Wilhite, B. A., Unconventional microreactor designs for process intensification in the distributed
606 reforming of hydrocarbons: a review of recent developments at Texas A&M University. *Current Opinion*
607 *in Chemical Engineering* **2017**, 17, 100-107.
- 608 4. Southall, G. D.; Khare, A., The feasibility of distributed hydrogen production from renewable
609 energy sources and the financial contribution from UK motorists on environmental grounds. *Sustainable*
610 *Cities and Society* **2016**, 26, 134-149.
- 611 5. Bolat, P.; Thiel, C., Hydrogen supply chain architecture for bottom-up energy systems models.
612 Part 2: Techno-economic inputs for hydrogen production pathways. *Int J Hydrogen Energ* **2014**, 39, (17),
613 8898-8925.
- 614 6. Ercolino, G.; Ashraf, M. A.; Specchia, V.; Specchia, S. In *Performance of SR or ATR fuel*
615 *processors integrated with WGS and PSA units for hydrogen production*, Roma, 2014; Roma, 2014; pp
616 232-233.
- 617 7. Ashraf, M. A.; Ercolino, G.; Specchia, S.; Specchia, V., Final step for CO syngas clean-up:
618 Comparison between CO-PROX and CO-SMET processes. *Int J Hydrogen Energ* **2014**, 39, (31), 18109-
619 18119.
- 620 8. Gandia, L. M.; Arzamedi, G.; Dieguez, P. M., *Renewable Hydrogen Technologies: Production,*
621 *Purification, Storage, Applications and Safety*. Elsevier: Amsterdam, 2013; p 472.
- 622 9. Vita, A.; Cristiano, G.; Italiano, C.; Pino, L.; Specchia, S., Syngas production by methane Oxy-
623 steam reforming on Me/CeO₂ (Me = Rh, Pt, Ni) catalyst lined on cordierite monoliths. *Appl Catal B-*
624 *Environ* **2015**, 162, 551-563.
- 625 10. Gupta, R. B., *Hydrogen Fuel: Production, Transport, and Storage*. CRC Press, Taylor & Francis
626 Group: Boca Raton, 2009.
- 627 11. Sanz, O.; Echave, F. J.; Romero-Sarria, F.; Odriozola, J. A.; Montes, M., Chapter 9 - Advances in
628 Structured and Microstructured Catalytic Reactors for Hydrogen Production. In *Renewable Hydrogen*
629 *Technologies*, Gandia, L. M.; Arzamendi, G.; Diéguez, P. M., Eds. Elsevier: Amsterdam, 2013; pp 201-
630 224.
- 631 12. Adris, A. M.; Pruden, B. B.; Lim, C. J.; Grace, J. R., On the reported attempts to radically
632 improve the performance of the steam methane reforming reactor. *The Canadian Journal of Chemical*
633 *Engineering* **1996**, 74, (2), 177-186.

- 634 13. Kumar, A.; Baldea, M.; Edgar, T. F., A physics-based model for industrial steam-methane
635 reformer optimization with non-uniform temperature field. *Computers & Chemical Engineering* **2017**,
636 105, 224-236.
- 637 14. Kumar, A.; Baldea, M.; Edgar, T. F., Real-time optimization of an industrial steam-methane
638 reformer under distributed sensing. *Control Engineering Practice* **2016**, 54, 140-153.
- 639 15. Zecevic, N.; Bolf, N., Advanced Operation of the Steam Methane Reformer by Using Gain-
640 Scheduled Model Predictive Control. *Ind Eng Chem Res* **2020**, 59, (8), 3458-3474.
- 641 16. Oechsler, B. F.; Dutra, J. C. S.; Bittencourt, R. C. P.; Pinto, J. C., Simulation and Control of
642 Steam Reforming of Natural Gas—Reactor Temperature Control Using Residual Gas. *Ind Eng Chem Res*
643 **2017**, 56, (10), 2690-2710.
- 644 17. Weinberg, F. J., Combustion Temperatures: The Future? *Nature* **1971**, 233, (5317), 239-241.
- 645 18. Hayes, R. E.; Kolaczkowski, S. T., *Introduction to catalytic combustion*. Gordon & Breach
646 Science Publishers: Amsterdam, 1997.
- 647 19. Pfefferle, W. C.; Pfefferle, L. D., Catalytically stabilized combustion. *Progress in Energy and*
648 *Combustion Science* **1986**, 12, (1), 25-41.
