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Incertitude induced by testing a small number of catalytic pellets in fixed beds

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Abstract

Heterogeneous catalyst pellets evaluation is performed in smaller and smaller reactors with the main objective of reducing catalyst development costs. Downscaling raises the question: is there a lower limit to the number of pellets that ought to be tested in a reactor so that the results do not depend on which pellets are sampled? Major sources of variability among a catalyst pellet population are dimensions and many parameters that can be grouped as “intrinsic kinetic activity” (porosity, tortuosity, active phase repartition and availability).

In this paper, we present a methodology to estimate the incertitude induced by variability on size and kinetics on the evaluation of the apparent kinetic constant in a fixed bed reactor. Analytical expressions are presented to predict this incertitude for sphere and cylinder shaped pellets, with a first order kinetic law in two limiting cases: absence of mass transfer limitations and presence of severe internal mass transfer limitations. The predicted incertitude scales as the square root of sample population: downsizing increases the incertitude. We propose criteria to evaluate the minimum number of pellets to sample, so that sampling induced variability is lower than an acceptable incertitude, expressed in °C. This acceptable incertitude could be for example a fraction of the experimental temperature incertitude.

Keywords

Fixed beds, downscaling, sampling, incertitude, criteria, catalyst testing

Highlights

- Methodology to evaluate the consequences of testing small catalyst samples in fixed beds
- Explicit equation to evaluate the incertitude for spherical and cylindrical pellets
- Criterion on minimum number of pellets required for a low variability catalytic test
- Incertitude scales with the square root of sample population

Nomenclature

c_x	concentration [mol/m ³], (x = inter, outlet)
D_{eff}	effective diffusion in the catalyst pellet [m ² /s]
d_p or d	particle diameter [m], random variable

$\overline{d_p}$	average particle diameter [m]
Δh	layer thickness [m]
k	intrinsic kinetic constant [s^{-1}], random variable
$\overline{k}$	average intrinsic kinetic constant [s^{-1}]
k_x	apparent kinetic constant [s^{-1}], (x = layer, reactor, particle)
L	pellet length [m]
u	superficial velocity [m/s]
E_a	activation energy [kJ/mol]
I	absolute incertitude on kinetic constant evaluation (at reactor scale) [s^{-1}]
I_k	absolute incertitude on intrinsic kinetic constant [s^{-1}]
$I^{\max}$	maximum allowable absolute incertitude on intrinsic kinetic constant evaluation (at reactor scale) [s^{-1}]
$I_{\Delta T}$	same as I but expressed in temperature [$^{\circ}C$]
$I_{\Delta T}^{\max}$	same as $I^{\max}$ but expressed in temperature [$^{\circ}C$]
I_{dp}	absolute incertitude on particle diameter [m]
I_L	absolute incertitude on particle length (cylindrical particle) [m]
L	pellet length [m]
M	total number of particles in the reactor
M_i	number of particles in the layer i
N	numbers of layers
S	external surface of particle [m^2]
V	volume of particle [m^3]
η	efficiency
ϕ	Thiele modulus

1 Introduction

Heterogeneous catalyst pellets evaluation is performed in smaller and smaller reactors with numerous benefits such as reduction of the amount of feedstock, waste products and catalyst, reduction of investment cost per reactor, etc... Data acquired in the test is used for kinetic parameters estimation in order to select the best catalyst and to predict its performance in an industrial size reactor. Here we focus on the case of millimetric size pellets, used for example in refining processes, whose performance is evaluated in fixed beds. In some High-Throughput Experiment catalyst testing, the number of catalyst pellets can be as low as one hundred, while catalyst pellets are never exactly identical with variability in size, structure, impregnation quality... This raises a quite crucial question: is there a lower limit to the

number of pellets that ought to be tested in the reactor so that the results do not depend on the laboratory test itself, i.e., mainly here on which pellets are sampled?

This question has received little attention in the literature. In 1988, Gierman (H. Gierman, 1988) has evoked sample inhomogeneity like impregnation quality as a potential limitation to scaling-down and proposed calculations for samples made of two populations, one normal and one abnormal. He estimated the maximum acceptable activity spread so that the average rate constant would be measured within 5% of the normal value depending of the reactor volume and abnormal population fraction. Regrettably, Gierman does not detail the methodology to estimate the average reactor kinetic. As expected, he concludes that larger reactors can level out excess activity better than small reactors. To our knowledge, the effect of catalyst sampling in small units has not been studied since.

