

Simulation of a structured catalytic reactor for exothermic methanation reactions producing synthetic natural gas

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Abstract

Aim of this work is a theoretical investigation of the catalytic methanation reactions in externally cooled tubular reactors filled with novel monolithic catalysts with high thermal conductivity.

Using the general purpose modelling tool gPromsTM we have developed a steady-state, heterogeneous 1D model, representing a single, externally cooled reactor tube loaded with cylindrical honeycomb catalysts with square channels, made of conductive material. The model equations include mass and energy balances for the gas and solid phases and the momentum balance for the gas phase. Two reactions are considered: carbon monoxide and carbon dioxide methanation, whose rate equations are taken from the literature.

By reactor simulation it is shown that the problem of temperature control typical of fixed-bed methanation reactors can be overcome by the monolith reactor herein proposed. The effects of space velocity on conversion and temperature profiles are discussed, with a fixed geometrical configuration of the monolithic reactor.

Keywords: Monolith reactors, Reactor modeling, Methanation, Synthetic Natural Gas

1. Introduction

The production of synthetic natural gas (SNG) from coal or biomass is an interesting opportunity both for exploiting coal and biomass, and for replacing oil products for transportation and other uses.

Natural gas is cleaner than coal and its production has been increasing for years; however, its price has been increasing as well, so the synthesis of SNG from coal and biomass is receiving strong interest especially in USA and China (<http://www.chinamining.org>). SNG has many important advantages: it can be transported efficiently and cheaply using existing natural gas pipelines and distributing networks, it is an easily convertible feedstock, both in natural-gas combined-cycle power plants and in petrochemical facilities, it can count on a high social acceptance with respect to coal, and it can be stored underground, enabling efficient operation throughout the year independent of a fluctuating demand.

Unfortunately, the commercial deployment of technologies for the production of SNG is currently constrained by technical barriers, so that more research is required before extensive applications at the industrial scale. An important issue to be addressed is the

strong exothermicity of the reactions, so that conventional fixed-bed catalytic reactors cannot be safely used (Sudiro *et al.*, 2009a).

The use of monolith catalyst supports offers at least two advantages with respect to conventional packed-bed reactors: pressure drops are greatly reduced (to less than 1%) and the radial heat transport can be more favorable, especially when metallic support are used. Such monoliths have in fact the advantage of favorable global heat-transfer properties resulting from heat conduction in the connected structure of their solid matrix; this problem has been extensively investigated theoretically (Groppi and Tronconi, 1996; Groppi and Tronconi, 2000). Application of monolith catalysts has already been shown as technically feasible, both by simulation in the case of the oxidation of methanol to formaldehyde and epoxidation of ethylene (Groppi and Tronconi, 2001) and experimentally at the pilot-reactor scale (Groppi *et al.*, 2008; Groppi *et al.*, 2000; Tronconi and Groppi, 2000) in the case of strongly exothermic gas/solid reactions, such as catalytic *o*-xylene selective oxidation and CO oxidation.

In this way significantly more heat can be removed and structured catalyst are eligible to be used for strongly exothermic gas/solid reactions. Favourable heat transfer properties permit reducing risk of thermal runaway and catalyst deactivation. To this end, our aim is to verify the possibility of overcoming the problem of temperature control, typical of fixed-bed, for methanation reactions, if they are carried out in monolith reactors.

2. Reactor modeling

It is assumed that catalytic methanation reactions occur in an externally cooled tubular reactors filled with novel monolithic catalysts with high thermal conductivity.

2.1. Model equations

The behavior of the methanation reactor is modelled by a dynamic 1D, heterogeneous, single-tube model of an externally cooled multi-tubular fixed-bed reactor, which is loaded with honeycomb catalysts.

The model includes the specie mass balances and the energy balances for the gas and solid phases, and the momentum balance for the gas phase.

Mass balances for the gas phase are expressed by:

$$\varepsilon \frac{\partial w_{i,g}}{\partial t} = -\frac{Wt}{\rho_g} \cdot \frac{\partial w_{i,g}}{\partial z} - \frac{K_{m,i}a}{\rho_g} \cdot (w_{i,g} - w_{i,s}) \quad (1)$$

whereas those for the solid phase are:

$$0 = \sum_{j=1}^{NR} v_{i,j} \frac{\tanh \vartheta_j}{\vartheta_j} R_j PM_i \xi + K_{m,i}a (w_{i,g} - w_{i,s}) \quad (2)$$

Energy balance for the gas phase is written as:

$$\varepsilon \rho c_p \frac{\partial T_g}{\partial t} = -Wt c_p \frac{\partial T_g}{\partial z} - ha (T_g - T_s) \quad (3)$$

whereas that for the solid phase is:

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$$\rho_s c_{p,s} (1-\varepsilon) \frac{\partial T_s}{\partial t} = k_{s,ax} (1-\varepsilon) \frac{\partial^2 T_s}{\partial z^2} + \frac{ha}{1-\varepsilon} (T_g - T_s) + \sum_{j=1}^{NR} \left(-\Delta H_{R,j} \frac{\tanh \vartheta_j}{\vartheta_j} R_j \right) \xi - h_{wall} (T_s - T_{wall}) \frac{4}{d} \quad (4)$$

The momentum balance is according to the following equation:

$$\left(-\frac{1}{\rho_g} + \frac{Wt}{\rho_g^2 P} \right) \frac{\partial P}{\partial z} - \frac{Wt^2}{\rho_g^2 T} \frac{\partial T_g}{\partial z} = \frac{1}{2} \frac{Wt^2}{\rho_g^2} af \quad (5)$$

Boundary conditions at reactor inlet and outlet are reported in Table 1.

Table 1. Boundary conditions

Reactor inlet (z=0)	Reactor outlet (z=L)
$w_{i,g} \Big _{z=0} = w_{i,feed} ; T_g \Big _{z=0} = T_{feed} ; P \Big _{z=0} = P_{feed}$	
$-k_{s,ax} \frac{\partial T_s}{\partial z} \Big _{z=0} = \sigma \cdot \varepsilon_s \cdot (T_g^4 - T_s^4 \Big _{z=0})$	$-k_{s,ax} \frac{\partial T_s}{\partial z} \Big _{z=L} = \sigma \cdot \varepsilon_s \cdot (T_g^4 - T_s^4 \Big _{z=L})$

Initial conditions are: $w_{i,g}(z, t=0) = w_{i,feed}$, $T_g(z, t=0) = T_{coolant}$, $T_s(z, t=0) = T_{coolant}$.

The following gas-solid heat and mass transfer correlations for honeycomb monoliths have been adopted to calculate Nusselt and Sherwood numbers in the square celled monoliths:

$$Nu = 3 + 6.874 \cdot \left(1000 \cdot z_{Nu}^* \right)^{-0.488} e^{-57.2 \cdot z_{Nu}^*}, \text{ where } z_{Nu}^* = \frac{z}{d_{eq} Re Pr} \quad (6)$$

$$Sh = 3 + 6.874 \cdot \left(1000 \cdot z_{Sh}^* \right)^{-0.488} e^{-57.2 \cdot z_{Sh}^*}, \text{ where } z_{Sh}^* = \frac{z}{d_{eq} Re Sc} \quad (7)$$

The following expression for calculation of friction factors in the square monolith channels was adopted in the model:

$$f Re = 14.227 + 17.76323 \cdot \left(1000 \cdot z_f^* \right)^{-0.4715} e^{-59.57 \cdot z_f^*}, \text{ where } z_f^* = \frac{z}{d_{eq} Re} \quad (8)$$

Dimensionless numbers are defined in Table 2:

Table 2. Dimensionless numbers

$$Pr = \frac{\mu_g c_{p,g}}{k_g} ; Re = \frac{d_{eq} Wt}{\varepsilon \mu_g} ; Nu = \frac{d_{eq} h}{k_g} ; Sc_i = \frac{\mu_g}{\rho_g D_{i,g}} ; Sh_i = \frac{K_{m,i} d_{eq}}{\rho_g D_{i,g}}$$

Thermal properties, such as specific heat and heat of reaction, were estimated according to the CHEMKIN correlations (Smith *et al.*, 2009), and gas properties, such as conductivity, viscosity and diffusivity, were calculated according to the correlations reported by Sudiro *et al.*, (2009b). The system of equations was solved by using the general purpose tool gProms™, adopting 200 grid points along the axial direction.

The reactor has a length of 1 m with an inner diameter of 0.254 m. The monolith pitch is set to 2 mm, values of the catalytic washcoat (ξ) and of fraction of metallic support (λ), are 0.2 and 0.25, respectively.

The wall heat transfer coefficient was set to 500 W/m² K, according to the results of Groppi and Tronconi, (2005) for a monolith in tight contact with the reaction tube, whereas the thermal conductivity of the monolith support was set to 200 W/m K (Al).

