HEAT AND MASS TRANSFER LIMITATIONS IN MONOLITH REACTOR SIMULATION WITH NON UNIFORM WASHCOAT THICKNESS

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Abstract—In this contribution, effectiveness factor (η) calculations are performed by a perturbation and matching technique developed by the authors which takes into account both the intrinsic kinetic expression and external heat and mass transfer resistances. The simplified method of Papadias et al. (2000) was used to consider the non-uniform washcoat thickness usually present in monolith channels. As a result a global effectiveness factor (ηg) is calculated at each point on the grid to simulate monolith reactor performance. The procedure was tested to predict experimental findings taking into account the actual kinetic expression to describe CO oxidation on Pt catalyst. Agreement among theoretical predictions and Ullah et al. (1992) and Holmgren and Andersson (1998) experimental results are fairly good.

Keywords—Monolith reactor, Diffusion, Reactor engineering, Effectiveness factor.

I. INTRODUCTION

Catalytic monolith reactors are widely used to reduce emissions of undesired products in automotive exhaust gases; the abatement of NOx emitted in the stack gases from power stations by the selective catalytic reduction processes, and the catalytic combustion of volatile organic compounds (VOCs) (Cybulski and Moulijn, 1994; Heck et al., 2001). Monoliths are increasingly under development and evaluation for many new reactor applications. As a consequence, the studies with monolithic catalysts are now more and more relevant in areas outside traditional chemical engineering and catalysis, e.g., energy fields such as production, car manufacturing and pollution control.

A monolith reactor is an array of channels with honeycomb like structure. The monolith catalyst is a structured substrate (e.g., cordierite, a material having a low thermal expansion coefficient) which is covered with a layer (washcoat) of material that serves as a catalyst. The low pressure drop of the monolith, compared to a packed catalyst bed, is a great and important advantage. Then, they must diffuse and react into the catalytic washcoat in a simultaneous process. Due to the importance assigned to external mass transfer in monolith reactors, there have been several theoretical (Balakotaih and West, 2002) and experimental (Holmgren and Andersson, 1998; Uberoi and Pereira, 1996) studies on this subject. Therefore, various external mass transport correlations are available for typical monolith reactor applications and for different channel geometry.

Several researchers, recognizing that washcoat layers are thin (e.g. 10 – 100 μm), have assumed that the effect of the internal mass transport is negligible (i.e. effectiveness factor of one) (Ullah et al., 1992; Uberoi and Pereira, 1996). Other studies have considered first or pseudo-first order kinetic expressions for the intrinsic chemical reaction (Groppi et al., 1995), oversimplified kinetic expression (Holmgren and Andersson, 1998) or global kinetics that included pore diffusion. Notwithstanding the small washcoat thickness, the influence of internal diffusion is significant for many reactions under operation conditions usually found in practice (Leung et al., 1996; Hayes et al., 2004).

Diffusion and reaction inside the washcoat are characterized by the intrinsic effectiveness factor ηi. Meanwhile the global effectiveness factor ηg is used to quantify the combination of limitations, the internal resistance (washcoat) and the external mass transfer. The use of the full expression of the intrinsic rate of reaction is necessary to account for the effect of the internal washcoat mass transport resistance. However, for complex non linear kinetic expressions the effectiveness factor calculation becomes computationally expensive. The solution of the heat and mass balance differential equations is quite difficult. Besides these difficulties, when a honeycomb like catalyst is prepared, there is a tendency for the coating to accumulate in the corners of monolith channel. Therefore, the varying thickness of the catalytic washcoat should be considered to estimate effectiveness factors. Papadias et al. (2000) reported a simplified method to calculate effectiveness factor in non uniform washcoat shapes. They proposed dividing the washcoat into a series of slices (or particles side by side on the monolith wall). A variable effectiveness factor ηi in each slice is calculated using a 1D analysis, assuming a characteristic length for each slice (Li) as the ratio between its area (Ai) and the length of the fluid solid interface (Li):

\[ L_i = \frac{A_i}{L_i} \]  \hspace{1cm} (1)

