# Very rich methanol-air combustion in microchannel-based reactors to produce hydrogen-rich syngas

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### Abstract

We examine very rich methanol-air combustion in a microchannel-based reactor consisting of multiple counter-current channels of finite length separated by thin solid conducting walls. Within the framework of the narrow-channel approximation, this problem can be formulated as a one-dimensional model for a single channel with an extra term representing heat transfer from hot stream products to fresh reactants in adjacent channels. The heat recirculation enables superadiabatic temperatures and promotes the oxidation of the fuel far beyond the conventional rich limit of flammability, resulting in a feasible thermal partial oxidation that produces hydrogen without the need for a catalyst. We present an analysis of the stationary model burner performance with detailed gas-phase kinetics in terms of operating variables such as the equivalence ratio and the gas inflow velocity, and for different physical parameters such as the length of the reactor and the conductivity of the wall material. The model predicts a hydrogen yield between 50 and 60% for a range of equivalence ratios between 3 and 6 and a wide range of reactant flow rates.

## 1 Introduction

Fuel cell technology is increasingly considered as an alternative to conventional electrochemical batteries (e.g. lithium-ion batteries) to power small portable systems for long operating times. Proton-exchange membrane fuel cells seem to be the most suitable due to the fast startup, however, they require pure hydrogen for operation. To avoid safety problems linked to hydrogen storage a proposed solution is to produce hydrogen on-site from hydrocarbons in a micro reformer. The obtention of large conversion rates of hydrogen in a small-volume reactor requires completion of the chemical process within a short residence time. The process is limited by the kinetics and for this reason catalyst layers or heat recirculation are frequently employed to accelerate the reactions. Among the main methods for hydrogen production from hydrocarbons (e.g. steam reforming, autothermal reforming or partial oxidation), for a microchannel-based reactor

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the simplest is by partial oxidation of a very rich mixture in a heat-recirculating configuration. Heat recirculation extends the rich flammability limit [1] and increases the  $H_2$  yield with no need for a catalyst, avoiding problems associated to catalyst degradation and poisoning.

Experimental works have demonstrated the feasibility of hydrogen production without catalysts using a configuration of multiple narrow channels with alternating flow directions, similar to the sketch in Fig. 1. The opposing combustion zones are self-stabilized as reactants are preheated by the product stream in the adjacent channels. Ellzey et al. [2] used four parallel counter-current channels separated by silicon carbide walls. This reactor prototype was investigated with methane, propane and liquid heptane fuel. Swiss-roll burners are conceptually similar. The heat transfer mechanism is based on a double-spiral geometry and a single combustion zone is stabilized in the center of the burner. Experiments using propane in a 6-turn Swiss-roll burner have been reported recently [3]. Combustion in inert porous media to produce hydrogen is another solution based on preheating of the reactants. Differently to the counter-current configuration, the combustion front in this case is not steady and propagates along the porous reactor material. To maintain the combustion front inside the reactor, additional techniques such as periodic restarting or reversal of the flow are required. The most compact porous reactor for hydrogen production was investigated by Pedersen-Mjaanes et al. [4] with different fuels (methanol, methane, octane and petrol) and different porous materials (foams and beads). With the addition of a second porous layer the porous media reactor supported stationary combustion. Methanol combustion was sustained up to an equivalence ratio  $\phi = 9.3$ , well beyond the conventional flammability limit of  $\phi = 4.1$ .

Two-dimensional numerical simulations with multistep chemical kinetics have been used to investigate the counter-current configuration [5], but a parametric study was no viable due to the high computational cost. Here we present an analysis of the partial oxidation of methanol in counter-current narrow channels with the use of detailed gas-phase chemical kinetics. Simplification to a one-dimensional problem is achieved in the framework of the narrow-channel approximation and periodicity reduces the problem to the analysis of a single channel. We investigate the effect of four variables (the equivalence ratio, the gas inflow velocity, the reactor length, and the conductivity of the solid wall material) on the hydrogen conversion rate.

## 2 Formulation

Consider very rich methanol-air oxidation in multiple counter-current narrow planar channels of width d and length L, separated by solid conducting walls of thickness  $d_w$ . We illustrate the design in Fig. 1. In this configuration each channel can be treated as thermally isolated from the exterior because of the multiple channels in the y-direction. The gas mixture is introduced at an initial temperature  $T_u = 343$  K (higher than the standard temperature to prevent condensation of the fuel) and velocity  $U_u$ .

