

Title: Theoretical analysis of tracer method for the measurement of wetting efficiency

Keywords: trickle-bed; wetting efficiency; tracer; liquid-solid contacting; internal diffusion; reactor modelling

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The numerical method for parameter optimisation implies a frequency domain least-squares procedure. A sensitivity analysis has been performed proving the wetting efficiency may be derived with convenient accuracy in usual trickle-bed conditions: high Peclet and Biot numbers.

For $f > 0.3$, it is shown that wetting efficiency can be accurately calculated from apparent particle diffusivities derived in liquid-full conditions ($De_{app,LF}$) and in partial wetting regime ($De_{app,TB}$), using the following relation: $f = \sqrt{De_{app,TB}/De_{app,LF}}$.

Theoretical analysis of tracer method for the measurement of wetting efficiency

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ABSTRACT

This work investigates the tracer technique for the measurement of catalyst wetting efficiency, f , in trickle-bed reactor.

The model of Ramachandran *et al.* (1986), based on a 2D description of the tracer diffusion, is applied for the full range of wetting efficiency. It is also extended to account for the effects of axial dispersion, liquid-solid mass transfer, pattern of the wetted zone on the pellet, and distribution of the partial wetting along the reactor.

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INTRODUCTION

Trickle bed reactors are extensively used in petroleum refining (hydrocracking, hydrodesulphurization, hydrodemetalization), but also in petrochemistry and fine chemistry, wastewater treatment, biochemical and electrochemical processes.

Bench-scale reactors used to design industrial units usually operate at the same liquid hourly space velocities as the commercial reactors, i.e. at very low liquid velocities.

Incomplete wetting of the catalyst may then be observed at laboratory-scale which can affect conversion and selectivity in a complex way.

Previous measurements of wetting efficiency f , i.e. the fraction of the external catalyst surface wetted by the flowing liquid, used chemical reactions (Ruecker and Akgerman (1987)), dynamic tracer methods (Colombo *et al.* (1976), Mills and Dudukovic (1981)), dissolution technique (Lakota and Levec (1990)), or more recently pressure drop (Pironti *et al.* (1999), Kundu *et al.* (2003)).

The tracer technique is the most popular one as it allows the determination of wetting efficiency with the actual bed under operating conditions. It consists in producing a step impulse of a tracer and analysing the time distribution of concentration at the outlet. From RTD variance, particle effective diffusivities for the reactor operating in liquid-full conditions – i.e. liquid phase flow without trapped gas – and in partial wetting regime can be calculated, respectively $D_{e_{app,LF}}$ which is actually the “true” effective diffusivity (D_e) and $D_{e_{app,TB}}$ an “apparent” (lower) diffusivity. Then f is deduced from

$$\text{either } f = \frac{D_{e_{app,TB}}}{D_{e_{app,LF}}} \text{ or } f = \sqrt{\frac{D_{e_{app,TB}}}{D_{e_{app,LF}}}} .$$

These relationships are intuitive, the second being based on the effectiveness factor under partial wetting. Deriving the exact relation would require an appropriate modelling of the tracer diffusion under non-symmetrical conditions due to non-uniform mass transfer flux on the outer surface of the catalyst.

In 1986, Ramachandran *et al.* proposed to calculate wetting efficiency from tracer measurement data. Using experimental RTD data, they identified in the Laplace domain both the wetting efficiency from their model and the apparent effective diffusivity from the conventional model of Colombo *et al.*. Surprisingly this pioneering work, performed at a single high wetting efficiency, has not been completed nor accounted for in the next studies. In this work, the model of Ramachandran *et al.* is applied for the full range of partial wetting. It is also extended to include the effects of axial dispersion, liquid-solid mass transfer, pattern of the wetted zone on a pellet, distribution of the wetting along the reactor length. Furthermore a detailed sensitivity analysis is performed.

MODELLING SECTION

Model hypothesis

The model is based on the following assumptions:

- Complete pore filling (i.e. internal wetting) due to capillary forces.
- Spherical catalyst pellets.
- Steady flow (no pulsation).
- The outer surface of the pellet is depicted in figure 1 with a wetted zone around the north pole ($0 \leq \theta \leq \alpha$) and a dry zone underneath:

$$f = (1 - \cos \alpha)/2 \quad (1)$$

The initial angle (α) of the wetted zone has also been varied to study the influence of the wetting pattern (polar or annular, figure 5).

