Short contact time reactors for hydrogen production

Terms of use:

Publisher copyright

(Article begins on next page)

04 May 2024

Short contact time reactors for hydrogen production

M. Bizzi, S. Specchia, G. Saracco & V. Specchia
Department of Materials Science and Chemical Engineering, Politecnico di Torino, Italy

Abstract

This work presents a model analysis of short contact time reactors for methane conversion. The analysis is focused on the maximization of hydrogen yield at very high space velocity. In particular, the effect of the diameter to length ratio in cylindrical reactors is investigated, and the variation in natural gas conversion and products selectivity is evaluated at different GHSVs.

1 Introduction

Natural gas is a very interesting resource for several reasons. At present it is an abundant source of energy, which is generally present in large amounts in oil fields. In the past years, associated gas was often flared but recently the need for a more rational use of existing resources has forced the development of processes for natural gas conversion. Currently, natural gas is seen as the most promising source of energy of the next decades. The power plants based on natural gas, namely CCGTs (Combined Cycle Gas Turbines), can reach fuel-to-electricity efficiencies in the order of 50% and process development currently in progress are aiming at reaching 60% of overall efficiency. Another very interesting use of natural gas is based on its conversion into synthesis gas, which can be used in a wide range of applications. In particular, it can be used to produce hydrogen, which can be converted into energy in fuel cell systems with an overall efficiency higher than 60%.

The present study deals with the conversion of natural gas into syngas in short contact time particles bed reactors [1–4], activated with a rhodium catalyst. A mathematical model of the reactor is presented and validated. Experiments [5]

have shown that hydrogen yield could rapidly fall, under certain conditions, as the GHSV is increased. In the perspective of achieving an effective process for hydrogen production, this issue must be addressed carefully. The objective of our study has been therefore to maintain the reactions inside the fixed bed reactor even at higher GHSV, thus preserving methane conversion and products selectivity. The main feature analysed here has been the "shape" of the cylindrical reactor employed in our study in terms of diameter and length. These parameters have been finally optimised therefore to maximize the system performance.

2 Model

The model conceived and numerically solved consisted of transient mono-dimensional conservation equations for gas phase species, separate energy equations for the gas and solid phases, and the ideal gas law.

Gas Phase Mass Balances:

$$S\varepsilon \frac{\partial(\rho_g Y_k)}{\partial t} + \dot{m}\frac{\partial Y_k}{\partial z} + \frac{\partial(V_k S\varepsilon\rho_g Y_k)}{\partial z} + J_k M_k \, aS = 0 \quad k=1,N \tag{1}$$

Gas Phase Energy Balance:

$$S\varepsilon \, \hat{c}_{pg} \frac{\partial(\rho_g T_g)}{\partial t} + \dot{m}\hat{c}_{pg}\frac{\partial T_g}{\partial z} + \frac{\partial}{\partial z}\left(-k_g S\frac{\partial T_g}{\partial z}\right) + hS(T_g - T_s) = 0 \tag{2}$$

Solid Phase Energy Balance:

$$S(1-\varepsilon)\rho_s \, \hat{c}_{ps} \frac{\partial T_s}{\partial t} + \frac{\partial}{\partial z}\left(-k_{s,eff} S\frac{\partial T_s}{\partial z}\right) =$$
$$\sum_k J_k a M_k \hat{H}_k S + hS(T - T_s) - \sigma e_r \left(T^4 - T_{room}^4\right)\pi d_r \tag{3}$$

Ideal gas law:

$$\rho_g = \frac{pM}{RT_g} \tag{4}$$

The model accounted for a detailed surface kinetic mechanism [6], to consider the complex transformations occurring on the active sites of the rhodium catalyst. However, the chemical reactivity was coupled with transport phenomena limitations, pointing out that the system mainly operates in a transport-controlled regime [1]. Therefore, the overall reaction rates were determined using both the transport velocity of the slowest reactant migrating towards the surface [2] and

the kinetic production/destruction rates of all species, as calculated by the model [7]:

$$J_k = \frac{R_k}{R_{k,rl}} J_{rl} \tag{5}$$

This approach is therefore based on the assumption that the catalyst reactivity is not influenced by any transport limitation, and the local conversion rates are determined reducing the reaction rates calculated by the surface kinetic model by a "transport limitation factor".