Assuming: 1) that the channel width d is much smaller than the flame thickness,  $d \ll \delta_T$  (narrow-channel approximation [6]), defined as  $\delta_T = \mathcal{D}_T/S_L$ , with  $\mathcal{D}_T$  and  $S_L$  the thermal diffusivity and the burning velocity of the planar flame, respectively; and 2) that the gas inflow velocity  $U_u$  is equal in all channels (so that flames are stabilized at symmetric positions  $\pm x_f$ ), the problem is reduced to integrating the following

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Figure 1: Sketch of the array of counter-current narrow channels and the coordinate system centered in the lower wall of channel *i*.

one-dimensional steady governing equations for a single channel *i*:

$$\rho U = \rho_u U_u = \text{const.},\tag{1}$$

$$\rho c_p U \frac{\mathrm{d}T}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x} \left( \lambda_g \frac{\mathrm{d}T}{\mathrm{d}x} \right) - \rho \sum_{k=1}^N c_{p,k} Y_k V_k \frac{\mathrm{d}T}{\mathrm{d}x} - \sum_{k=1}^N \dot{\omega}_k h_k W_k - \frac{2\lambda_w}{d d_w} \left[ T(x) - T(-x) \right], \tag{2}$$

$$\rho U \frac{\mathrm{d}Y_k}{\mathrm{d}x} = -\frac{\mathrm{d}}{\mathrm{d}x} \left(\rho Y_k V_k\right) + \dot{\omega}_k W_k, \qquad k = 1, 2, \dots, N, \tag{3}$$

$$\rho = \frac{p_{\rm atm} W}{\mathcal{R}T},\tag{4}$$

with the corresponding flux conditions at the left and right boundaries given by

$$x = -L/2: \begin{cases} \rho_u U_u h_u = \rho U h - \lambda_g \frac{\mathrm{d}T}{\mathrm{d}x} + \sum_{k=1}^N \rho Y_k V_k h_k, \\ \rho_u U_u Y_{k_u} = \rho U Y_k + \rho Y_k V_k, \end{cases} \qquad x = L/2: \quad \frac{\mathrm{d}T}{\mathrm{d}x} = 0, \quad (5)$$

for k = 1, 2, ..., N, where  $h = \sum_{k=1}^{N} h_k(T)Y_k$  and  $h_u = \sum_{k=1}^{N} h_k(T_u)Y_{k_u}$  are the specific enthalpy of the mixture at the inlet of the reactor and at the fresh unburned mixture, respectively. In the present study the heat flux through a thin wall is taken to be proportional to the differences of the temperatures at each side of the wall multiplied by the wall thermal conductivity,  $\lambda_w$ , and divided by its thickness,  $d_w$ .

In the above equations,  $Y_k$ ,  $c_{p,k}$ ,  $\dot{\omega}_k$ ,  $h_k$ ,  $V_k$ , and  $W_k$  are, respectively, the mass fraction, the specific heat, the molar rate of production per unit volume, the specific enthalpy, the diffusion velocity (calculated with the multicomponent diffusion model), and the molecular weight of the  $k^{\text{th}}$  species.  $p_{\text{atm}}$  is the ambient (atmospheric) pressure,  $\rho$  is the gas density,  $c_p$  is the specific heat of the mixture at constant pressure,  $\overline{W}$  is the mean molecular weight,  $\mathcal{R}$  is the universal gas constant, and N stands for the total number of chemical species. The last term on the right-hand side of Eq. 2 represents the heat recirculation between

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adjacent, symmetric with respect to x = 0, channels. The parameter  $b = 2\lambda_w/(d d_w)$  stands for the reduced conductivity factor of the wall. For a microburner with d = 4 mm and  $d_w = 1$  mm, the order of magnitude of b lies typically between 10<sup>5</sup> W/(m<sup>3</sup>K) for less conductive materials such as quartz to 10<sup>7</sup> W/(m<sup>3</sup>K) for more conductive materials such as silicon carbide [2]. The partial oxidation process is modeled with the 247-step C3 San Diego mechanism that involves N = 50 reactive species [7].

## 3 Inlet/outlet boundary conditions



Figure 2: Profiles of temperature, CH<sub>3</sub>OH, O<sub>2</sub>, H<sub>2</sub>, and CO molar fractions along channel calculated using an infinite three-zone model (dashed curves) and using a finite one-zone model (solid curves). Calculated for  $\phi = \{1, 3\}$ , with  $U_u = 100$  cm/s,  $T_u = 343$  K,  $b = 4 \cdot 10^5$  W/(m<sup>3</sup> K), and L = 2 cm. Dot-dashed lines correspond to adiabatic temperatures. The insets show zooms of the inlet, combustion zone and outlet.

The validity of flux boundary conditions in Eq. (5) is checked in Fig. 2 by comparing results of the system of equations (1)-(4) with conditions (5) to computations assuming an infinite channel. The infinite channel domain comprises three zones: the heat-recirculating channel itself (zone 2) and two semi-infinite sections outside the channel where heat recirculation is excluded (zones 1 and 3). As can be seen in Fig. 2, differences in the results inside the reactor are insignificant. We found differences far downstream the exit of the reactor in some circumstances, namely, for stoichiometric mixtures, as the equilibrium composition is not attained at the outlet. For fuel-rich mixtures the composition reaches a metastable state at the exit so boundary conditions (5) suffice to integrate the problem (1)-(4) from x = -L/2 to x = L/2.