In this paper we will examine major sources of sample inhomogeneity, present a methodology to estimate its effect on kinetic evaluation, and present analytical solutions and criterions for spherical and cylindrical catalyst pellets.

2 How can pellets from the same sample be different?

Before addressing the question of a lower limit on the number of grains, one must explore the potential sources of sample inhomogeneity that may affect chemical activity. We have identified variations in size, shape, structural properties and, for supported catalysts, impregnation quality.

Shape and size control depend only on the support manufacturing process. Samples of spherical beads produced by the oil drop method are very uniform as the shape and diameter is determined by surface tension and gravity. Another process to produce spherical beads is continuous coating of successive layers of support. It results in roughly spherical particles with large diameter distributions (Figure 1). Regarding extruded pellets, also called extrudates, extrusion guarantees a very precise shape and diameter (within a batch production). Due to extrusion die wear, some evolution can be observed in the long term, potentially inducing some batch to batch differences. Extruded pellets length results from random breakages occurring on the manufacturing lines like free fall from one equipment to the next: the extrudates length is therefore not homogeneous (Figure 1). Additional dimensional variability can be observed if the pellets are subjected to attrition, or agglomeration. Dimensional variations will lead to some effects on the pellets apparent kinetics, for cases where internal mass transfer limitations occur.

Figure 1 : Left: Sample of spherical beads with near spherical shape and various diameter (around 2 mm) -
 Right: Sample of triloblic extrudates with various length (around 3 mm). Glass container internal diameter:
 16 mm.

(single column figure)

Little has been published about structural properties dependence on process fabrication: catalyst manufacturer would certainly not publish data hinting toward lack of homogeneity. Similarly, little has been published about impregnation homogeneity except of course for egg-shell and egg-yolk type catalyst. Both structural and impregnation quality variations result in variations in the intrinsic grain kinetic activity and may be accounted for in changes of the kinetic activity.

Other sources of variability in kinetic activity can result in variable exposure, in quantity and duration, to chemicals (oxygen or moisture), temperature ... The potential change in kinetic activity will then depend on the position of the pellet in the storage container: pellets near the lid or at the bottom of the container may not be affected the same way. Similarly, during container filling, segregation of pellets according to their size is quite likely. For this reason, mixing the source container before sampling is highly recommended.

In the rest of the paper, we assume that storage procedures were adequate and that before sampling the pellets, the source batch was well mixed so that the pellets present random dimensional and intrinsic kinetic variability around “average” values.

3 Evaluation of sampling induced incertitude for spherical pellets

In this part, we present a methodology to estimate the effect of sampling a low number of spherical pellets, less than 1000 to set a number (representing a few grams), on the catalyst activity evaluation. More precisely, we are interested in assessing the incertitude on the catalyst activity evaluation induced by some randomness on diameter and activity.

3.1 Reactor based model

The first part of the methodology deals with establishing a mathematical relationship between the apparent catalyst activity at the reactor scale (k_{reactor}) and the random characteristics of the M particles tested in the reactor.

The particle properties are randomly drawn assuming: 1) known probability distributions on diameter and activity; 2) sampling reservoir is infinite. Using Thiele modulus approach, for each particle an apparent kinetic constant is computed based on diameter and intrinsic activity. We further assume a first order kinetic law. For a sphere, the equations are:

$$k_{\text{apparent}} = \eta k \quad \text{Eq. 1}$$

$$\eta = \frac{1}{\phi} \left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi} \right) \quad \text{Eq. 2}$$

$$\phi = \frac{d_p}{6} \sqrt{\frac{k}{D_{\text{eff}}}} \quad \text{Eq. 3}$$

The reactor apparent kinetic constant, $k_{reactor}$, is computed as follows. Let's split the fixed bed in N successive thin layers of thickness Δh . For these thin layers, we approximate the activity in each layer as the average activity of all particles in that layer¹.

$$k_{layer_i} = \frac{1}{M_i} \sum_{j=1}^{M_i} k_{apparent,particle_j} \quad \text{Eq. 4}$$