- 649 20. Coker, A. K., *Petroleum Refining Design and Applications Handbook*. John Wiley & Sons: USA,
650 2018; Vol. Volume 1.
- 651 21. Kolb, G., Review: Microstructured reactors for distributed and renewable production of fuels and
652 electrical energy. *Chemical Engineering and Processing: Process Intensification* **2013**, 65, 1-44.
- 653 22. Colorado, A.; McDonell, V.; Samuelsen, S., Direct emissions of nitrous oxide from combustion
654 of gaseous fuels. *Int J Hydrogen Energ* **2017**, 42, (1), 711-719.
- 655 23. Karagiannidis, S., *Catalytic Microreactors for Portable Power Generation*. Springer-Verlag:
656 Heidelberg, 2011.
- 657 24. He, L.; Fan, Y.; Bellettre, J.; Yue, J.; Luo, L., A review on catalytic methane combustion at low
658 temperatures: Catalysts, mechanisms, reaction conditions and reactor designs. *Renewable and*
659 *Sustainable Energy Reviews* **2020**, 119, 109589.
- 660 25. Kolios, G.; Gritsch, A.; Glöckler, B.; Eigenberger, G., Enhancing Productivity and Thermal
661 Efficiency of High-Temperature Endothermic Processes in Heat-Integrated Fixed-Bed Reactors. In
662 *Integrated Chemical Processes*, Sundmacher, K.; Kienle, A.; Seidel-Morgenstern, A., Eds. WILEY-VCH
663 Verlag GmbH & Co. KGaA: Weinheim, 2005; pp 1-43.
- 664 26. Meloni, E.; Martino, M.; Palma, V., A Short Review on Ni Based Catalysts and Related
665 Engineering Issues for Methane Steam Reforming. *Catalysts* **2020**, 10, (3).
- 666 27. Luk, H. T.; Lei, H. M.; Ng, W. Y.; Ju, Y.; Lam, K. F., Techno-economic Analysis of Distributed
667 Hydrogen Production from Natural Gas. *Chinese J Chem Eng* **2012**, 20, (3), 489-496.

- 668 28. Stefanidis, G. D.; Vlachos, D. G., Millisecond Methane Steam Reforming Via Process and
669 Catalyst Intensification. *Chem Eng Technol* **2008**, 31, (8), 1201-1209.
- 670 29. Chen, J.; Gao, X.; Xu, D., Catalytic Combustion Characteristics of Methane-Air Mixtures in
671 Small-Scale Systems at Elevated Temperatures. *Catalysts* **2018**, 8, (10), 439.
- 672 30. Venkataraman, K.; Redenius, J. M.; Schmidt, L. D., Millisecond catalytic wall reactors:
673 dehydrogenation of ethane. *Chem Eng Sci* **2002**, 57, (13), 2335-2343.
- 674 31. Venkataraman, K.; Wanat, E. C.; Schmidt, L. D., Steam reforming of methane and water-gas
675 shift in catalytic wall reactors. *Aiche J* **2003**, 49, (5), 1277-1284.
- 676 32. Kolb, G.; Schürer, J.; Tiemann, D.; Wichert, M.; Zapf, R.; Hessel, V.; Löwe, H., Fuel processing
677 in integrated micro-structured heat-exchanger reactors. *J Power Sources* **2007**, 171, (1), 198-204.
- 678 33. Specchia, S., Fuel processing activities at European level: A panoramic overview. *Int J Hydrogen*
679 *Energ* **2014**, 39, (31), 17953-17968.
- 680 34. Dodds, P. E.; Staffell, I.; Hawkes, A. D.; Li, F.; Grünewald, P.; McDowall, W.; Ekins, P.,
681 Hydrogen and fuel cell technologies for heating: A review. *Int J Hydrogen Energ* **2015**, 40, (5), 2065-
682 2083.
- 683 35. Specchia, S.; Specchia, V., Modeling Study on the Performance of an Integrated APU Fed with
684 Hydrocarbon Fuels. *Ind Eng Chem Res* **2010**, 49, (15), 6803-6809.
- 685 36. Zafir, M.; Gavriilidis, A., Catalytic combustion assisted methane steam reforming in a catalytic
686 plate reactor. *Chem Eng Sci* **2003**, 58, (17), 3947-3960.