- Tracer is transferred to the catalyst pores through the wetted zone only.
- Same effective internal diffusivity in radial and angular directions.
- Negligible tracer vaporization.
- Instantaneous and linear adsorption equilibrium.
- Liquid plug-flow with axial dispersion.

Model equations

Mass balance at the pellet scale:

$$(\epsilon_p + \rho_s(1 - \epsilon_p)K) \frac{\partial C_i}{\partial t} = D_e \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_i}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial C_i}{\partial \theta} \right) \right) \quad (2)$$

with D_e , effective internal diffusivity of the tracer (m^2/s),

K , adsorption equilibrium constant of the tracer (m^3/kg),

ϵ_p , catalyst internal porosity,

ρ_s , "true" density of the solid (kg/m^3).

Boundary conditions:

$$r = 0 \quad \forall \theta \quad \lim_{r \rightarrow 0} \left(r^2 \frac{\partial C_i}{\partial r} \right) = 0 \quad (3)$$

(pellet centre is neither a well nor a source of tracer)

$$\theta = 0, \pi \quad \forall r \quad \frac{\partial C_i}{\partial \theta} = 0 \quad (\text{axial symmetry}) \quad (4)$$

$$r = r_p \quad \begin{cases} -D_e \frac{\partial C_i}{\partial r} = k_s (C_i - C_L) & 0 \leq \theta \leq \alpha \\ \frac{\partial C_i}{\partial r} = 0 & \alpha \leq \theta \leq \pi \end{cases} \quad (5a,b)$$

(5a: liquid-solid flux from/to the wetted surface, 5b: no flux from/to the dry zone).

When the catalyst wetting is complete, equation (2) can be simplified into:

$$(\epsilon_p + \rho_s(1 - \epsilon_p)K) \frac{\partial C_i}{\partial t} = D_e \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_i}{\partial r} \right) \right) \quad (6)$$

with boundary conditions:

$$r = 0 \quad \lim_{r \rightarrow 0} \left(\frac{\partial C_i}{\partial r} \right) = 0 \quad (\text{spherical symmetry}) \quad (7)$$

$$r = r_p \quad -D_e \frac{\partial C_i}{\partial r} = k_s (C_i - C_L) \quad (8)$$

(which corresponds to the conventional model used by Colombo *et al.* (1976)).

Mass balance at the reactor scale:

$$\epsilon_L \frac{\partial C_L}{\partial t} = -u_{SL} \frac{\partial C_L}{\partial z} + \epsilon_L D_{ax} \frac{\partial^2 C_L}{\partial z^2} - \frac{(1 - \epsilon_B)}{V_p} \int_0^\alpha 2\pi r_p^2 D_e \frac{\partial C_i}{\partial r} \Big|_{r=r_p} \sin \theta d\theta \quad (9)$$

with D_{ax} , liquid axial dispersion coefficient based on interstitial velocity (m²/s),

ε_L , external liquid hold up,

u_{SL} , liquid superficial velocity (m/s).

Boundary conditions:

$$\varepsilon_L D_{ax} \left. \frac{\partial C_L}{\partial z} \right|_{z=0^+} = u_{SL} (C_L|_{z=0^+} - C_{inlet}) \quad (10)$$

$$\left. \frac{\partial C_L}{\partial z} \right|_{z=L} = 0 \quad (11)$$

The methods for resolution and parameter optimisation using Laplace transform and frequency domain least-squares procedure (Fast Fourier Transform) are detailed elsewhere (Baussaron, 2005).

RESULTS AND DISCUSSION

For the simulations, the normalized tracer response curves measured by Ramachandran *et al.* (1986) were used as experimental signals. Table 1 summarizes the corresponding operating conditions.

Preliminary simulations

The accuracy of the FFT reconstruction was first checked for the classical cases of plug flow with axial dispersion in both non-porous and porous particles bed.