The model accounts for thermal conduction and radiation inside the fixed bed by an effective thermal conductivity approach [8]. Longitudinal heat transfer inside the fixed bed has indeed been pointed out as extremely important for the reactor operation in previous investigations [2].

Longitudinal mass transfer has been included in the model. However, the model solution showed that this phenomenon is relatively unimportant. The same conclusion can be obtained by calculating the longitudinal Peclet number, as shown in [2].

Appropriate boundary conditions have been used. Fixed compositions and gas phase temperature were specified at the domain inlet and flat profiles for these variables were set at the outlet. For the solid phase thermal balance equation, a radiation boundary condition was imposed at both the inlet and the outlet of the computational domain:

$$-k_{s,eff} \left.\frac{\partial T_s}{\partial z}\right|_{z=0} = \sigma\, e_s \left(T_{room}^{\;4} - \left.T_s^4\right|_{z=0} \right) \tag{6}$$

$$-k_{s,eff} \left.\frac{\partial T_s}{\partial z}\right|_{z=L} = \sigma\, e_s \left(\left.T_s^4\right|_{z=L} - T_{room}^{\;4} \right) \tag{7}$$

3 Results

To validate the model, the simulation results have been compared to experiments reported in the literature [1–3], as shown in Figures 1 and 2.

The experimental reactor reference is described in [3]. Figures 1 and 2 report the typical behaviour of a short contact time reactor for methane conversion. An increase in the space velocity (i.e. a reduction in contact time) determines a series of concatenated effects:

- an increment in methane conversion (Figure 1);
- an increase in the average fixed bed temperature (Figure 2);
- an increase in products selectivity (Figure 1).

These effects can be explained by considering that the system operates in transport-controlled regime. The increase in mass flow rate improves mass and heat transfer within the fixed bed. Therefore, this induces an improvement in methane conversion that in turn enhances the system temperatures. A higher thermal level on its side increases the products yields, since syngas production is favoured both kinetically and thermodynamically at high temperature.
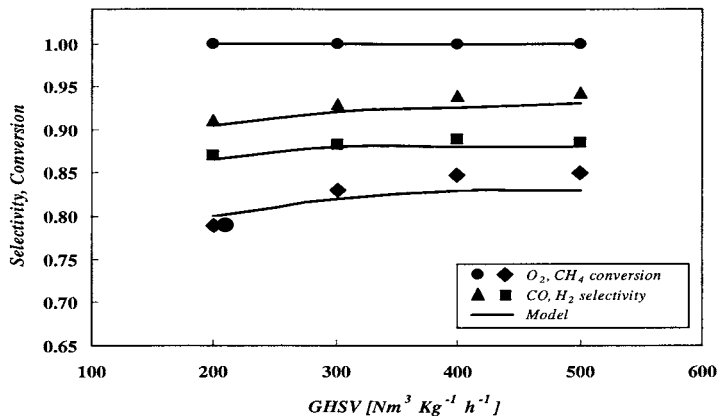
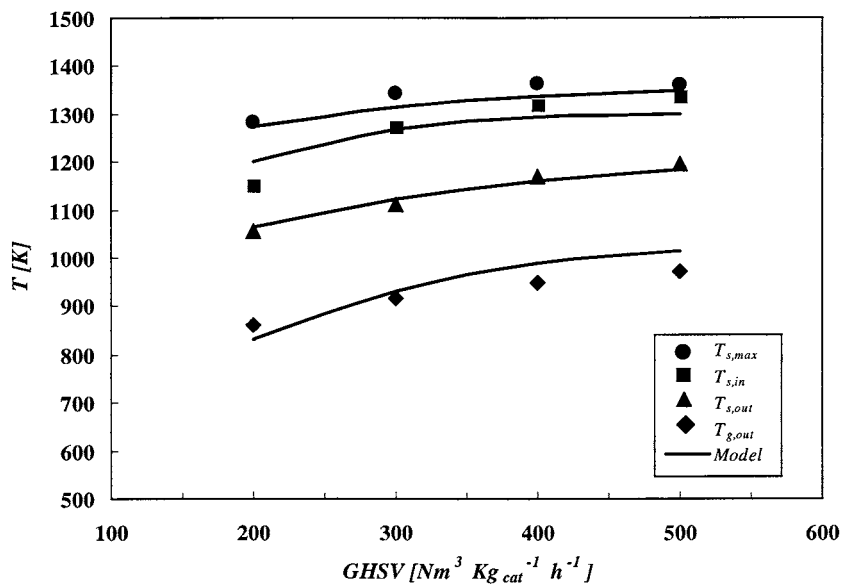Figure 1: Conversion and selectivity versus space velocity (data from [3]).