## 4 **Results**

Spatially resolved profiles of gas temperature and mole fractions of H<sub>2</sub> and CO along channels of length L = 2 and 10 cm are presented in Fig. 3 at a fixed mixture equivalence ratio  $\phi = 3$  by varying the inflow velocity. Three different stages are observed: 1) an inert preheat zone, where heat transfer with the adjacent channels increases the temperature of the fresh gas until ignition occurs. 2) A reaction zone, where the fuel is partially oxidated at high temperature and H<sub>2</sub>O and CO molecules, as well as a significant amount of H<sub>2</sub>, are produced. Because of its relative importance in the total amount of produced hydrogen, we shall call primary the hydrogen production in this zone [8]. 3) A post-combustion zone, where H<sub>2</sub>O reacts through reforming and water-gas-shift reactions with CH<sub>4</sub> and CO producing smaller amounts of hydrogen (secondary hydrogen formation).



Figure 3: Profiles of gas temperature, H<sub>2</sub> and CO molar fractions along the channel for L = 2 cm and L = 10 cm. Calculated for inflow velocities  $U_u = \{100, 200, 300, 400, 800, 1200, 1600, 2000\}$  cm/s, with  $\phi = 3$ ,  $T_u = 343$  K, and  $b = 10^6$  W/(m<sup>3</sup> K). Dot-dashed lines correspond to chemical equilibrium values.

Our calculations show that primary H<sub>2</sub> formation does not depend on the inflow velocity. The value of  $X_{\text{H}_2}^{\text{primary}}$  measured in the reaction zone (i.e. where CO peaks) corresponds to  $X_{\text{H}_2}^{\text{primary}} \approx 0.19$  for all cases at the given equivalence ratio. We found that the amount of hydrogen obtained by secondary formation, however, does depend on the inflow velocity. In our calculations we observed low secondary hydrogen formation for large inflow velocities (corresponding to flames near the middle of the channel and thus short post-combustion zones) or small inflow velocities (corresponding to flames near the inlet and thus low combustion temperatures). In Fig. 4 we plot the gas temperature and mole fraction profiles of H<sub>2</sub> and CO for a fixed inlet velocity  $U_u = 200$  cm/s as  $\phi$  is varied. As can be seen, combustion can be sustained for mixtures very far from the rich flammability limit, with the H<sub>2</sub> mole fraction obtained at the outlet increasing with the equivalence ratio.

The hydrogen conversion efficiency (or H<sub>2</sub> yield) variation with the inflow velocity and the equivalence ratio is shown in Fig. 5. The H<sub>2</sub> yield is defined as the ratio of H<sub>2</sub> moles produced per unit time at the exit of the reactor over the H<sub>2</sub> moles that would be produced if all the atomic hydrogen in the fuel was converted to H<sub>2</sub> ( $\eta_{\text{H}_2} = \dot{N}_{\text{H}_2,\text{out}}/2\dot{N}_{\text{CH}_3\text{OH},u}$ , where  $\dot{N}_k$  is the molar flow rate of the species k). The process reaches a conversion efficiency between 50 and 60% in a range of equivalence ratios between  $\phi = 3$  and 6 and for inflow velocities between  $U_u = 100$  and 200 cm/s. Longer reactors and higher wall conductivities result in better efficiencies.



Figure 4: Profiles of gas temperature, H<sub>2</sub> and CO molar fractions along the channel for L = 2 cm and L = 10 cm. Calculated for  $\phi = \{2, 3, 4, 5, 6, 7\}$  with  $U_u = 200$  cm/s,  $T_u = 343$  K and  $b = 10^6$  W/(m<sup>3</sup> K).

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Figure 5: The H<sub>2</sub> yield variation at the exit of the channel. Left: for fixed  $\phi = 3$ . Right: for fixed  $U_u = 200$  cm/s (solid curves) and  $U_u = 50$  cm/s (dashed curves). Calculated for  $b = 10^6$  W/(m<sup>3</sup> K) (solid curves) and  $b = 10^5$  W/(m<sup>3</sup> K) (dashed curves) with  $T_u = 343$  K. Dot-dashed curves correspond to equilibrium.

## 5 Conclusions

We presented a simplified one-dimensional model for a reactor consisting in multiple counter-current narrow channels and applied it to the numerical analysis of rich methanol oxidation for hydrogen production. The results showed three stages in the process: (1) an inert preheat zone, (2) an exothermic reaction zone, where partial oxidation produced most of the H<sub>2</sub> (primary formation), and (3) a post-combustion zone, where slow endothermic reforming reactions contributed to a small amount of H<sub>2</sub> (secondary formation). The primary formation of H<sub>2</sub> only depends on the equivalence ratio, whereas the secondary formation depends mainly on the inflow velocity. The model reactor presented hydrogen yields between 50 and 60% in a range of equivalence ratios between 3 and 6 and for inflow velocities between 100 and 200 cm/s. Although soot formation is an important issue in the present problem it was not investigated here. It could be evaluated a posteriori through the study of the gas-phase precursors  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$ .

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