With the set of parameters used by Ramachandran *et al.* similar results were given by the partial wetting program in the Laplace domain.

Sensitivity analysis

The influence of hydrodynamic and mass transfer parameters on the outlet signal and the optimized values of both D_e (liquid-full conditions) and f (trickle-bed) may be summarized as:

- Using only moments instead of the complete set of data should be avoided as even the most complete model does not perfectly match experimental data.
- Great attention should be paid to mass transfer coefficient and even more to Péclet number. At $Pe=10$, axial dispersion is highly predominant and no significant wetting efficiency can be derived.

Influence of wetting efficiency on the dynamic response

The outlet signals shown on figure 2 were simulated for the case of plug flow with non limiting external mass transfer and using parameters given in table 1.

For $f < 0.3$, the wetting efficiency being very low the resulting curves show an early peak corresponding to the mean residence time in the interstitial liquid, and a long tail representing the slow transfer to the pellets.

Wetting efficiency plays a similar role as diffusion or external mass transfer: the lower it is, the wider the response curve is.

Influence of tracer adsorption

The adsorption capacity of the catalyst for the tracer also influences its dynamic response. An adsorbing tracer has a longer residence time and also leads to a wider outlet signal. Figure 3 illustrates the influence of K on estimated liquid hold up (ϵ_L varies from 0.12 to 0.24 when K is set to 0.125 g/cm^3) and wetting efficiency (15% deviation).

Wetting heterogeneity at the reactor scale

To illustrate the effect of the wetting heterogeneity on f evaluation, two cases were examined.

In the first case (figure 4a), a fraction of particles exhibits a wetting efficiency f_1 (for instance 50% of particles are half-wetted) and the rest a different value ($f_2=0.9$), so that the mean wetting efficiency of the bed is $f_{\text{mean}}=0.7$. The two types of particles are homogeneously distributed along the reactor. Nearly no difference can be observed when varying the wetting distribution with same f_{mean} , excepting in the extreme case ($f_1=0.1$ and $f_2=0.9$).

In the second case (figure 4b), the reactor is equally divided in two consecutive zones, the first one with particles 90% wetted and the second one 50% wetted particles (the outlet signal calculated for the first section is used as inlet signal for the second one). The difference is again very low comparing to a bed with all particles at $f=0.7$.

Location of the wetting zone

The calculation algorithm was modified so that to compare the outlet signals for catalyst pellets with either polar or annular wetted zone of same surface. The location of the wetted zone was found to have only a very slight effect on the tracer response (figure 5).

Wetting efficiency vs. diffusivity ratio

The partial wetting model was also used to check for the validity of the simple formulas proposed to calculate f from the apparent particle diffusivities measured in liquid-full conditions and partial wetting regime.

The tracer response was simulated by the partial wetting program for different values of particle effective diffusivity (D_e) and wetting efficiency (using the inlet signal of Ramachandran *et al.*).

Then 1D diffusion model was used to optimize the apparent particle diffusivity ($D_{e_{app,TB}}$) in partial wetting conditions from the inlet signal and the simulated response. The

wetting efficiency calculated from this optimized diffusivity using $f = \frac{D_{e_{app,TB}}}{D_e}$ or

$f = \sqrt{\frac{D_{e_{app,TB}}}{D_e}}$ was compared to the initial value (f_{model}).

Figure 6 shows that $f = \sqrt{\frac{D_{e_{app,TB}}}{D_e}}$ provides a very accurate estimation (less than 4% deviation) when $f > 0.3$.

CONCLUSION

A theoretical analysis of tracer responses in trickle-bed reactors was performed, showing that tracer method may be performed to derive wetting efficiency in usual low axial dispersion conditions.

External mass transfer resistance, adsorption of the tracer, pattern of the wetted zone, and heterogeneity of wetting at the reactor scale were found to have only a slight effect on the outlet signal and the resulting wetting efficiency.

This work demonstrates that in usual hydrodynamic and wetting conditions of trickle-beds, the wetting efficiency can accurately be evaluated from RTD data, using a 1D

diffusion model and the following formula: $f = \sqrt{\frac{D_{e_{app,TB}}}{D_{e_{app,LF}}}}$, where $D_{e_{app,LF}}$ and $D_{e_{app,TB}}$ are

the apparent particle diffusivities measured respectively in liquid-full conditions and in

partial wetting regime. This tracer technique has been experimentally carried out and satisfactorily compared to direct measurements of partial wetting obtained by dye adsorption (Baussaron et al., 2007).