- 687 37. Chen, J.; Han, J.; Xu, D., Efficient operation of autothermal microchannel reactors for the
688 production of hydrogen by steam methane reforming. *Int J Hydrogen Energ* **2019**, 44, (23), 11546-11563.
- 689 38. Mundhwa, M.; Thurgood, C. P., Improved performance of a catalytic plate reactor coated with
690 distributed layers of reforming and combustion catalysts for hydrogen production. *Reaction Chemistry &*
691 *Engineering* **2018**, 3, (4), 487-514.
- 692 39. Chen, J.; Gao, X.; Yan, L.; Xu, D., Computational fluid dynamics modeling of the millisecond
693 methane steam reforming in microchannel reactors for hydrogen production. *Rsc Adv* **2018**, 8, (44),
694 25183-25200.
- 695 40. Mundhwa, M.; Thurgood, C. P., Numerical study of methane steam reforming and methane
696 combustion over the segmented and continuously coated layers of catalysts in a plate reactor. *Fuel*
697 *Process Technol* **2017**, 158, 57-72.
- 698 41. Mundhwa, M.; Parmar, R. D.; Thurgood, C. P., A comparative parametric study of a catalytic
699 plate methane reformer coated with segmented and continuous layers of combustion catalyst for
700 hydrogen production. *J Power Sources* **2017**, 344, 85-102.

- 701 42. Chen, J.; Yan, L.; Song, W.; Xu, D., Methane steam reforming thermally coupled with catalytic
702 combustion in catalytic microreactors for hydrogen production. *Int J Hydrogen Energ* **2017**, 42, (1), 664-
703 680.
- 704 43. Cao, C.; Zhang, N.; Dang, D.; Cheng, Y., Numerical evaluation of a microchannel methane
705 reformer used for miniaturized GTL: Operating characteristics and greenhouse gases emission. *Fuel*
706 *Process Technol* **2017**, 167, 78-91.
- 707 44. Cao, C.; Zhang, N.; Dang, D.; Cheng, Y., Hybrid modeling of integrated microchannel methane
708 reformer for miniaturized GTL application using an effectiveness factor submodel based on complex
709 surface chemistry. *Chem Eng J* **2017**, 316, 715-726.
- 710 45. Cao, C.; Zhang, N.; Cheng, Y., Numerical analysis on steam methane reforming in a plate
711 microchannel reactor: Effect of washcoat properties. *Int J Hydrogen Energ* **2016**, 41, (42), 18921-18941.
- 712 46. Lakhete, P.; Janardhanan, V. M., Modeling process intensified catalytic plate reactor for
713 synthesis gas production. *Chem Eng Sci* **2014**, 110, 13-19.
- 714 47. Jeon, S. W.; Yoon, W. J.; Baek, C.; Kim, Y., Minimization of hot spot in a microchannel reactor
715 for steam reforming of methane with the stripe combustion catalyst layer. *Int J Hydrogen Energ* **2013**, 38,
716 (32), 13982-13990.
- 717 48. Mettler, M. S.; Stefanidis, G. D.; Vlachos, D. G., Enhancing stability in parallel plate
718 microreactor stacks for syngas production. *Chem Eng Sci* **2011**, 66, (6), 1051-1059.
- 719 49. Zhai, X.; Ding, S.; Cheng, Y.; Jin, Y.; Cheng, Y., CFD simulation with detailed chemistry of
720 steam reforming of methane for hydrogen production in an integrated micro-reactor. *Int J Hydrogen*
721 *Energ* **2010**, 35, (11), 5383-5392.
- 722 50. Stefanidis, G. D.; Vlachos, D. G., Intensification of steam reforming of natural gas: Choosing
723 combustible fuel and reforming catalyst. *Chem Eng Sci* **2010**, 65, (1), 398-404.
- 724 51. Mettler, M. S.; Stefanidis, G. D.; Vlachos, D. G., Scale-out of Microreactor Stacks for Portable
725 and Distributed Processing: Coupling of Exothermic and Endothermic Processes for Syngas Production.
726 *Ind Eng Chem Res* **2010**, 49, (21), 10942-10955.
- 727 52. Tonkovich, A. L. Y.; Yang, B.; Perry, S. T.; Fitzgerald, S. P.; Wang, Y., From seconds to
728 milliseconds to microseconds through tailored microchannel reactor design of a steam methane reformer.