Figure 2: System temperatures versus GHSV (experimental data from [3]).

Figure 3 represents the comparison between the thermal profiles measured by IR-thermography [2,3] and model calculations. Two distinct regions can be singled out, respectively before and after the temperature peak:

- exothermic region: the main reactions taking place in the system are partial oxidation of methane to CO and H_2O.
- endothermic region: the main reaction after the maximum is steam reforming, that contributes in increasing methane conversion and improves hydrogen selectivity.
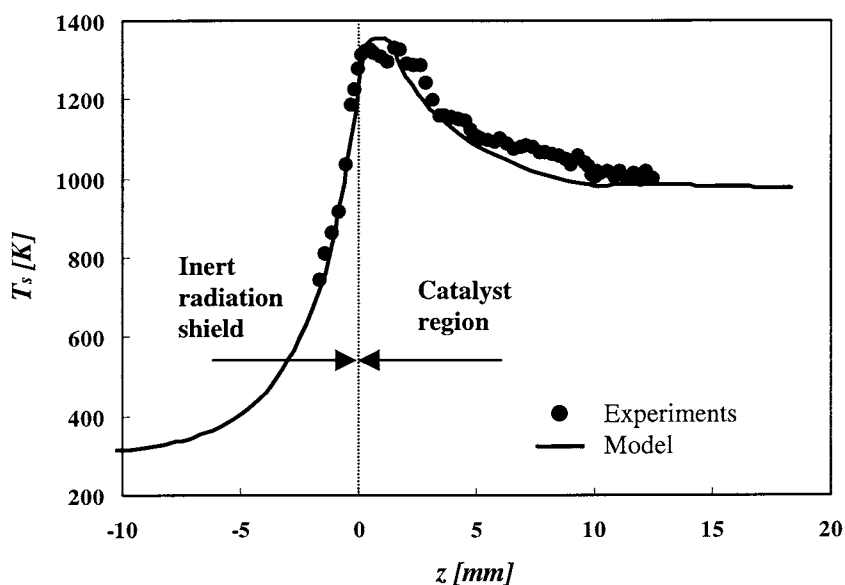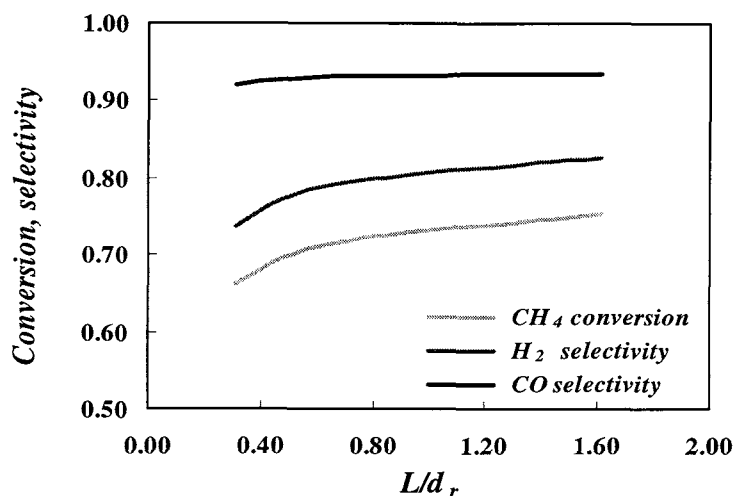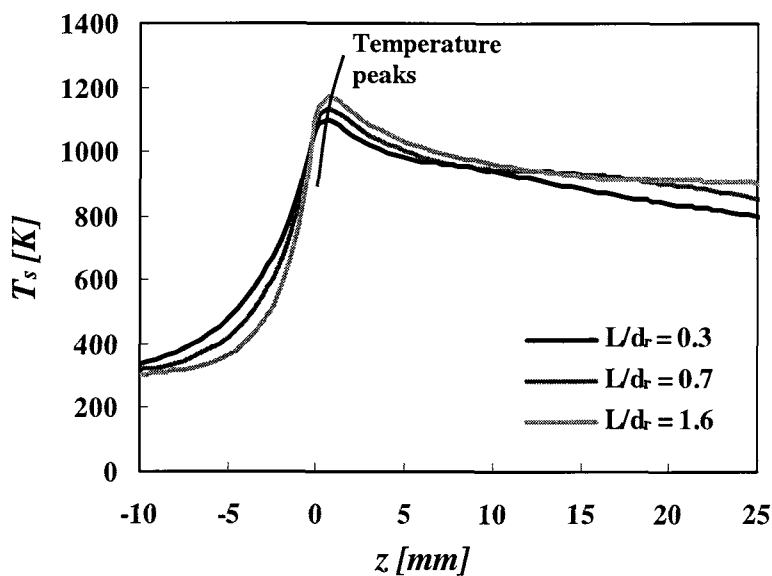