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FIGURE CAPTIONS

Figure 1: The partially wetted catalyst pellet

Figure 2: Effect of f on the dynamic response

Figure 3: Effect of tracer adsorption on the dynamic response

Figure 4: Effect of wetting heterogeneity on the dynamic response: (a) distribution of particles with different f , (b) repartition of wetting along the reactor length

Figure 5: Effect of the pattern of the wetting zone on the dynamic response

Figure 6: Comparison between f and $(De_{app,TB}/De)^p$: $p=0.5$ and $p=1$

Table 1: Data for the calculation of RTD responses in liquid-full (LF) and trickle-bed (TB) reactors

Figure
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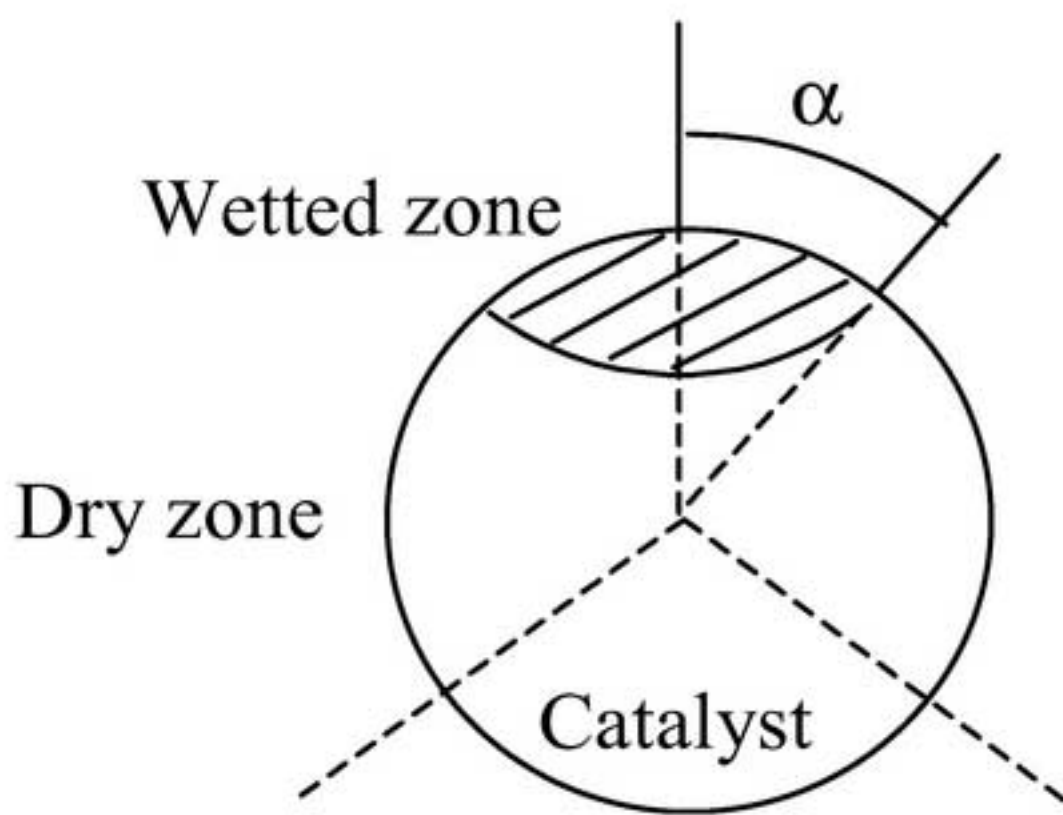
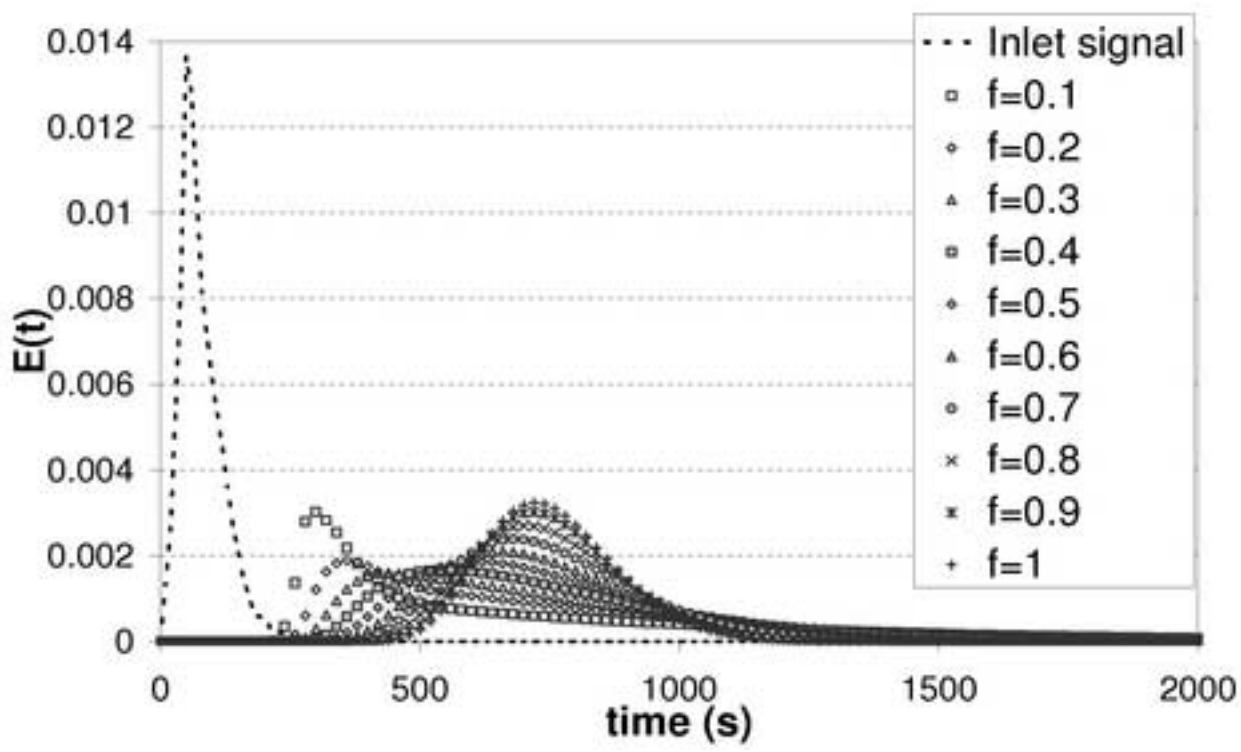