729 *Catal Today* **2007**, 120, (1), 21-29.
- 730 53. Zafir, M.; Gavriilidis, A., Influence of Flow Arrangement in Catalytic Plate Reactors for
731 Methane Steam Reforming. *Chemical Engineering Research and Design* **2004**, 82, (2), 252-258.
- 732 54. Kolios, G.; Frauhammer, J.; Eigenberger, G., Efficient reactor concepts for coupling of
733 endothermic and exothermic reactions. *Chem Eng Sci* **2002**, 57, (9), 1505-1510.

- 734 55. Nikačević, N. M.; Huesman, A. E. M.; Van den Hof, P. M. J.; Stankiewicz, A. I., Opportunities
735 and challenges for process control in process intensification. *Chemical Engineering and Processing:
736 Process Intensification* **2012**, 52, 1-15.
- 737 56. Pattison, R. C.; Estep, F. E.; Baldea, M., Pseudodistributed Feed Configurations for Catalytic
738 Plate Microchannel Reactors. *Ind Eng Chem Res* **2014**, 53, (13), 5028-5037.
- 739 57. Ohi, T.; Miyata, T.; Li, D.; Shishido, T.; Kawabata, T.; Sano, T.; Takehira, K., Sustainability of
740 Ni loaded Mg–Al mixed oxide catalyst in daily startup and shutdown operations of CH₄ steam reforming.
741 *Applied Catalysis A: General* **2006**, 308, 194-203.
- 742 58. Granlund, M. Z.; Gorke, O.; Pfeifer, P.; Pettersson, L. J., Comparison between a micro reactor
743 with multiple air inlets and a monolith reactor for oxidative steam reforming of diesel. *Int J Hydrogen
744 Energ* **2014**, 39, (31), 18037-18045.
- 745 59. Zafir, M.; Baldea, M.; Daoutidis, P., Optimizing the catalyst distribution for countercurrent
746 methane steam reforming in plate reactors. *Aiche J* **2011**, 57, (9), 2518-2528.
- 747 60. Jeon, S. W.; Yoon, W. J.; Jeong, M. W.; Kim, Y., Optimization of a counter-flow microchannel
748 reactor using hydrogen assisted catalytic combustion for steam reforming of methane. *Int J Hydrogen
749 Energ* **2014**, 39, (12), 6470-6478.
- 750 61. Herdem, M. S.; Mundhwa, M.; Farhad, S.; Hamdullahpur, F., Catalyst layer design and
751 arrangement to improve the performance of a microchannel methanol steam reformer. *Energ Convers
752 Manage* **2019**, 180, 149-161.
- 753 62. Pattison, R. C.; Baldea, M., A thermal-flywheel approach to distributed temperature control in
754 microchannel reactors. *Aiche J* **2013**, 59, (6), 2051-2061.
- 755 63. Pattison, R. C.; Donahue, M. M.; Gupta, A. M.; Baldea, M., Localized Temperature Control in
756 Microchannel Reactors Using Bimetallic Thermally-Actuated Valves. *Ind Eng Chem Res* **2015**, 54, (24),
757 6355-6361.
- 758 64. Welty, J.; Rorrer, G. L.; Foster, D. G., *Fundamentals of Momentum, Heat, and Mass Transfer*.
759 7th ed.; John Wiley & Sons: Hoboken, NJ,, 2019; p 784.
- 760 65. Tonkovich, A. Y.; Perry, S.; Wang, Y.; Qiu, D.; LaPlante, T.; Rogers, W. A., Microchannel
761 process technology for compact methane steam reforming. *Chem Eng Sci* **2004**, 59, (22-23), 4819-4824.
- 762 66. Irankhah, A.; Rahimi, M.; Rezaei, M., Performance Research on a Methane Compact Reformer
763 Integrated with Catalytic Combustion. *Chem Eng Technol* **2014**, 37, (7), 1220-1226.
- 764 67. Commenge, J. M.; Falk, L.; Corriou, J. P.; Matlosz, M., Optimal design for flow uniformity in
765 microchannel reactors. *Aiche J* **2002**, 48, (2), 345-358.