Finally, by considering an approximate average surface concentration all over the washcoat perimeter, the aver-
The literature offers a great deal of attention to establish accurate predictions of heat and mass transfer coefficients mainly through empirical correlations. Clearly, it was thought that the external convective resistances were dominant since the reaction would only take place on the solid-fluid interface. It is interesting to note that in such a case most of the valuable catalytic species dispersed in the washcoat were not used and consequently the effectiveness factor for the reaction would be very small. On the other hand when the rate of reaction is very slow, the effectiveness factor is almost one. However the length of the reactor, to achieve the desired conversion, is very large from a practical and economic point of view. Thus, it is not surprising that the working regime, of most well known operating monolith reactors, is the intermediate with effectiveness factors ranging 0.4 to 0.8. However at these intermediate values the influence of both, kinetic expression and washcoat geometry, cannot be oversimplified to estimate accurate effectiveness factors along the reaction length. It should be stressed that this estimation must be performed repeatedly at each point of the grid, to simulate the performance of a monolith reactor.

In this contribution, calculations are performed by an early perturbation and matching technique developed by the authors (Gottifredi and Gonzo, 1986) which allows very accurate estimates taking into account both, the actual kinetic expression to properly describe the chemical event and the influence of heat and mass transfer coefficients. Papadias method is used to take into account the proper washcoat resulting geometry which usually presents a non uniform thickness along the flow section perimeter as shown below (Fig. 1). As it will be shown, the whole procedure to calculate \( \eta \) at each point of the grid is carried out very fast since a non linear algebraic equation must be solved; whose initial guess, can be assumed from the final values of the previous point at the grid.

Reactor behavior predictions are compared with experimental results. An excellent agreement is found in all cases. To estimate external fluid flow convective transport coefficients most accepted correlations were used. However we found interesting to establish the parametric sensitivity of conversion in relation to the values of these transport coefficients. The results are very attractive since, although the effect of coefficients is important in establishing the concentration, and eventually temperature variations between bulk fluid and interfacial values, the overall effect on reactor conversion is negligible. As a whole this contribution presents a number of original results in the specific field of monolith reactor performance.

II. MATHEMATICAL

The global and intrinsic effectiveness factors estimation were carried out according to the procedure presented by Gottifredi and Gonzo, (2005) (Gomez-Barea and Ollero, 2006). The dimensionless continuity equation for the key component in a washcoat slice assuming constant effective diffusivity, isothermal condition within the catalyst layer and single reaction can be written as:

\[
\frac{d^2 C}{dx^2} = \phi^2 R(C),
\]

where \( C(x, z) \) and \( R(C) = r / r_s \), are the dimensionless concentration and rate of reaction related to its washcoat surface value at each point in the reactor.

\[
\phi = \frac{L_s r_s / D_e f C_i}{}, \quad (4)
\]

\( \phi \) is the Thiele modulus, \( D_{ef} \) the key component effective diffusivity and \( x \) the dimensionless washcoat coordinate, respectively.

Equation (3) must be solved subject to the following boundary conditions:

\[
\frac{dC}{dx} = 0 \text{ at } x = 0, \quad (5)
\]

\[
\frac{dC}{dx} = B_{in} \left( 1 - C_i / C_s \right) \text{ at } x = 1, \quad (6)
\]

\[
\frac{dT}{dx} = -B_{ie} \left( 1 - T_i / T^* \right) \text{ at } x = 1, \quad (7)
\]

where \( C_i \) and \( T_i \) are dimensionless surface concentration and temperature with respect to its bulk fluid value at each point of the monolith reactor, and \( B_{in} \) and \( B_{ie} \) denote Biot numbers for mass and energy fluid film transfer, respectively: \( B_{in} = k_{gt} L_{gt} / D_{eff} \) and \( B_{ie} = h_e L_{gt} / k_{teff} \).

\( k_{gt} \) and \( h_e \) are the mass and heat transfer coefficients, \( k_{teff} \) the effective thermal conductivity of the washcoat, and \( L_{gt} \) the global characteristic length defined as the ratio between the washcoat total cross section and the fluid-washcoat interface perimeter.