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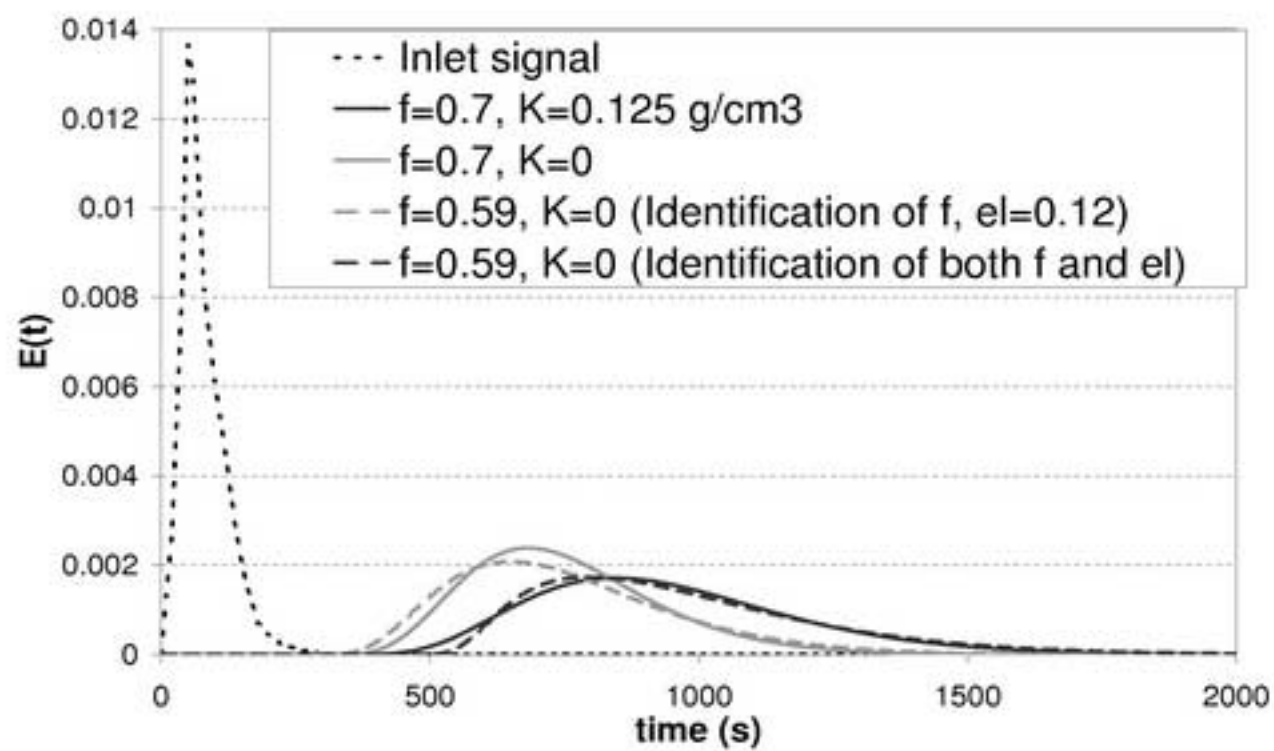
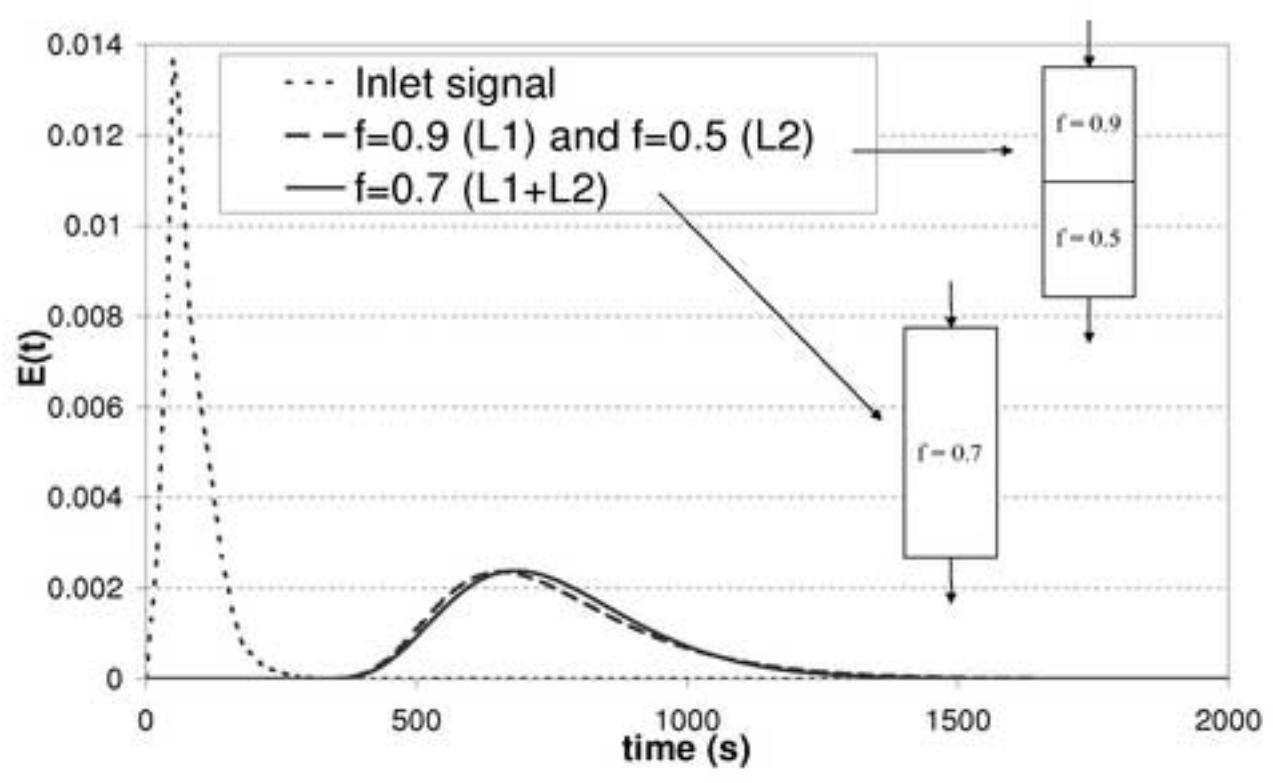