Assuming ideal reactor hydrodynamics, the concentration evolution through each layer can be computed as follow.

$$\int_{c_{inlet,layer_i}}^{c_{outlet,layer_i}} \frac{dc}{c} = -k_{layer_i} \frac{\Delta h}{u} \quad \text{Eq. 5}$$

Combining all the layers, we have then:

$$\int_{c_{reactor_inlet}}^{c_{reactor_outlet}} \frac{dc}{c} = -\frac{\Delta h}{u} \sum_{i=1}^N k_{layer_i} \quad \text{Eq. 6}$$

Assuming the apparent kinetics at the reactor scale is also of 1st order, then

$$\int_{c_{reactor_inlet}}^{c_{reactor_outlet}} \frac{dc}{c} = -k_{reactor} \cdot N \cdot \frac{\Delta h}{u} \quad \text{Eq. 7}$$

Comparing equations 6 and 7, we deduce that, for all reaction orders, the kinetic constant measured at the reactor scale can be estimated as the average of all particles apparent activity:

$$k_{reactor} = \frac{1}{N} \sum_{i=1}^N k_{layer_i} = \frac{1}{N} \sum_{i=1}^N \frac{1}{M_i} \sum_{j=1}^{M_i} k_{apparent,particle_j} \approx \frac{1}{M} \sum_{j=1}^M k_{apparent,particle_j} \quad \text{Eq. 8}$$

In Equation 8, we further assumed that the particles are perfectly homogeneously distributed in the fixed bed and that all layers possess the same number of particles.

Before getting on with the use of Eq. 8 to assess incertitude due to sampling, it is interesting to comment on the chosen assumptions. The model assumes ideal hydrodynamics (plug flow) and no external mass transfer limitations. Usually, reactors for kinetic parameters evaluation are chosen and designed to be operated close to those ideal conditions so that this assumption is not restrictive. Underlying basic assumptions of the work are 1) dividing the bed in thin layers with uniform concentration and number of particles (Eq. 5) and 2) evaluating the apparent activity at thin layer scale by averaging the activity of the catalyst in the layer (Eq. 4). These assumptions are equally at the basis of all mono-dimensional models of fixed bed reactors who have proved over decades to be quite good at representing fixed bed reactors. In chemical engineering, it is quite common to model fixed beds as a cascade of stirred tank reactors. In appendix, we show that this would lead to identical results.

The aforementioned derivation is based on the integration over each layer (Eq. 5) or reactor (Eq. 7) by separating variables. This is mathematically correct if and only if the right term of the equations, more particularly k_{layer} , is not a function of concentration. This condition is met when the efficiency is not a function of the concentration, which is always the case for a 1st order kinetic law (Eq. 1 to 3) and at low Thiele modulus for other reaction orders, in which

¹ Strictly speaking, one should account for the solid fraction, but as it cancels out we prefer not to include it in the equations for clarity reasons.

case the efficiency is equal to 1. It is probably possible to find other cases where variable separation is possible but this further analysis is not in the scope of this paper.

In the rest of the paper, we will assume isothermal conditions but the methodology holds as well for non-isothermal reactors: if a temperature profile is known (by measuring or by simulation), it is possible to correct the activity of each particle using for example the Arrhenius law (in Eq. 1 and 3).

The approach is also valid for any solid catalyst stacked in a fixed bed reactor. A special mention has to be made about egg shell catalyst where the active phase is impregnated on only a limited depth, generally thin but normally thicker than the reactant penetration depth. In those catalysts, concentration profiles are identical to those that would be calculated if the catalysts were fully impregnated so that proposed methodology is still valid without modifications.

3.2 Estimation of incertitude

In the previous part, we derived a set of equation to compute an apparent kinetic constant at reactor scale (k_{reactor}) based on the random characteristics of a sample made of M particles. Using this set of equations, it is possible to derive information about the statistics k_{reactor} .

The incertitude on k_{reactor} is denoted as I and is defined so that 95% of the measured values of k_{reactor} are within I of the real kinetic constant. Assuming that the kinetic constant follows a Gaussian distribution, the incertitude I is equal to twice the standard deviation of the k_{reactor} distribution. The determination of I requires therefore calculating the standard deviation of a rather complex function of two random variables: diameter, d , and intrinsic kinetic constant, k .

