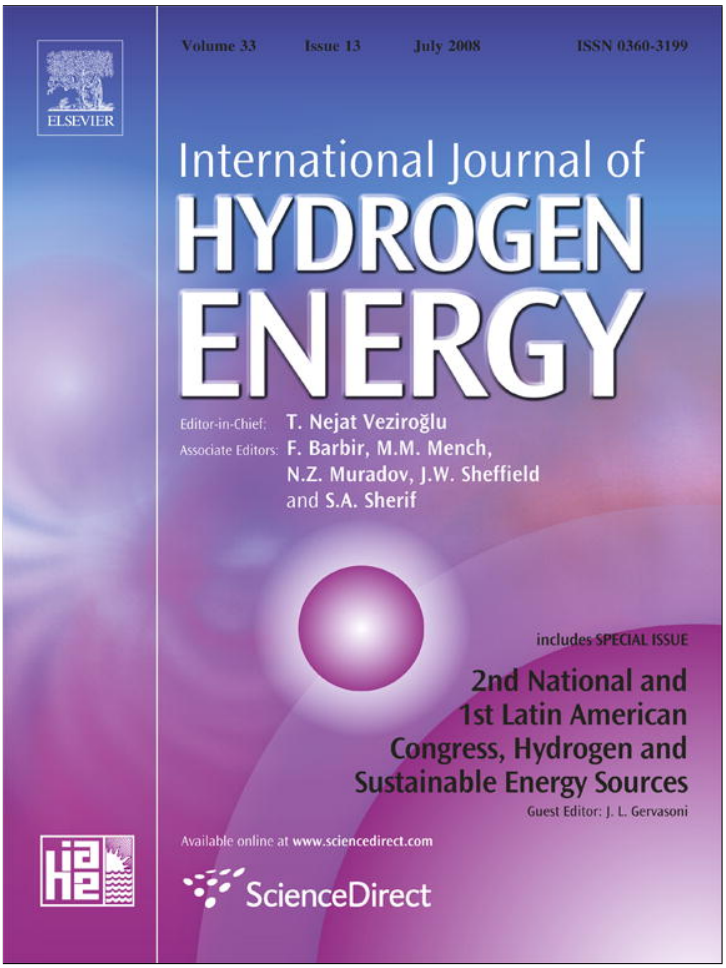

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Hydrogen from methanol-steam reforming. Isothermal and adiabatic monolith reactors' simulation

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ABSTRACT

In this work a simple, precise and fast procedure to simulate monolith reactors where the methanol-steam reforming reaction is carried out is presented. The technique accounts for the interfacial heat and mass transport limitations and the diffusion reaction process in monolith reactors with catalytic washcoat of nonuniform thickness. The monolithic reactor simulations were carried out considering a square channel of various sizes, different washcoat distributions (filled in square, circle in square) and taken into account isothermal or adiabatic operation. The global effectiveness factor profiles for the isothermal and adiabatic processes are shown. The bulk fluid temperature, the difference between bulk fluid and washcoat temperature profiles, and methanol conversion curves are also depicted. Comparison with experimental data of other authors as well as with results obtained using a robust, but time-consuming, numerical method for computing effectiveness factor showed a very good agreement.

1. Introduction

Hydrogen is considered to be the most viable energy carrier for the future [1,2]. Generally, there are several ways to produce hydrogen gas from hydrocarbons like natural gas, oil or alcohols. It can be efficiently converted to electricity by fuel cells. The steam reforming of methanol is feasible on copper–zinc catalysts in a low temperature range of 200–300 °C [3]. The produced hydrogen has to have a low level of harmful impurities, in particular the carbon monoxide content has to be lower than 20 ppm. The design of a simple and compact hydrogen production system that integrated the production and purification reaction steps is the main target nowadays [4].

Efficient heat transfer is important in the reforming reactions because steam reforming of methanol is a highly endothermic reaction. Compared to large industrial scale reactors, micro reactors offer advantages of improved heat and mass transfer and more precise control of reaction temperature. Between them, catalytic monolith reactors are widely used to reduce the emissions of undesired products in automotive exhaust gases, the abatement of NO_x emitted in the stack gases from power stations and the catalytic combustion of volatile organic compounds (VOCs) [5–7]. A monolith reactor is a wall reactor that consists of arrays of channels with honeycomb structure. Conventional reactor configurations such as a packed bed reactor operate in a heat transfer limited mode for this reaction. On the other hand, the wall-coated monolith reactor was found to be the most efficient configuration to carry out the methanol-steam-reforming reaction [8]. When a monolith reactor operates, the reactants should be transported from the bulk fluid to the fluid–solid interface. Then they should be diffused and made to react into the catalytic washcoat in a simultaneous process. Diffusion and reaction inside the washcoat layer is characterized by the intrinsic effectiveness factor (η).