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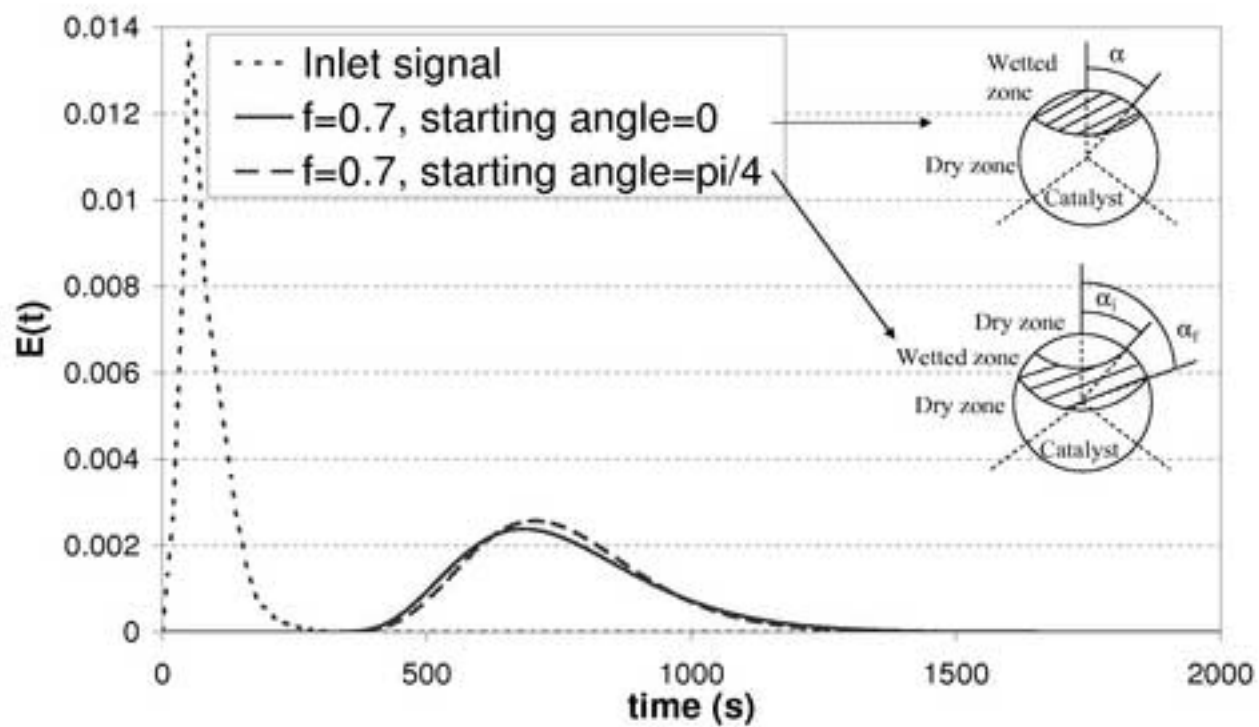
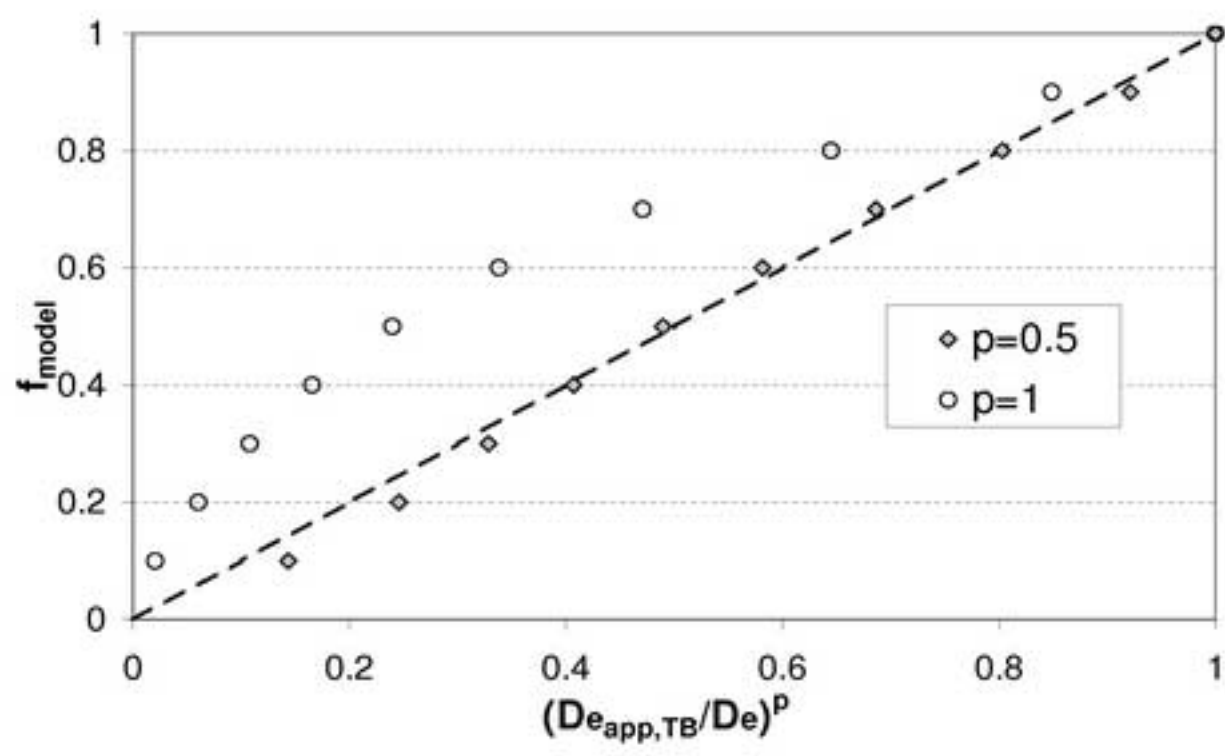