The incertitude can be computed using a Monte Carlo numerical approach and in some particular cases using analytical equations. In the Monte Carlo approach, numerous numerical experiments are repeated and the deviations to the homogeneous case are statistically analyzed. A single numerical experiment consists of the following steps:

- Selecting randomly M particles, each being defined by a random diameter and a random activity,
- Estimate the overall kinetic constant at fixed bed scale,
- Compare the activity to the homogeneous case.

The numerical experiment is repeated 500 times, which has been observed to be high enough for results to be statistically representative and independent of the number of repeats. The incertitude induced by the random sampling is set to twice the standard deviations of the activity distribution. The particle properties are randomly drawn assuming: 1) known probability distributions on diameter and activity; 2) sampling reservoir is infinite.

At low and high Thiele moduli, for an isothermal reactor, equations 1-3 can be simplified and it is possible to derive analytical expressions for incertitude. In the Appendix, the mathematical tools and derivations are summarized. At a low Thiele modulus, $k_{\text{apparent_particle}}$ is equal to the intrinsic activity and does not depend on particle diameter. Kinetic constants

estimated on the reactor are equal to the average of the particle intrinsic kinetics. We then deduce that² :

$$\phi \ll 1, I = \frac{I_k}{\sqrt{M}} \quad \text{Eq. 9}$$

In this case, the incertitude does not depend on the number of pellets and scales as the inverse of the square root of the number of particles.

At a high Thiele modulus, a good approximation of Eq. 2 is:

$$\phi \gg 1, \eta = \frac{1}{\phi} \quad \text{Eq. 10}$$

So that

$$\phi \gg 1, k_{\text{reactor}} = \frac{1}{M} \sum_{j=1}^M 6\sqrt{D_{\text{eff}}} \frac{\sqrt{k_{\text{particle}_j}}}{d_{p,\text{particle}_j}} \quad \text{Eq. 11}$$

Using classical composite incertitude formulas and after a few mathematical operations (see the Appendix), the incertitude on the kinetic constant measured at reactor scale, if particle diameter and intrinsic kinetic are not correlated is given by:

$$\phi \gg 1, I = \frac{\bar{k}}{\sqrt{M}} \sqrt{\left(\frac{I_{dp}}{d_p}\right)^2 + \frac{1}{4} \left(\frac{I_k}{k}\right)^2} \quad \text{Eq. 12}$$

Similarly to low Thiele modules, I_k scales as the inverse of the square root of the number of particles. The contribution of incertitude on diameter is larger than that of incertitude on intrinsic kinetic constant; this results from difference of exponent in Eq. 11.

3.3 Defining an acceptable incertitude on kinetic constant evaluation

The proposed methodology makes it possible to compute the incertitude on the apparent kinetic constant. In order to define a suitable particle number, a maximum acceptable incertitude ought to be defined beforehand by comparison with the other sources of incertitude in screening tests. These other sources of incertitude can result from measurement of process parameters (flow-rates, pressure, and temperature) or of feedstock properties (physical properties, chemical analysis).

An interesting way to present the incertitude, and common in the industrial practice, is to express it in the form of a temperature: what is the incertitude in the temperature of a reactor filled with identical pellets that would result in the same incertitude as the one induced by sampling a low number of non-ideal particles? The reasons for this choice are 1) that catalysts are very often compared on temperature difference basis; 2) the temperature difference can be straightforwardly compared to the incertitude on repeatability of temperature measurements in fixed bed pilot units. With this definition, an incertitude of 1°C means that in 95% of the

² Averaging N times a random variable reduces the incertitude by $\sqrt{N}$. See appendix for derivation.

cases, the kinetic at reactor scale is estimated within ± 1 °C of that of the reactor loaded with perfectly identical pellets.

With a first order development of the Arrhenius law, one can link absolute incertitude and incertitude expressed in temperature using:

$$I = \bar{k} \frac{E_a^{apparent}}{R} \frac{I_{\Delta T}}{T_{ref}^2} \quad \text{Eq. 13}$$

Relative incertitude and incertitude expressed in temperature are directly proportional, with a slope related to activation energy and reference temperature. Transposition from one to the other is graphically straightforward.