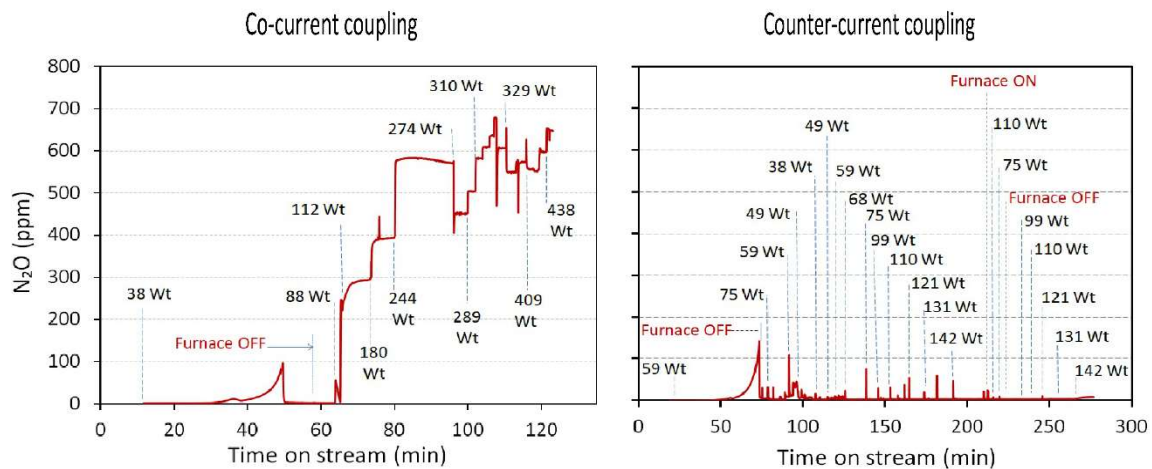
- 766 68. Stefanidis, G. D.; Vlachos, D. G.; Kaisare, N. S.; Maestri, M., Methane steam reforming at
767 microscales: Operation strategies for variable power output at millisecond contact times. *Aiche J* **2009**,
768 55, (1), 180-191.
- 769 69. Farrauto, R. J., New catalysts and reactor designs for the hydrogen economy. *Chem Eng J* **2014**,
770 238, 172-177.
- 771 70. Ashraf, M. A.; Sanz, O.; Italiano, C.; Vita, A.; Montes, M.; Specchia, S., Analysis of Ru/La-
772 Al₂O₃ catalyst loading on alumina monoliths and controlling regimes in methane steam reforming. *Chem*
773 *Eng J* **2018**, 334, 1792-1807.
- 774 71. Ashraf, M. A.; Sanz, O.; Montes, M.; Specchia, S., Insights into the effect of catalyst loading on
775 methane steam reforming and controlling regime for metallic catalytic monoliths. *Int J Hydrogen Energ*
776 **2018**, 43, (26), 11778-11792.
- 777 72. Amjad, U.-E. S.; Vita, A.; Galletti, C.; Pino, L.; Specchia, S., Comparative Study on Steam and
778 Oxidative Steam Reforming of Methane with Noble Metal Catalysts. *Ind Eng Chem Res* **2013**, 52, (44),
779 15428-15436.
- 780 73. Ercolino, G.; Stelmachowski, P.; Specchia, S., Catalytic Performance of Pd/Co₃O₄ on SiC and
781 ZrO₂ Open Cell Foams for Process Intensification of Methane Combustion in Lean Conditions. *Ind Eng*
782 *Chem Res* **2017**, 56, (23), 6625-6636.
- 783 74. Tacchino, S.; Vella, L. D.; Specchia, S., Catalytic combustion of CH₄ and H₂ into micro-
784 monoliths. *Catal Today* **2010**, 157, (1), 440-445.
- 785 75. Otto, K., Methane oxidation over Pt on γ -alumina: kinetics and structure sensitivity. *Langmuir*
786 **1989**, 5, (6), 1364-1369.
- 787 76. Peela, N. R.; Mubayi, A.; Kunzru, D., Washcoating of γ -alumina on stainless steel
788 microchannels. *Catal Today* **2009**, 147, S17-S23.
- 789 77. Zhang, Q.; Sakurai, M.; Kameyama, H., Performance Simulations of a Compact Plate Methane
790 Steam Reformer Using an Electrically Heated Alumite Catalyst. *Journal of Chemical Engineering of*
791 *Japan* **2007**, 40, (4), 319-328.
- 792 78. Haruta, M.; Sano, H., Catalytic combustion of hydrogen—III. Advantages and disadvantages of a
793 catalytic heater with hydrogen fuel. *Int J Hydrogen Energ* **1982**, 7, (9), 737-740.