Figure 3: Longitudinal thermal profiles (GHSV=300,000 $Nm^3/h/Kg$).

The validated model was then used to study the effects of the reactor shape in a cylindrical reactor configuration. This analysis was carried out calculating the reactor performance variation related to different length-to-diameter ratios (L/d_r) at fixed reactor volume (cylindrical reactor).

Figure 4 shows that an increment in the length-to-diameter ratio enhances the system performance in terms of feedstock conversion and products selectivity. This feature can be explained considering that the system operates under transport-controlled regime. Therefore, at constant reactor volume, an L/d_r increase entails a reduction in the reactor cross section. This induces in turn:

- an increment in the gas phase linear velocity;
- an increment in the Reynolds number, at constant mass flow rate and GHSV;
- an increment in the Sherwood and Nusselt numbers;
- an increment in the local conversion rates ([2,7] and eqn. 7).

Figure 4: Reactor performance versus L/d$_r$ (GHSV=300,000 Nm^3/h/kg).

Figure 5: Longitudinal thermal profiles (GHSV=300,000 Nm^3/h/Kg).

An increment in the overall pressure drops across the reactor is of course a defect of the system, however methane conversion increases, thus improving the system temperatures and the products selectivity, as previously mentioned.

This effect can be noticed also in Figure 5 that shows the calculated thermal profiles along the reactor at different L/d$_r$ values. As the cross-section decreases,

the increased linear velocity forces the peak of the thermal profiles to move slightly downstream. Moreover, the increased conversion determines an increment in the overall catalyst temperature, as previously stated.