It is worth emphasizing here that due to our definition of the incertitude expressed in temperature, the activation energy to be used in Eq. 13 is the apparent activation energy : it has to be estimated accounting for internal mass transfer limitations. A classical result is that for high Thiele modulus, the apparent activation energy is half of the intrinsic one.

Typically, an overall experiment incertitude should remain below 1 °C in order to ensure a correct ranking of catalysts. Thus an acceptable incertitude for sampling ought to be even lower, ideally in the 0.1-0.3°C range, depending on the quality of the control and measure of process parameters and catalyst improvement target. This acceptable range has to be expressed back in incertitude on the kinetic constant evaluation, which depends strongly on both activation energy and temperature of reference.

Figure 2 presents maximum acceptable relative values, I^{max} , for various temperatures and activation energies (10 to 150 kJ/mol) assuming a maximum sampling induced incertitude of 0.2 °C. Large acceptable values are preferred to lower sensibility to sample inhomogeneity. A reaction presenting a low activation energy and/or operated at high temperature is more sensitive to eventual sample inhomogeneity. This conclusion may be counter-intuitive but results from our choice of expressing incertitude as a temperature. For a given experimental incertitude on the kinetic constant, a higher activation energy will results in lower incertitude expressed in °C.

Figure 2: Maximum acceptable relative incertitude as a function of activation energy for 3 temperatures (80, 200 and 350°C) assuming a sampling induced incertitude of 0.2°C.

(single column figure)

Combining Eq. 13 with previous expressions of I (Eq. 9 and 12) for low and high Thiele moduli, and the remark on the apparent activation energy, a minimum number of pellets to be used can be estimated by:

$$\begin{aligned} \phi \ll 1, M_{\min} &= \left(\frac{R}{E_a^{\text{apparent}}} \frac{T_{\text{ref}}^2}{I_{\Delta T}^{\max}} \right)^2 \left(\frac{I_k}{k} \right)^2 \\ \phi \gg 1, M_{\min} &= \left(\frac{2R}{E_a^{\text{apparent}}} \frac{T_{\text{ref}}^2}{I_{\Delta T}^{\max}} \right)^2 \left(\left(\frac{I_{dp}}{d_p} \right)^2 + \frac{1}{4} \left(\frac{I_k}{k} \right)^2 \right) \end{aligned} \quad \text{Eq. 14}$$

3.4 Special cases

3.4.1 Constant activity, Random diameter: same mean value, different spread

For pellets whose intrinsic activity is not random ($I_k=0$), but depends only on diameter spread, analytical solutions at low and high Thiele number (Eq. 9 and Eq. 12) reduce to:

$$\phi \ll 1, I = 0 \quad \text{Eq. 15}$$

$$\phi \gg 1, \frac{I}{k} = \frac{1}{\sqrt{M}} \frac{I_{dp}}{d_p}$$

In these conditions, the relative incertitude ($I/\bar{k}$) is proportional to the relative incertitude on diameter. The high Thiele modulus solution is an upper-bound estimation.

3.4.2 Random activity, fixed diameter

When diameter is well controlled, and intrinsic activity presents some randomness, Eq. 9 and 12 becomes:

$$\phi \ll 1, I = \frac{I_k}{\sqrt{M}} \quad \text{Eq. 16}$$

$$\phi \gg 1, I = \frac{I_k}{2\sqrt{M}}$$

In this case, there is more incertitude at a low Thiele modulus: at high a Thiele modulus, internal mass transfer limitations dampen the effect of activity variations. The number 1/2 at the denominator comes from the exponent of k (1/2) in the Thiele modulus expression. For the same reason, the apparent activation energy is halved at high Thiele modulus. This leads to an interesting result: in absence of spread on the diameter, the expression for the minimum number of pellets are identical for low and high Thiele modulus (See Eq. 14 with $I_{dp} = 0$). The same can be said about the incertitude expressed in °C. As expected, Monte Carlo simulations indicate that this observation still holds for intermediate Thiele moduli.