- 794 79. Maximini, M.; Engelhardt, P.; Brenner, M.; Beckmann, F.; Moritz, O., Fast start-up of a diesel
795 fuel processor for PEM fuel cells. *Int J Hydrogen Energ* **2014**, 39, (31), 18154-18163.
- 796 80. Chen, F.; Chang, M.-H.; Kuo, C.-Y.; Hsueh, C.-Y.; Yan, W.-M., Analysis of a Plate-Type
797 Microreformer for Methanol Steam Reforming Reaction. *Energy & Fuels* **2009**, 23, (10), 5092-5098.
- 798 81. Rodríguez-Guerra, Y.; Gerling, L. A.; López-Guajardo, E. A.; Lozano-García, F. J.; Nigam, K.
799 D. P.; Montesinos-Castellanos, A., Design of Micro- and Milli-Channel Heat Exchanger Reactors for

- 800 Homogeneous Exothermic Reactions in the Laminar Regime. *Ind Eng Chem Res* **2016**, 55, (22), 6435-
801 6442.
- 802 82. Ahmed, K.; Föger, K., Fuel Processing for High-Temperature High-Efficiency Fuel Cells. *Ind*
803 *Eng Chem Res* **2010**, 49, (16), 7239-7256.
- 804 83. Janicke, M. T.; Kestenbaum, H.; Hagendorf, U.; Schüth, F.; Fichtner, M.; Schubert, K., The
805 Controlled Oxidation of Hydrogen from an Explosive Mixture of Gases Using a Microstructured
806 Reactor/Heat Exchanger and Pt/Al₂O₃ Catalyst. *J Catal* **2000**, 191, (2), 282-293.
- 807 84. Ryi, S. K.; Park, J. S.; Cho, S. H.; Kim, S. H., Fast start-up of microchannel fuel processor
808 integrated with an igniter for hydrogen combustion. *J Power Sources* **2006**, 161, (2), 1234-1240.
- 809 85. Yang, J.; Salman, A. D.; Blanco-García, P., A Review of Measurement Techniques of
810 Mechanical Properties of the Catalyst Layer in Catalytic Converters. *Johnson Matthey Technology*
811 *Review* **2019**, 63, (3), 177-190.
- 812 86. Vican, J.; Gajdeczko, B. F.; Dryer, F. L.; Milius, D. L.; Aksay, I. A.; Yetter, R. A., Development
813 of a microreactor as a thermal source for microelectromechanical systems power generation. *Proceedings*
814 *of the Combustion Institute* **2002**, 29, (1), 909-916.
- 815 87. Belmont, E. L.; Schoegl, I.; Ellzey, J. L., Experimental and analytical investigation of lean
816 premixed methane/air combustion in a mesoscale counter-flow reactor. *Proceedings of the Combustion*
817 *Institute* **2013**, 34, (2), 3361-3367.
- 818 88. He, L.; Fan, Y.; Luo, L.; Bellettre, J.; Yue, J., Preparation of Pt/ γ -Al₂O₃ catalyst coating in
819 microreactors for catalytic methane combustion. *Chem Eng J* **2020**, 380, 122424.
- 820 89. Zafir, M.; Gavriilidis, A., Modelling of a catalytic plate reactor for dehydrogenation-
821 combustion coupling. *Chem Eng Sci* **2001**, 56, (8), 2671-2683.
- 822 90. Lee, J. H.; Trimm, D. L., Catalytic combustion of methane. *Fuel Process Technol* **1995**, 42, (2),
823 339-359.
- 824 91. Chen, J.; Gao, X.; Liu, B.; Xu, D., Management of the gas-phase and surface chemistry in
825 methane-fueled catalytic micro-combustors. *Int J Hydrogen Energ* **2017**, 42, (30), 19079-19095.
- 826 92. Wang, Y.; Yang, W.; Zhou, J.; Yang, H.; Yao, Y.; Cen, K., Heterogeneous reaction
827 characteristics and its effects on homogeneous combustion of methane/air mixture in microchannels II.
828 Chemical analysis. *Fuel* **2019**, 235, 923-932.
- 829 93. Robinson, C.; Smith, D. B., The auto-ignition temperature of methane. *Journal of Hazardous*
830 *Materials* **1984**, 8, (3), 199-203.