Consequently \( \eta \) is calculated from:

\[
\eta = \int_0^1 R(C) \, dx, \quad (9)
\]

\[
\eta_i = \eta \left( \frac{r_s}{r_0} \right) \quad \phi_i^2 = \phi^2 \left( \frac{r_s}{r_0} \right) \left( \frac{C_i}{C_0} \right), \quad (10)
\]

\[
C_i^* = \frac{C_i}{C_0} = 1 - \frac{\phi_i^2 \eta_i}{B_{in}}, \quad (11)
\]

\[
T_i^* = \frac{T_i}{T_0} = 1 + \frac{\phi_i \eta_i \beta_e}{B_{ie}}, \quad (12)
\]

where \( \beta_e \) is the Prater number.
The subscript “0” is used for parameters calculated at the bulk fluid phase conditions. The intrinsic effectiveness factor was calculated using the following expression (Gottifredi et al., 1986):

\[ \eta = \left[ \phi^* + \exp\left(-a \phi^*\right) \right]^{-1/2}, \]  

where

\[ a = 1 - 2 \sigma \]

\[ \sigma = \sigma^* R^3, \]

\[ p = \left[ 2 \int_0^1 R(C) dC \right]^{1/2} \]

\[ \phi^* = \frac{\phi}{p}, \]

\[ R'(1) \] is the first derivative of \( R(C) \) respect of \( C \) evaluate at \( C=1 \).

Therefore, besides effectiveness factors, \( \eta \) and \( \eta_0 \), temperature and reactant concentrations on the washcoat-fluid interphase are calculated at each point of the axial reactor position by a trial and error algebraic procedure.

### III. RESULTS AND DISCUSSION

Let us consider a square monolith channel of side \( L \) covered by a non uniform washcoat layer. It is characterized by the minimum washcoat thickness \( \delta \) and the radius of washcoat in the corner \( R_N \). For this type of geometrical configuration, symmetry allows to consider \((1/8)^{th}\) of the total washcoat cross section (see Fig. 1).

Using the normalized representation of a square channel presented by Papadias et al. (2000) (e.g. \( \delta_N = \delta \times 2/L \)), the normalized characteristic geometric length \( L_{cov} \) of a slice is given by (Fig. 1):

\[ A = 1 - R_N - \delta_N, \]

“\( A \)” being the coordinate of point \((A, A)\) in the normalized square channel (Fig. 1). The segments:

\[ db = (1 - A) \tan(\phi + \Delta \phi), \]

\[ cb = (1 - A) \tan \phi. \]

Then

\[ L_{cov} = \frac{\text{Area slice } i}{\text{Perimeter slice } i} \]

While \( \omega_i \), is given by:

\[ \omega_i = \frac{\text{Area slice } i}{\text{washcoat area}} \]

\[ \omega_i = 0.5 \left[ 1 - 2 (A \Delta \phi) - \frac{\Delta \phi R_N^2}{8 A} \right] \]

\[ \text{and} \]

\[ L_{cov} = \frac{8 A \delta_N + 4(1 - A)^2 - \pi R_N^2}{8 A + 2 \pi R_N} \]

Provided the values of the radius of washcoat in the corner \( R_N \), the minimum washcoat thickness \( \delta \) and the side of a particular monolith sample \( L \); parameters \( A \), \( R_N \) and \( \delta_N \) can be calculated.

Nevertheless, there are several works that have considered a uniform washcoat characterized by the global length \( L_{cov} \).

#### A. Reactor Simulation

Concentration and temperature profiles, along a monolith channel, obtained by the simple but accurate method for estimating effectiveness factor for the specific case of CO oxidation reaction are investigated in this section. Estimates obtained with the procedure here presented are compared with experimental findings of Ullah et al. (1992) and Holmgren and Andersson (1998).

A single monolith one-dimensional 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. \( \text{Re} < 600 \).
3. Single adiabatic or isothermal channel. For adiabatic operation, there is no heat exchange through the connecting walls.
4. No conducting wall in the axial direction.