2.2. Kinetic scheme

The following two reactions (CO and CO₂ methanation) have been considered:



The CO methanation kinetic was derived from Sughrue, 1982, the one of CO₂ methanation from Weatherbee, 1982. Rate expression for CO methanation on Ni catalyst is:

$$r_{\text{CO}} \left(\frac{\text{mol}}{\text{m}^3 \text{s}} \right) = \frac{0.2 \cdot k_1 k_2 p_{\text{H}_2}}{k_1 \left(1 + K_{\text{H}_2}^{0.5} p_{\text{H}_2}^{0.5} + K_{\text{CO}} p_{\text{CO}} \right)^2 + k_2 \left(1 + K_{\text{CO}} p_{\text{CO}} \right)^2} \cdot \rho_{\text{catalyst}} \quad (11)$$

where k_1 , k_2 , k_{H_2} , k_{CO} depend on the temperature according to an Arrhenius/power law expression. The rate expression for CO₂ methanation on Ni catalyst is:

$$r_{\text{CO}_2} \left(\frac{\text{mol}}{\text{m}^3 \text{s}} \right) = \frac{0.2 \cdot A \cdot p_{\text{CO}_2}^{0.5} p_{\text{H}_2}^{0.5}}{\left(1 + B \left(\frac{p_{\text{CO}_2}}{p_{\text{H}_2}} \right)^{0.5} + C \left(p_{\text{CO}_2} p_{\text{H}_2} \right)^{0.5} + \frac{p_{\text{CO}}}{D} \right)^2} \cdot \rho_{\text{catalyst}} \quad (12)$$

Constant A, B, C and D are tabulated as a function of temperature. In order to explore intensified process conditions, r_{CO} and r_{CO_2} were incremented by 40% in all the simulations.

3. Results and discussion

Figure 1 shows the calculated axial profiles of gas temperature (1a) and conversion of H₂, CO and CO₂ along the reactor (1b). Coolant temperature was set to 573K, as reactions start at $T \gg 240^\circ\text{C}$ (Odermatt, 2008). A feed (60% mol H₂, 20% mol CO and 20% mol CO₂) with a H₂/CO molar ratio of 3 was assumed, and the GHSV was set to 15000 h⁻¹, as reported by Rostrup-Nielsen, 2007, which is a typical value for pilot plants. The inlet pressure was set to 6.9 bar.

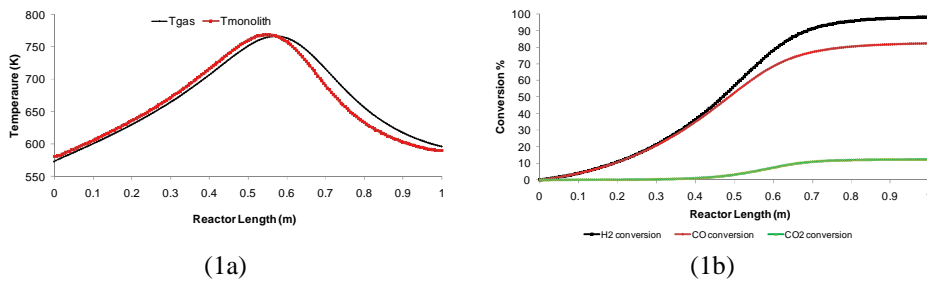


Figure 1. Axial profiles of temperatures and conversions

It is interesting to show that with only one monolithic reactor a high conversion of hydrogen and carbon monoxide can be obtained (98 and 83%, respectively), with a

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moderate and acceptable increase of temperature along the reactor, avoiding catalyst deactivation with respect to existing methanation processes. Here at least three reactors and a recycle of a part of the products are required (Sudiro *et al.*, 2009a, Topsøe, 2009): recycle is needed for controlling the temperature using products as inert and three reactors are required to achieve high conversion.

For comparison, if the same gas flow rate were sent to an equilibrium adiabatic reactor the output temperature would be higher (about 1000K), with a CO conversion of 81%, similar to that obtained with the monolith reactor, but with the consequence of a total deactivation of the catalyst.

3.1. Sensitivity analysis

The effect of a progressive increase of the flow rate value was investigated in order to improve the productivity (see Figure 2). A higher gas flow rate, and correspondingly a greater value of GHSV, results in the shift of the hot-spot towards the bed exit (in this conditions the reactions tend to the extinction). In fact, the increase of gas flow rate results in an enhanced convective heat removal, so that the temperature increment generated by the reaction heat is lower, which in turn slows down the reaction rate.

As a result, at increasing space velocity a decrease of CO conversion can be observed.