- 831 94. Farrauto, R. J.; Liu, Y.; Ruettinger, W.; Ilinich, O.; Shore, L.; Giroux, T., Precious Metal
832 Catalysts Supported on Ceramic and Metal Monolithic Structures for the Hydrogen Economy. *Catalysis*
833 *Reviews* **2007**, 49, (2), 141-196.

- 834 95. Boldrini, D. E.; Sanchez, J. F.; Tonetto, G. M.; Damiani, D. E., Monolithic Stirrer Reactor:
835 Performance in the Partial Hydrogenation of Sunflower Oil. *Ind Eng Chem Res* **2012**, 51, (38), 12222-
836 12232.
- 837 96. Ertl, G.; Knözinger, H.; Weitkamp, J., *Handbook of heterogeneous catalysis*. VCH
838 Verlagsgesellschaft mbH: Weinheim, 1997.
- 839 97. Ismagilov, Z. R.; Pushkarev, V. V.; Podyacheva, O. Y.; Koryabkina, N. A.; Veringa, H., A
840 catalytic heat-exchanging tubular reactor for combining of high temperature exothermic and endothermic
841 reactions. *Chem Eng J* **2001**, 82, (1-3), 355-360.
- 842 98. Baukal, C. E., *The John Zink Hamworthy Combustion Handbook: Fundamentals*. CRC Press:
843 Danvers, MA, 2013; Vol. Vol. 1.
- 844 99. Bowman, C. T., Gas-Phase Reaction Mechanisms for Nitrogen Oxide Formation and Removal in
845 Combustion. In *Pollutants from Combustion: Formation and Impact on Atmospheric Chemistry*, Vovelle,
846 C., Ed. Springer: Dordrecht, 2000; pp 123-144.
- 847 100. Muzio, L. J.; Montgomery, T. A.; Samuelsen, G. S.; Kramlich, J. C.; Lyon, R. K.; Kokkinos, A.,
848 Formation and measurement of N₂O in combustion systems. *Symposium (International) on Combustion*
849 **1991**, 23, (1), 245-250.
- 850 101. Kumar, A.; Baldea, M.; Edgar, T. F.; Ezekoye, O. A., Smart Manufacturing Approach for
851 Efficient Operation of Industrial Steam-Methane Reformers. *Ind Eng Chem Res* **2015**, 54, (16), 4360-
852 4370.
- 853 102. Glarborg, P.; Miller, J. A.; Ruscic, B.; Klippenstein, S. J., Modeling nitrogen chemistry in
854 combustion. *Progress in Energy and Combustion Science* **2018**, 67, 31-68.
- 855 103. Wójcik, S.; Ercolino, G.; Gajewska, M.; Quintero, C. W. M.; Specchia, S.; Kotarba, A., Robust
856 Co₃O₄| α -Al₂O₃|cordierite structured catalyst for N₂O abatement – Validation of the SCS method for
857 active phase synthesis and deposition. *Chem Eng J* **2019**, 377, 120088.
- 858 104. Hayhurst, A. N.; Lawrence, A. D., Emissions of nitrous oxide from combustion sources.
859 *Progress in Energy and Combustion Science* **1992**, 18, (6), 529-552.
- 860 105. Kolios, G.; Glockler, B.; Gritsch, A.; Morillo, A.; Eigenberger, G., Heat-integrated reactor
861 concepts for hydrogen production by methane steam reforming. *Fuel Cells* **2005**, 5, (1), 52-65.
- 862 106. Plee, S. L.; Mellor, A. M., Review of flashback reported in prevaporizing/premixing combustors.
863 *Combustion and Flame* **1978**, 32, 193-203.
- 864 107. Kolios, G.; Frauhammer, J.; Eigenberger, G., A simplified procedure for the optimal design of
865 autothermal reactors for endothermic high-temperature reactions. *Chem Eng Sci* **2001**, 56, (2), 351-357.
- 866 108. Dhingra, A. Modeling and Development of Compact Onboard Fuel Processors for PEM Fuel Cell
867 Applications. The University of Michigan, USA, 2012.

868 109. Frauhammer, J.; Eigenberger, G.; Hippel, L. v.; Arntz, D., A new reactor concept for
869 endothermic high-temperature reactions. *Chem Eng Sci* **1999**, 54, (15), 3661-3670.

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871