3.5 Results for spheres

3.5.1 Random diameter

In Figure 3, we present the incertitude induced by the distribution of diameter for 3 levels of activity corresponding to Thiele modulus ranging from 0.1 (negligible internal limitations) to 10 (strong internal limitations). In these simulations, the intrinsic activity is identical for all particles, and diameter distribution is a Gaussian distribution centered on 3 mm with a standard deviation of 0.35 mm. As expected, severe internal mass transfer limitation (high Thiele modulus) are required for diameter distribution to have an impact on the results. Figure 3 additionally shows that: 1) Monte-Carlo simulations based on 500 repeats are in very close agreement with the analytical solutions; 2) High Thiele modulus analytical solution can greatly overestimate incertitude at moderate Thiele Modulus (~ 1). In those conditions, Monte-Carlo simulations can help in assessing the risks.

Figure 3 : Incertitude for random diameters and various Thiele Modulus (0.1: negligible internal limitations, 1: medium internal limitations and 10: large internal limitations).

(single column figure)

3.5.2 Random activity

In Figure 4, we present the incertitude induced by the distribution of activity for Thiele modulus ranging from 0.1 (negligible internal limitations) to 10 (strong internal limitations). In these simulations, the particle diameter is constant at 3 mm and the activity follows a Gaussian distribution of standard deviation 10% of average activity. This confirms that the

validity of the analytical solutions (Eq. 16) and again that High Thiele modulus analytical solution can greatly overestimate incertitude at moderate Thiele Modulus (~ 1).

Figure 4 : Incertitude for random activity and various Thiele Modulus (0.1: negligible internal limitations, 1: medium internal limitations and 10: large internal limitations).

3.5.3 Random activity, random diameter, independent variability

When introducing independent variability of diameter (standard deviation of 0.35 mm) and on the intrinsic kinetic constant (standard deviation of 10%), as shown in Figure 5, incertitudes do not add up. This case would correspond to a quite inhomogeneous batch on the active phase. At low and moderate Thiele modulus, the incertitude is equal to the incertitude on the intrinsic constant of the pellet. The effect of diameter only becomes visible with severe internal limitation.

Figure 5 : Incertitude induced by independent variability on diameter (Gaussian distribution, average of 3 mm, standard deviation of 0.35 mm) and intrinsic kinetic constant (Gaussian distribution, standard deviation of 10%) for Thiele modulus of 0.1, 1 and 10.

(single column figure)

3.5.4 Random activity, random diameter, coupled variability

During sample preparation, one may assume that larger particles can retain more (or less) active phase than smaller particles. Hence our idea to test the consequences of a coupling between diameter and intrinsic kinetic constant.

Figure 6 presents results obtained for 500 particles drawn from a Gaussian distribution (average 3mm, standard deviation 0.35 mm). The activity is a linear of the diameter: the slope is such that a change in diameter of 0.35 mm corresponds to a change of 10% of the catalytic activity (same as uncoupled case). When the coupling is negative (a larger particle retains less metals and its intrinsic activity is lower), a very large incertitude emerges for high Thiele modulus reactions: smaller particle are more active due to their lower internal limitations and higher kinetic constant. When the coupling is positive, i.e. a larger particle retains more metals and its intrinsic activity is higher, a quite interesting result emerges: on a limited Thiele modulus range, the incertitude is nearly 0. In that range, it is possible to sample a very low number of particles without increasing incertitude. This peculiar effect is maximal around a Thiele modulus of 1, at a location that depends on the random parameters chosen for diameter distribution and coupling. At a low Thiele modulus, the main source of incertitude is rare and very active large particles, and equally rare but very inactive small particles. At high Thiele modulus, the “large particle” source of incertitude is dampened by internal mass transfer limitations but not the “small particle” source, hence a lower but non-zero incertitude.

In the intermediate range of Thiele modulus, we propose that all particles present near equal activity as both diameter effects compensate (a smaller diameter results in both a smaller intrinsic activity and lower limitations): sensibility to diameter is very weak and incertitude quite small.

Figure 6 : Relative Incertitude as a function of Thiele modulus for a fixed bed of 500 particles for positive and negative coupling between diameter and activity.