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Meanwhile the global effectiveness factor (η_0) is used to quantify the combination of external and internal diffusion limitations. For complex non-linear kinetic expressions, the effectiveness factor calculation becomes computationally expensive. Besides these difficulties, when a honeycomb catalyst is prepared, there is a tendency for the coating to accumulate in the corners of monolith channel [9]. Therefore, the varying thickness of the catalytic washcoat should be considered in the effectiveness factor calculations.

Recently, Gonzo [10] presented a fast and precise procedure to simulate monolith reactors. The procedure takes into account the Papadias method [11] to consider the non uniform washcoat thickness around the channel perimeter, and the perturbation and matching technique [12] that allows the effectiveness factor estimation through a single and simple algebraic equation. Consequently, the complete simulation of a monolith reactor, where both internal and external diffusion phenomena as well as the non-uniform catalytic washcoat thickness are considered, can be done.

In this paper a procedure for the calculation of effectiveness factor in non uniform washcoat shapes in monolithic channels is presented. Simulations of monolith reactors with squared channels of different sizes and washcoat distributions, where the methanol-steam reforming reaction is carried out, are presented. The results of the simulation are compared with experimental data of other authors and with those obtained with numerical methods.

2. Effectiveness factor estimation

To calculate the intrinsic effectiveness factor in non uniform washcoat, Papadias et al. [11] proposed dividing the washcoat cross section into a series of slices. A variable effectiveness factor (η_i) in each slice is calculated using a 1D analysis, assuming a characteristic length for each slice (L_{ci}) as the ratio of its cross section area (A_i) to the arc length of the fluid–washcoat interface (L_i) (see Fig. 1):

$$L_{ci} = \frac{A_i}{L_i}. \tag{1}$$

The overall intrinsic effectiveness factor for the whole washcoat in a point along the monolith is obtained using a weighted average. The weights for each slice's effectiveness factor would be the fraction of the total washcoat cross-section (A) in the slice ($\omega_i = A_i/A$) [13]:

$$\eta = \sum_i \omega_i \eta_i. \tag{2}$$

Let us consider a square monolith channel of side (L) covered by a non uniform washcoat layer with minimum thickness (δ) and a radius in the corner (R_c). For this type of geometrical configuration, symmetry allows one to consider (1/8)th of the total washcoat cross-section. According to Fig. 1, the slice characteristic length (L_{ci}) and the weighting factor (ω_i) are given by

$$L_i = \frac{0,5\{[\mathrm{tag}(\varphi+\Delta\varphi)-\mathrm{tag}(\varphi)](R_c+\delta)^2 - R_c^2\,\Delta\varphi\}}{R_c\,\Delta\varphi}, \tag{3}$$

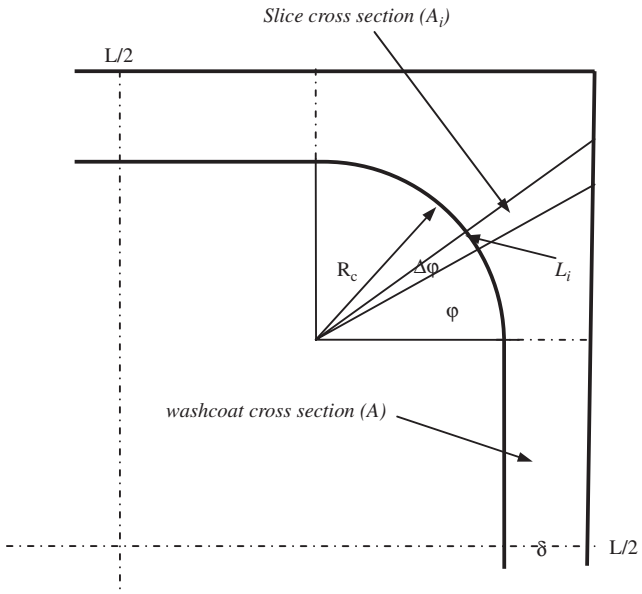

Fig. 1 – (1/4) of a monolith channel scheme.