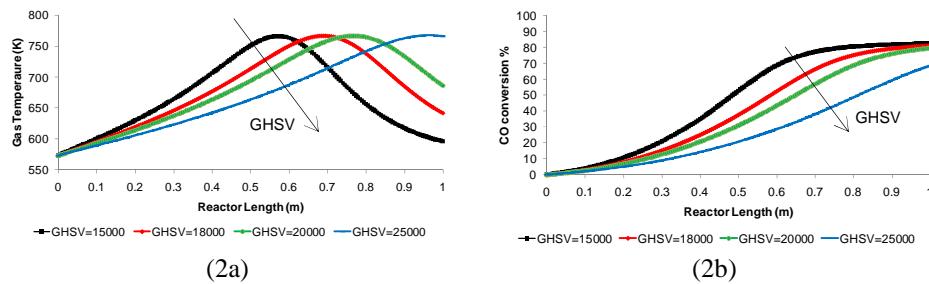


Figure 2. Gas temperature (a) and CO conversion (b) axial profiles at four different GHSV

4. Final remarks

In this work the possibility of using monolithic reactors carrying out exothermic methanation reactions from syngas was investigated by process simulation. A model of a dynamic 1D, heterogeneous, single-channel model of an externally cooled fixed-bed reactor, loaded with honeycomb catalysts, was developed and solved, using gProms™ as process simulator.

It was shown that synthetic natural gas can be produced in a single pass monolithic catalyst reactor, with acceptable conversion values and temperature hot spots compatible with the catalyst stability. This system improves the presently adopted process configurations, as it overcomes the problem of temperature control typical of fixed-bed methanation reactors.

The use of monolith reactors is also useful in view of process intensification: we have verified that the GHSV can be increased up to 20000 h⁻¹, with minimal pressure drops, increasing the cooling temperature correspondingly, without the risk of reactor runaway. Further improvements might be obtained by adopting more active catalyst formulations.

Nomenclature

a = specific area (1/m), $a = 4\epsilon/d_{eq}$

c_p = mass specific heat (J/kg K),

k_w = active washcoat conductivity (1.2 W/m K)

L = reactor length (m)

m = monolith pitch (m) (2 mm)

($c_{p,s}=865$ kJ/kg)
 D = diffusivity (m^2/s)
 d = monolith (or reactor) diameter (m)
 d_{eq} = hydraulic diameter of the monolith channel (m), $d_{eq} = m\sqrt{\varepsilon}$
 f = friction factor
 h = gas-solid heat transfer coefficient in the monolith channel ($W/m^2 K$)
 h_{wall} = wall heat transfer coefficient
 k_g = gas mixture conductivity ($W/m K$)
 $K_{m,i}$ = gas-solid mass transfer coefficient in the monolith channel ($kg/m^2 s$)
 $k_{s,ax}$ = effective axial conductivity (W/mK),
 $k_{s,ax} = k_s \left(\lambda + \xi \frac{k_w}{k_s} \right)$
 k_s = support conductivity ($Al=200$ $W/m K$)

Greek Letters

δ_w = thickness washcoat (m),
 $\delta_w = \left(\sqrt{\varepsilon + \xi} - \sqrt{\varepsilon} \right)$
 ε = bed void fraction (0.7)
 ε_s = emissivity of solid phase (0.7 for Al)
 λ = volume fraction of inert support (0.25)

Subscripts and Superscripts

ax = axial
g = gas phase
s = solid phase

Nu = Nusselt number
 P = pressure (Pa); p = partial pressure
 PM_i = molecular weight of the specie i ($kg/kmol$)
 Pr = Prandtl number
 Re = Reynolds number
 R_j = j reaction rate ($kmol/m^3 s$)
 R = universal gas constant (8314 $J/kmol K$)
 Sc_i = Schmidt number
 Sh_i = Sherwood number
 T = temperature (K)
 t = time (s)
 v = gas velocity (m/s)
 w_i = weight fraction of the specie i
 W_t = specific mass flow rate ($kg/m^2 s$)
 W_{tot} = mass flow rate (kg/s)
 z_{f}^* = axial coordinate for friction factor
 z_{Nu}^* = axial coordinate for Nusselt number
 z_{Sh}^* = axial coordinate for Sherwood number

μ = viscosity ($kg/m s$)
 ξ = volume fraction of active phase (0.2)
 $\Delta H_{R,j}$ = heat of reaction ($J/kmol$)
 θ = Thiele modulus
 ρ = density (kg/m^3), $\rho_s=3800$ kg/m^3 , $\rho_w=900$ kg/m^3
 σ = Stefan-Boltzmann constant ($5.67 \cdot 10^{-8}$ $W/m^2 K^4$)
 ν = stoichiometric coefficient

w = active washcoat or catalytic phase
wall = reactor wall

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