The analysis considered then the variation of the reactor performance with independent variation of the shape factor L/d_r and space velocity. The methane conversion curve in the top left panel of Figure 6 shows a typical behaviour with a peak, that suggests the presence of two distinct regions before and after the maximum, respectively.
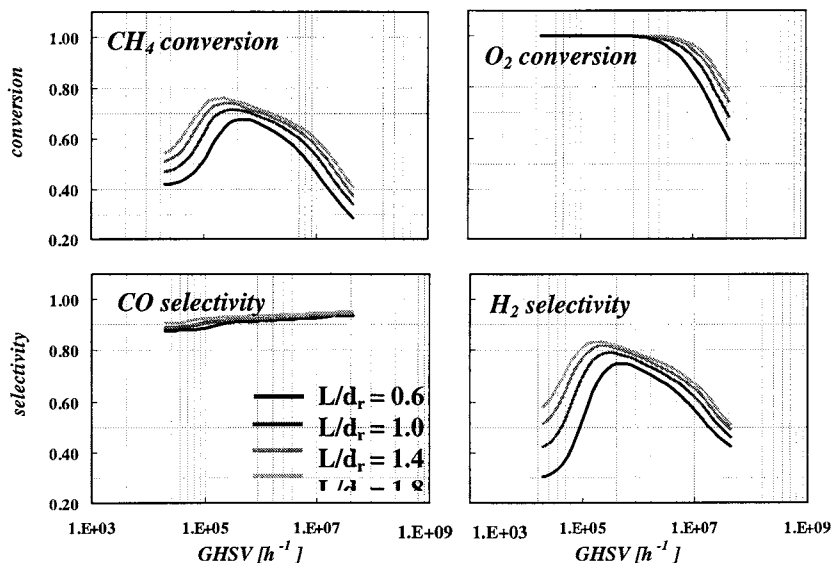

Figure 6: Reactor performance at different L/d_r and GHSVs.

These regions can be described as follows:

- *Mass transfer limitation region: at lower GHSV, an increment in mass flow rate improves transport phenomena and therefore methane conversion, catalyst temperature and products selectivity.*
- *Blow out region: at higher GHSV, the reduction in residence time prevails over the beneficial transport phenomena improvement.*
    - *Incomplete steam reforming limits methane conversion and hydrogen selectivity.*
    - *If GHSV is further enhanced, also the oxidation reactions can not come to completion and also oxygen conversion start to decrease.*

It can be noticed that CO selectivity never drops under the conditions here employed. This is due to the kinetic scheme used that generally takes into account a direct CO formation without intermediates.

172   *Energy and the Environment*

The increment in the L/d_r ratio determines a general improvement in the system performance, that can be described by the same considerations proposed so far: the reactor cross section is reduced at constant GHSV and this entails an improvement in both conversion and selectivity.

The thermal behaviour of the reactor reproduces the same features proposed in this last paragraph. Figure 7 reports the solid phase temperature at the catalyst region inlet, at different L/d_r and GHSV.
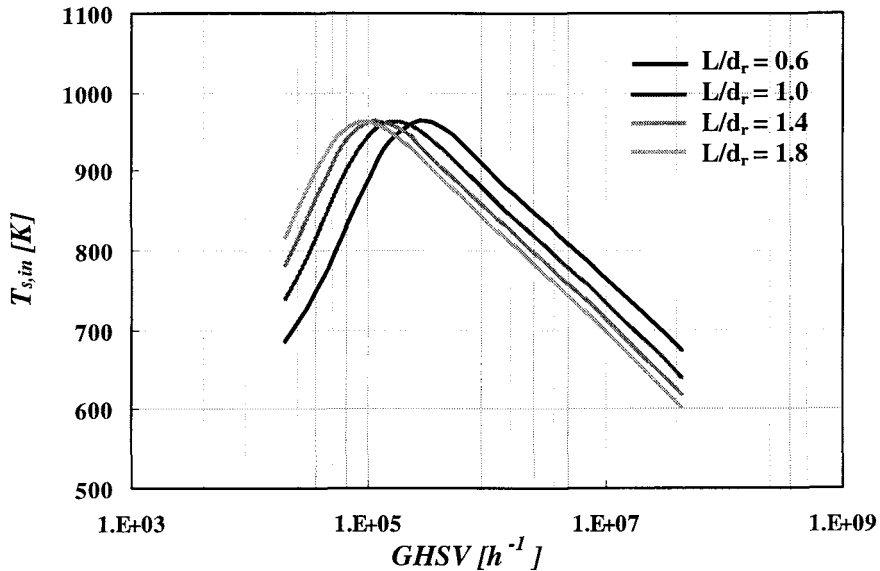

Figure 7: Solid phase temperature at the catalyst region inlet.