$$\omega_i = \frac{0,5\{[\mathrm{tag}(\varphi+\Delta\varphi)-\mathrm{tag}(\varphi)](R_c+\delta)^2 - R_c^2\,\Delta\varphi\}}{4[L-2(R_c+\delta)]\delta + 4(R_c+\delta)^2 - \pi R_c^2}. \tag{4}$$

The intrinsic effectiveness factor for each slice (η_i) was calculated using the expression [12]

$$\eta_i = [\phi_i^{*2} + \exp(-a\phi_i^{*2})]^{-1/2}, \tag{5}$$

where

$$a = 1 - 2\sigma, \quad \sigma = \sigma^* p^2, \tag{6}$$

$$p = \left[2\int_0^1 R(C)\,dC\right]^{1/2}, \quad \sigma^* = \frac{R'(1)}{3} \tag{7}$$

and

$$\phi_i^* = \frac{\phi_i}{p}, \quad \phi_i^2 = \frac{L_{ci}^2 r_s}{D_{eff} C_s}, \tag{8}$$

where $\phi_i^2 = L_{ci}^2(r_s/D_{eff}C_s)$ is the Thiele modulus, D_{eff} is the effective diffusivity of the key component and C_s, T_s and r_s are the concentration, temperature and rate of reaction evaluated with the washcoat surface value at each point in the reactor, respectively. $R(C) = r/r_s$ and $R'(1)$ is the first derivative of $R(C)$ with respect to C evaluated at $C = 1$.

The global effectiveness factors (η_0) were calculated from [12] considering the boundary conditions at the fluid–washcoat interface:

$$\eta_0 = \eta\left(\frac{r_s}{r_0}\right), \quad \phi_0^2 = \phi^2\left(\frac{r_0}{r_s}\right)\left(\frac{C_s}{C_0}\right), \tag{9}$$

$$\frac{C_s}{C_0} = 1 - \frac{\phi_0^2\eta_0}{Bi_m}, \tag{10}$$

$$\frac{T_s}{T_0} = 1 + \frac{\phi_0^2\eta_0\beta_0}{Bi_e}. \tag{11}$$

Bi_m and Bi_e denote Biot numbers for mass and energy fluid film transfer, and subscript "0" indicates bulk fluid value. The

Biot numbers are defined as

$$Bi_m = \frac{k_{gA} L_g}{D_{Aeff}} \quad \text{and} \quad Bi_e = \frac{h_e L_g}{k_{Teff}}.$$

Here k_{gA} and h_e are the mass and heat transfer coefficients, k_{Teff} the effective thermal conductivity of the washcoat and L_g the global characteristic length defined as the ratio of the washcoat total cross section to the fluid–solid interface perimeter.

Therefore, besides effectiveness factors η and η_0, bulk and washcoat–fluid interphase temperature and reactants' concentrations are calculated at each point of the axial reactor position.

3. Reactor simulation

A single monolith 1D model channel with square cross-section has been developed under the following assumptions:

(1) Steady-state conditions.
(2) Laminar flow, i.e. Reynolds number lower than 600 ($Re < 600$).
(3) Single adiabatic or isothermal channel.
(4) No conducting wall in the axial direction.

Using the heterogeneous 1D model [14], accounting for interfacial and intra-washcoat gradients, methanol conversion (X) and axial bulk fluid temperature changes over an elementary monolith reactor volume may be written as

$$\frac{dX}{dz} = \Omega \left(\frac{\Lambda_V}{F_M^0} \right) \eta_0 r_0, \tag{12}$$

$$\frac{dT}{dz} = \left(\frac{\Lambda_V}{GCp} \right) \eta_0 r_0 (-\Delta H). \tag{13}$$

Here, Λ_V, Ω, F_M^0, ΔH, G and Cp are the washcoat to monolith channel volume ratio, cross section of the monolith channel, methanol flow rate at the reactor entrance, heat of reaction, total mass velocity and specific heat of the mixture, respectively.