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Solvent	n-hexane
Tracer	n-pentane (non-adsorbing)
Reactor length (m)	0.4
Bed porosity ϵ_B (-)	0.374
External liquid holdup ϵ_L (-)	0.374 (LF) 0.120 (TB)
u_{SL} (mm/s)	0.23
Particle radius (mm)	0.359
Particle porosity ϵ_p	0.428

Dear Dr Nick

Thank you for helping us to improve our manuscript.

Finally we did not modify very much the first version as the two reviewers have rather different opinions and according to the restricted size of the format (2000 words) we cannot add detailed information from Baussaron's PhD thesis. This would help only specialists aiming to perform such calculations. INP Ph D theses are available on line.

We only partly agree with reviewer 2: yes, it is an old problem, but no, it was not completely solved. We did not find in literature any clear demonstration of the result obtained here and especially the accuracy of the approximation using the square root formula based on usual 1D approach.

If we missed any, of course it should be added.

Dr Ramachandran confirmed that he did not do more on this topic since his first work.

The second important novelty of this work is the sensitivity analysis suggesting the feasibility of such measurement in usual trickle bed conditions.

Finally, we completely agree with reviewer 1, and have added the reference of an experimental work - to be presented as invited lecture at CAMURE 6 (Catalysis in Multiphase Reactors) and now submitted to IEC Research - proving this tracer method to give similar results as a direct but very heavy one, based on dye adsorption and image analysis.

Yours sincerely.

Professor A.M. Wilhelm