Using the heterogeneous one dimensional model (Bishoff and Fromot, 1980), accounting for interfacial and intra-washcoat gradients, key component conversion \( \Delta X \) and temperature \( \Delta T \) axial changes over an elementary monolith reactor volume may be written as:

\[ \frac{dT}{dz} = \left( \frac{\Lambda}{G C_p} \right) \eta_0 r_0 (\Delta H), \]

\[ \frac{dX}{dz} = \Omega \left( \frac{\Lambda}{F_{CO}} \right) \eta_0 r_0. \]

Here, \( \Lambda \) is the washcoat to monolith channel volume ratio, \( G \) the total mass velocity \( \text{g/m}^2 \text{s} \), \( \Omega \) the total cross section of the monolith channel \( \text{m}^2 \), \( C_p \) the specific heat of the mixture \( \text{cal/g K} \), \( F_{CO} \) the key component flow rate at the reactor entrance \( \text{mol/s} \) and \( \Delta H \) the heat of reaction \( \text{cal/mol} \).

It must be noticed that the appropriate definition of \( \eta_0 \) allows to deal with a plug flow homogeneous reactor.
This is so, because in \( \eta_c \) calculation the fluid dynamic of the system was taken into account through the interphase mass and heat transfer coefficients (Biot numbers).

**B. Reaction Rate Kinetic Expression**

Kinetic expression and parameter values for CO oxidation over Pt supported catalyst were taken from Oh and Cavendish, (1985):

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2,
\]

\[
r_{CO} = \frac{k_1 \text{C}_{CO} \text{C}_{O2}}{(1 + k_2 \text{C}_{CO})^2},
\]

\[
k_1 = 6.802 \times 10^8 \exp \left( \frac{-13108}{T} \right) \frac{m^4}{\text{mol s}},
\]

\[
k_2 = 8.099 \exp \left( \frac{409}{T} \right) \frac{m^3}{\text{mol}}.
\]

Where \( k_1 \) also depends upon platinum surface concentration. To estimate its value, in terms of unit washcoat volume, a surface site density of 1.25 \( \times 10^{15} \) Pt surface atoms per metal area and a washcoat density of 1.3 \( \text{g/cm}^3 \) were assumed. In each experimental case studied, the corresponding washcoat platinum loading and dispersion was utilized.

**C. Heat and Mass Transfer Coefficients**

In this work the Holmgren and Andersson, (1998), correlation for heat and mass transfer coefficients calculations were used. Assuming Colburn analogy applies, the same correlation can be used for \( Sh \) and \( Nu \) numbers:

\[
Sh = 3.53 \exp(0.0298 \text{Re Sc} d_s / L_s),
\]

As usual, Pr replaces Sc to calculate Nu. \( L_s \) is the reactor length and \( d_s \) the hydraulic diameter of the channel. In all cases, fluid properties were evaluated at an average temperature between washcoat surface and bulk temperatures. It must be pointed out that negligible conversion differences have been found when Uberoi and Pereira (1996) correlations were used.

**D. Properties Temperature Dependence**

The temperature \([K]\) dependence of the gas mixture properties, at 101.3 kPa, has been accounted for according to the following equations (Bird et al., 2002):

\[
k_T = 9.336 \times 10^{-5} T^{0.75} \frac{\text{cal}}{m \text{s} K},
\]

\[
\mu_s = 4.09 \times 10^{-4} T^{0.67} \frac{\text{g}}{m \text{s}},
\]

\[
\rho_s = 341257.5 T^{-1} \frac{\text{g}}{m^3}.
\]

The molecular diffusivity of compounds (reacting species) in the gaseous mixture was calculated according to Fuller method (Poling et al., 2004):

\[
D_{CO} = 9.1446 \times 10^{-10} T^{1.41} \frac{m^2}{s},
\]

and

\[
D_{O2} = 1.0115 D_{CO}.
\]

Specific heat as well as the heat of reaction variations have been neglected due to the smooth dependence with temperature. In the 500 – 700 K range a value of \( C_P = 0.2594 \text{cal/g.K} \) and \( \Delta H = -67777 \text{cal/mol} \), were used.

Taking into account the typical morphology of \( \gamma \)-Al\(_2\)O\(_3\) washcoat Pt catalyst, the effective diffusivity for CO in the washcoat was estimated from (Hayes and Kolaczkowski, 1994):

\[
D_{CO,ef} = 2.8 \times 10^{-9} T^4 \frac{m^2}{s},
\]

and

\[
D_{O2,ef} = 0.935 D_{CO,ef}.
\]

A constant effective washcoat thermal conductivity, \( k_{raf} = 0.09556 \text{cal/m.s.K} \), was used as previously reported (Gonzo, 2002).