The methanol-steam reforming reaction is expressed as

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2, \quad \Delta H = 57\,\text{kJ/mol (at 200°C)}. \tag{14}$$

In the temperature range between 200 and 300 °C over $Cu/ZnO/Al_2O_3$ catalyst, the reaction obeys the kinetic expression [3]:

$$r = 2.19 \times 10^9 \exp\left(-\frac{103\,\text{kJ/mol}}{RT} \right) P_M^{0.564} \times (11.6\,\text{kPa} + P_H)^{-0,647} \quad (\text{mol M/kg s}), \tag{15}$$

where P_M and P_H are the partial pressures of methanol and hydrogen in kPa, respectively. The properties of the catalytic

Table 1 – Characteristics of monoliths and washcoats studied

Monolith	Ω (mm^2)	A (mm^2)	δ (μm)	R_c (mm)	L (mm)^2	Cell density (cm^{-2})
200-fs[a]	4.3681	1.6474	200	0.3971	2.09	16
250-fs[a]	4.3681	1.9900	250	0.418	2.09	16
300-cs2[b]	4.3681	2.6244	300	0.745	2.09	16
200-cs1[b]	1.00	0.7173	200	0.30	1.00	62

[a] Fillet in square (fs).
[b] Circle in square (cs) washcoat geometries.

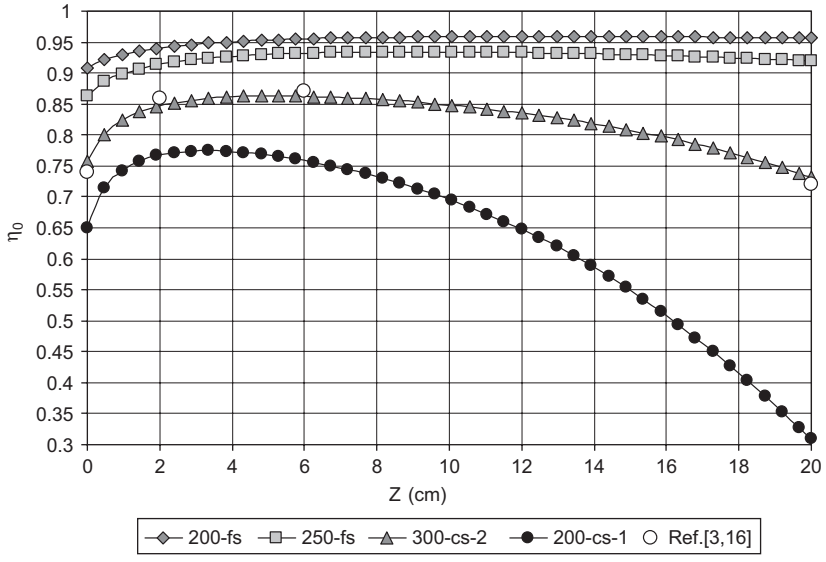

Fig. 2 – Global effectiveness factor profiles. Isothermal cases; $T = 533$ K.

washcoat are as follows [3]: density 2.4 g/cm^3; average pore radius 8 nm; BET area 66 m^2/g; porosity $\varepsilon = 0.47$ and a tortuosity factor (τ) of 3. The (mol%) feed compositions were water/methanol: 0.3/0.15; nitrogen/methanol: 0.55/0.15; and $G = 4400\,\mathrm{g/m^2\,s}$. Total pressure of 101.3 kPa, feed temperature of 533 K and 20 cm long monoliths were used. All these parameters were maintained constant for the different cases studied for comparison purposes. Table 1 resumes the characteristics of the monoliths and washcoat considered. The effective diffusivity of each component was calculated according to

$$D_{\mathrm{Aeff}} = \frac{D_{Am}\varepsilon}{\tau}, \tag{16}$$

where the diffusivity of component A in the porous washcoat (D_{Am}) was calculated following Ref. [3], taking into account the molecular Maxwell–Stefan binary diffusion and the Knudsen diffusivity.

In this work the Holmgren–Andersson [15] correlation for heat and mass transfer coefficient calculations was used. Assuming Colburn analogy applies, the same correlation can be used for *Sh* and *Nu* numbers:

$$Sh = 3.53\exp(0.0298\,Re\,Sc\,d_{\mathrm{h}}/L_Z), \tag{17}$$

where L_Z is the reactor length and d_{h} the hydraulic diameter of the fluid flow channel. Here, $Re = Gd_{\mathrm{h}}/\mu$, $Sh = k_{gA}d_{\mathrm{h}}/D_{\mathrm{A}}$ and