As far as transport limitations hold, the improvement in GHSV determines an increment in the system temperature. If GHSV is further enhanced, the temperature peak is shifted downstream, as already indicated in Figure 5. As a result, the inlet solid phase temperature drops. If the L/d_r ratio is increased, the gas phase linear velocity rises *ceteris paribus*. Therefore, a lower GHSV is required to shift the solid phase temperature peak downstream and therefore to make the $T_{s,in}$ versus GHSV curve decrease.

4 Conclusions

In the present paper, a model analysis was carried out to investigate the possibility to maximize methane conversion and hydrogen production in short contact time particles bed reactors. The following topics have been investigated:

- The effects of high space velocity
- The reactor shape factor L/d_r (length to diameter ratio)

The analysis carried out showed the following results:

- The model employed a surface kinetic model coupled with transport phenomena, in transfer-limited conditions. The reactor model was able to reproduce the major experimental evidences of a short contact time system.
- A high L/d_r ratio is beneficial to conversion and selectivity, due to heat and mass transfer improvement. This conclusion remains true also if the GHSV remarkably increased, and in particular resistance to blow-out is improved.
- The corresponding increase in performance is obtained at the expense of higher pressure drops: if energy demand for compression is a major issue to be considered, such as in an industrial system for syngas production that operates at relatively high pressure, a trade-off condition should be found between performance improvement and pressure drop increase.

Notation

$\hat{c}_p$	Specific heat [J kg^{-1}]
d	Diameter [m]
D	Diffusivity [m^2 s^{-1}]
e	Solid phase emissivity [-]
$\hat{H}$	Enthalpy of a chemical species [J g^{-1}]
h	Heat transfer coefficient [J K^{-1} m^{-2} s^{-1}]
J	Molar flux [mol m^{-2} s^{-1}]
K	Thermal conductivity [J s^{-1} m^{-1} K^{-1}]
L	Reactor length [m]
M	Molar weight [kg mol^{-1}]
N	Total number of gas phase chemical species involved in the reaction environment
p	Pressure [atm]
Pe	Peclet number [-]
R	Universal gas constant [J K^{-1} mol^{-1}]
Re	Reynolds number [-]
S	Reactor cross-flow section [m^2]
T	Time variable [s]
T	Temperature [K]
V	Diffusion velocity [m s^{-1}]

X	Mole fraction [-]
Y	Mass fraction [-]
Z	Reactor axial coordinate [m]
Greek letters	
ε	Porosity [-]
ρ	Gas phase density [kg m^{-3}]
σ	Stefan – Boltzman constant [W m^{-2} K^{-4}]
Subscripts	
Eff	Effective
G	Gas phase
K	Generic species
In	Reactor inlet
out	Reactor outlet
P	Particle
Room	Ambient conditions
S	Solid phase

References

[1]   Bizzi M., Basini L., Saracco G., Specchia V., *Chem. Eng. J.*, in press, 90 (1-2), 97-106, 2002.

[2]   Bizzi M., Basini L., Saracco G., Specchia V., 2002b, *Ind. & Eng. Chem. Res*, in press, 2002.

[3]   Basini L., Aasberg-Petersen K., Guarinoni A., Østberg M., *Catalysis Today*, 64, 9-20, 2001.

[4]   Deutschmann O., Schmidt L.D., "Modelling the partial oxidation of methane in a short contact time reactor", *AIChe J.*, 44, 11, 2465-2477, 1998.

[5]   Hohn K.L., Schmidt L.D., "Partial oxidation of methane to syngas at high space velocities over Rh-coated spheres", *Applied Catalysis A: General*, 211, 53-68, 2001.

[6]   Deutschmann O., Schwiedernoch R., Maier L. I., Chatterjee D., in *Natural Gas Conversion VI, Studies in Surface Science and Catalysis 136*, E. Iglesia, J.J. Spivey, T.H. Fleisch (eds.), p. 251-258, Elsevier, 2001.

[7]   Bizzi M., Deutschmann O., Schwiedernoch R., Saracco, G., in preparation.

[8]   Wakao N., Kaguei S., *Heat and Mass Transfer in Packed Beds*, Gordon and Breach, 1982.