Pressure drop in the experimental cases studied was relatively low. A figure of 1.2 kPa, near 1% of the total pressure, was found in the experiments carried out by Ullah et al. (1992). While in the Holmgren and Andersson (1998) case, \( \Delta P \) is 86 Pa. Due to the small pressure changes along the channel found in both cases; constant pressure along the reactor was assumed.

**D. Global and Intrinsic Effectiveness Factors**

Taking into account kinetic expression given by Eq. (26), the dimensionless rate of reaction \( R(C) \), using CO as the limiting reactant, is:

\[
R(C) = \frac{\left[ \Gamma (C - 1) + 1 \right] \left( 1 + K \right)^2}{(1 + K C^2)} C,
\]

where:

\[
C = \frac{C_{CO}}{C_{CO}} K - C_{CO} k_2,
\]

\[
\Gamma = \left[ \frac{1}{2} \left( \frac{D_{CO,ef}}{D_{O2,ef}} \right) \left( \frac{C_{CO}}{C_{O2}} \right) \right].
\]

Thus, the intrinsic effectiveness factor was calculated using the expression (13) with:

\[
R'(1) = \Gamma (1 + K) + 1 - K \frac{(1 + K)}{(1 + K)},
\]

**E. Comparison with Experimental Results**

A) Ullah et al. (1992) carried out their experiments under isothermal conditions, using a commercial monolith of cordierite with a cell density 62 cell/cm\(^2\). Experiments were started with a 15 cm long ceramic monolith core. After completion of the initial run, the monolith core was removed and cut 1 or 2 cm before being reinserted in the reactor for a new run. Thus, outlet CO conversions for different reactor length were obtained.

The inlet gaseous mixture was 0.5 mol\% CO, 0.25 mol\% O\(_2\), with the balance N\(_2\). A total mass flow rate of 5.24 \( \times 10^3 \) g/s in each channel was used. The monolith characteristics are: \( L = 1 \text{mm}; \delta = 10 \mu \text{m}, A = 0.325 \).
The bulk concentration profiles along the reactor, considering a 1% Pt catalytic washcoat with 55% dispersion, are shown in Fig. 2. In this figure, the bulk CO concentration estimated with our procedure (non uniform washcoat), and using $L_{cG}$ (the global characteristic length, uniform washcoat), are compared with the experimental results observed by Ullah et al. (1992), at 623 K. Fitting with the procedure herewith presented is remarkably good, especially when the washcoat non uniformity was taken into account.

Figure 3 shows the values of the intrinsic and global effectiveness factors along the reactor, estimated considering the non uniform washcoat.

The global effectiveness factor changes from 0.621 at the entrance to 0.872 at the outlet, with a minimum of 0.585 at $z = 0.9$ cm from the reactor entrance. In this case the calculated Reynolds number was 172 and the Sherwood number 3.64. Consequently, the CO and O$_2$ mean mass transfer coefficients were 0.259 and 0.262 m/s, respectively.

![Figure 2: CO bulk concentration estimated (our procedure), considering uniform washcoat ($L_{cG}$); experimental results observed by Ullah et al. (1992).](image)

![Figure 3: Estimated intrinsic and global effectiveness factors along the reactor. Ullah et al. (1992) case.](image)

B) Holmgren and Andersson (1998) have also investigated experimentally the CO oxidation, in an adiabatic monolith reactor. They used cordierite square monolith samples of 0.1 m long. Monoliths were coated with a catalytic washcoat consisting of 1% Pt on $\gamma$-Al$_2$O$_3$. The hydraulic diameter of the square monolith was 2.09 mm with a minimum washcoat thickness of 87 $\mu$m and $A = 0.404$. Mass flow was kept at 4500 g/m$^2$.s, which implies a Re of 300 in the channel, and 1% CO concentration in air, was fed. Initial pressure and temperature were 101.3 kPa and 573 K, respectively. A Pt dispersion of 25% (Holmgren and Andersson, 1998) was used to calculate $K_1$. Isothermal conditions within the washcoat were assumed, since under maximum CO concentration, Prater number (maximum dimensionless temperature gradient in the washcoat) was $\beta_0 = 4.83 \times 10^{-3}$. Fig. 4 shows CO conversion along the reactor. It should be noticed that in this experiment concentration was only measured at the reactor exit. Its reported value agrees fairly well with the obtained estimate with our procedure taking into account full kinetic expression.