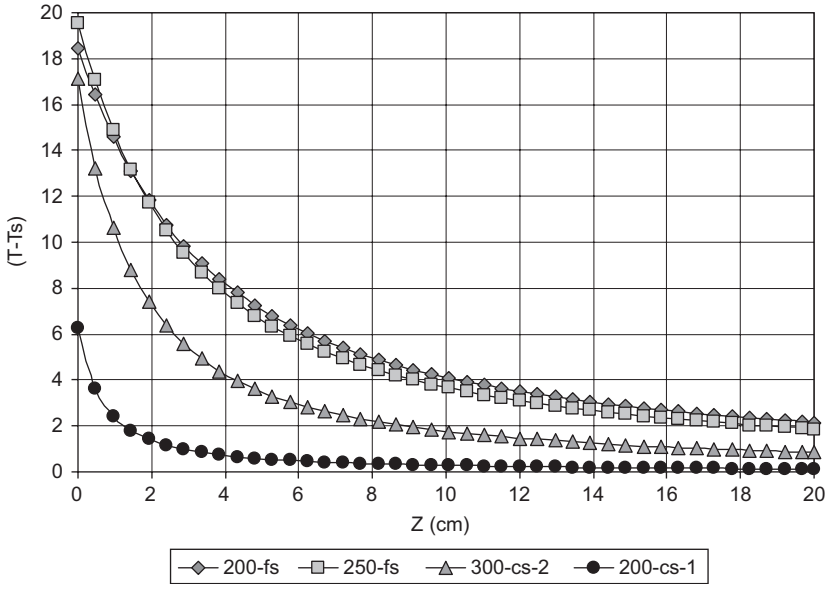

Fig. 3 – Difference between bulk fluid and washcoat temperatures. Adiabatic cases. Feed temperature $T^o = 533$ K.

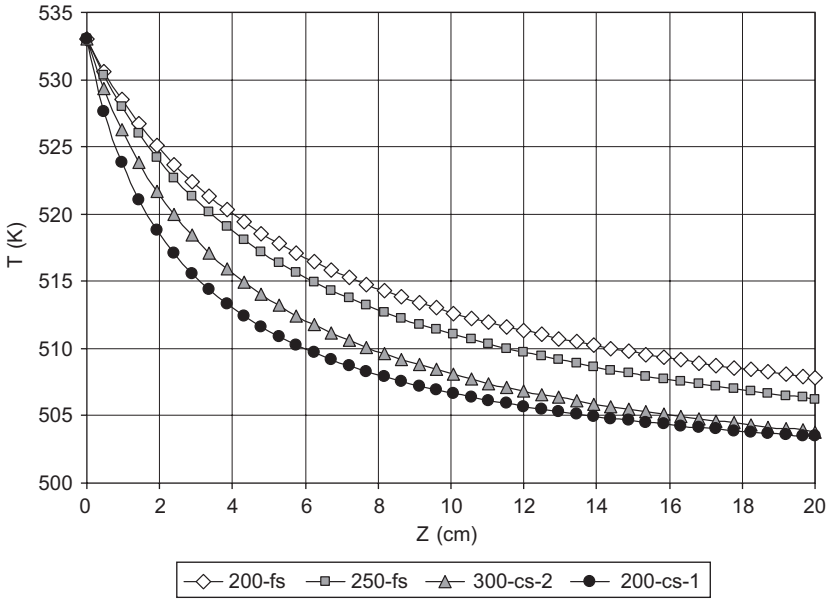

Fig. 4 – Bulk fluid temperature profiles. Adiabatic cases.

$Nu = h_e d_h / k_T$, k_T and μ being the thermal conductivity and viscosity of the fluid.

As usual, *Pr* replaces *Sc* for the calculation of *Nu*. In all cases, fluid properties were evaluated at an average temperature between washcoat surface and bulk fluid temperatures.

4. Results and discussion

Fig. 2 shows the global effectiveness factor along the reactor. It also depicts the result of [3] and numerical values obtained with the very time-consuming but robust numerical procedure [16] for the isothermal cases.

When the reactor works adiabatically, the temperature difference between bulk fluid and washcoat surface values is shown in Fig. 3; while in Fig. 4 bulk fluid temperature profiles for all the cases studied are presented. In Fig. 5, the global effectiveness factor as a function of the axial reactor coordinate can be seen for the four cases studied. This figure also shows results obtained with the numerical method [16]. Finally, Fig. 6 depicts the methanol conversion as a function of the axial reactor coordinate for adiabatic operation.

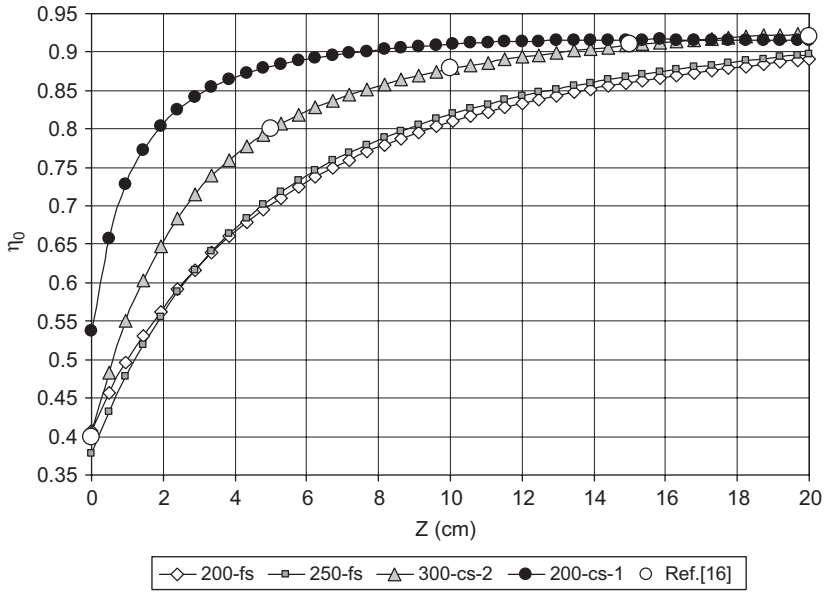

Fig. 5 – Global effectiveness factor along the reactor. Adiabatic cases; $T^o = 533$ K.

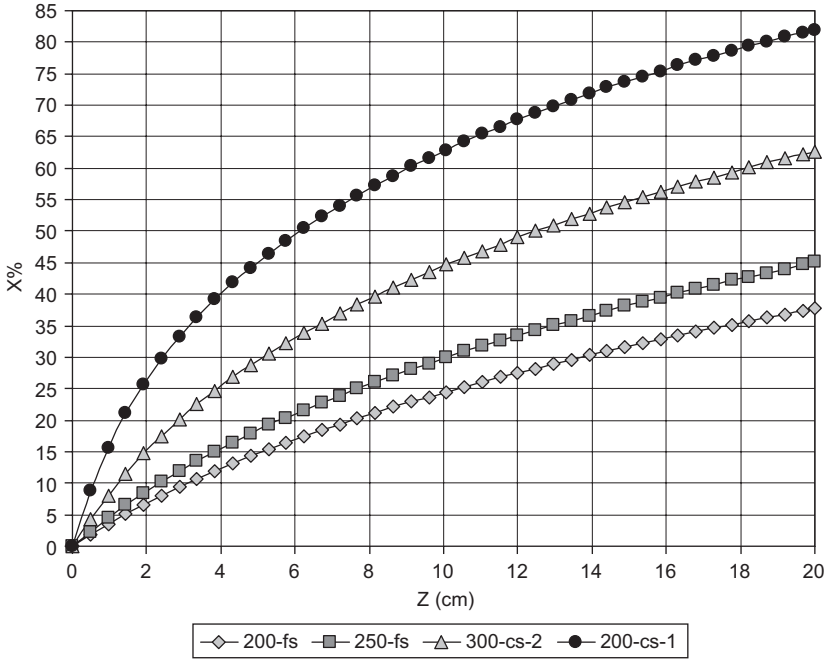

Fig. 6 – Methanol conversion along the reactor. Adiabatic operation; $T^o = 533$ K.

The agreement observed demonstrated that the fast and simple method for simulation monolith reactors with non uniform washcoat thickness, where the methanol reforming reaction is carried out, can be safely used.

5. Conclusions

In this paper a simple, precise and fast procedure for the effectiveness factor calculation in washcoats with variable thickness, to simulate monolith reactors where the methanol-steam reforming reaction is carried out, was presented. It was considered non uniform washcoat shapes included the extreme case of circle in square geometry. This procedure takes into account the external and internal (diffusion–reaction) transfer limitations. The agreement with results obtained experimentally and with numerical method by other authors is very good. The procedure here presented provides an effective and general tool for simulating monolith reactors with minor calculations. This procedure is fast enough to be used as an advanced process control.

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