In Fig. 5, differences between the bulk fluid and washcoat surface temperatures and percent relative difference concentration $[(C_0 - Cs)/C_0] \%$, along the reactor are presented. The bulk fluid and washcoat surface temperatures vary from 573K to 588.2K and from 660.4K to 662.4K, respectively. The relative concentration difference $[(C_0 - Cs)/C_0]$ varies from 0.21, at the reactor entrance, to 0.36, at the reactor exit, with a maximum of 0.47 at $z = 4.5$ cm. This indicates a strong external mass transfer resistance. Fig. 6 presents global and intrinsic effectiveness factor values along the reactor. While $\eta_0$ varies from 1.27 to 0.19 with a minimum of 0.172 at $z = 7.2$ cm, $\eta$ changes from 0.7646 to 0.404, with a minimum of 0.347 at $z = 5.76$ cm.

![Figure 4: CO conversion along the reactor. (a) Exit conversion experimental value. Holmgren and Andersson (1998).](image)

The effect of mass and heat transfer coefficient values on conversion was also simulated for the particular Holmgren and Andersson (1998) case. The coefficients, as estimated by the correlations Eq. (29), were then increased 10%, 20% and 40%, and the reactor performance simulation was carried out for each case.

Figures 7 and 8 show concentration and temperature differences between bulk and interfacial values along the reactor, showing a mild effect in relation with the normal case. However the effect on conversion along the reactor becomes negligible as can be seen in Fig. 9. The main reason to explain these results is that the overall effectiveness factor, $\eta_0$, is only slightly modified in every step of the reactor length. Thus a compensation
between external and internal resistances is produced which, as a whole, does not modify $\eta_0$ and consequently conversion. In actual facts our numerical results shows that the maximum deviation in $\eta_0$ presents a maximum decrease of 6% at reactor entrance and after 1 cm from the entrance there is no sensible difference between $\eta_0$ values although transfer coefficients have been increased up to 40%.

Figure 5: Difference between the bulk fluid and washcoat surface temperature and percent relative difference concentration $[(C_0 - Cs)/C_0] \%$ along the reactor. Holmgren and Andersson (1998) case.

Figure 6: Average global $\eta_o$ and intrinsic $\eta$ effectiveness factor along the reactor.

Figure 7: Parametric sensitivity of heat and mass transfer coefficients values on concentration differences between bulk and interfacial values along the reactor. Holmgren and Andersson (1998) case.

IV. CONCLUSIONS

This contribution presents a simple, accurate and fast procedure to predict monolith reactor performance by taking into account realistic kinetics, external and internal mass and heat transfer resistances as well as geometrical parameters to describe non uniform washcoat thickness along reactor section perimeter. It was developed from a simple and accurate method to predict effectiveness factor with complex kinetics and a one dimensional model able to describe non uniform washcoat thickness.

As a result the global effectiveness factor ($\eta_0$) can be calculated at each point of the grid by a simple algebraic iterative routine, where the initial guess of the dependent variable is taken from the previous point on the grid. The simulations presented in this work have clearly shown a fair agreement with experimental finding taking into account the true kinetic expression to describe CO oxidation on Pt catalyst, which is most acceptable for engineering purposes.

The agreement among our theoretical predictions with Ullah et al. (1992) reported conversion results along the reactor length are fairly good. It is also shown that both intrinsic kinetics and washcoat thickness variations are needed to achieve these good levels of agreement.
Almost the same conclusion can be drawn when our predictions are compared with overall conversion reported by experimental investigation of Holmgren and Andersson (1998). In this case however the only comparison that can be established refers to reactor exit conversion.

From each simulation a number of interesting results can be extracted. The changing role of internal and external transfer resistances was clearly shown. In fact, as reaction proceeds along the reactor, concentration depletion between bulk fluid and washcoat surface changes from a very modest value to almost 50%. Thus, as expected, the external resistances play an increasingly important role as conversion increases along the reactor although the internal diffusion-reaction phenomenon can never be neglected.

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