(single column figure)

4 Extension to cylindrical catalytic pellets

4.1 Extension of methodology by modified Thiele modulus

The methodology proposed for spheres can be extended to any particle shape provided it exists some way, either analytical or numerical, to compute the efficiency knowing the dimensions (random) of the particle. There exists some analytical expression for the Thiele modulus and efficiency for infinite cylinders:

$$\phi = \frac{d_{cylinder}}{4} \cdot \sqrt{\frac{k}{D_{eff}}} \quad \text{Eq. 17}$$

$$\eta = \frac{1}{\phi} \frac{I_1(2\phi)}{I_0(2\phi)} \quad \text{Eq. 18}$$

where I_1 and I_0 are Bessel function of the 1st and 0th order respectively.

Aris (Aris, 1957) proposed a generalized Thiele modulus valid for any particle shape:

$$\phi = \frac{V}{S} \cdot \sqrt{\frac{k}{D_{eff}}} \quad \text{Eq. 19}$$

$$\text{With } \frac{V}{S} = \frac{d.L}{2.d + 4.L}$$

We have checked using finite element simulations that for cylinders Eq. 11 combined with infinite cylinder efficiency (Eq. 18) predicts the actual efficiency with an error of less than 6% and opted to use these analytical functions rather than tabulated numerical results.

It is very likely that the results still holds for other extruded pellets like lobed shapes.

4.2 Analytical solutions for cylinders

Exactly like the sphere case, the expression for efficiency (Eq. 18) can be simplified for low and high Thiele modulus.

$$\phi \ll 1, \eta = 1 \quad \text{Eq. 20}$$

$$\phi \gg 1, \eta = \frac{1}{\phi}$$

As discussed in the introduction, we will assume now that there is no variability on the pellets diameter and some variability on activity and length.

Using the mathematical tools described in the Appendix, we can derive expressions for incertitude:

$$\phi \ll 1, I = \frac{I_k}{\sqrt{M}} \quad \text{Eq. 21}$$

$$\phi \gg 1, I = \frac{\bar{k}}{\sqrt{M}} \sqrt{4 \frac{\left(\frac{V}{S}\right)^2}{L^2} \left(\frac{I_L}{L}\right)^2 + \frac{1}{4} \left(\frac{I_k}{\bar{k}}\right)^2}$$

The sampling incertitude can be expressed in a form quite similar to that of spherical beads with a shape factor correction. Combining with Eq. 13, we can derive criterion for cylinders:

$$\phi \ll 1, M_{\min} = \left(\frac{R}{E_a^{\text{apparent}}} \frac{T_{\text{ref}}^2}{I_{\Delta T}^{\max}} \right)^2 \cdot \left(\frac{I_k}{\bar{k}} \right)^2 \quad \text{Eq. 22}$$

$$\phi \gg 1, M_{\min} = \left(\frac{2R}{E_a^{\text{apparent}}} \frac{T_{\text{ref}}^2}{I_{\Delta T}^{\max}} \right)^2 \cdot \left(4 \frac{\left(\frac{V}{S}\right)^2}{L^2} \left(\frac{I_L}{L}\right)^2 + \frac{1}{4} \left(\frac{I_k}{\bar{k}}\right)^2 \right)$$

As commented earlier, it is very likely that the results still holds for other extruded pellets like lobed shapes.

5 Discussion and conclusion

In this paper we present a novel methodology to estimate incertitude induced by sampling a limited number of particles in fixed bed kinetic studies. The methodology limits are given by its basic assumptions: first order kinetic law, ideal hydrodynamics, dimension and intrinsic activity as main source of variability. The predicted incertitude scales as the square root of the size of the sample: downsizing increases the incertitude especially in presence of mass transfer limitations.

For spherical and cylindrical particles, analytical formulas have been derived for low and high Thiele modulus to 1) predict incertitude induced by sampling a limited number of pellets and 2) propose a criterion on the minimum number of pellets that ought to be tested to keep sampling incertitude below an acceptable level. Results may differ greatly depending on the applications. If dimensional variability is larger than intrinsic activity variability, the minimum number of catalyst pellets to test can be lowered by narrowing the catalyst size distribution (sieving or sorting for example).

If the criterion on minimum number of pellets is not satisfied, we recommend first to try to increase the amount of catalyst loaded in the reactor paying attention to thermal issues. A next step would be to experimentally quantify the effect of sample inhomogeneity by comparing test response with reconstructed catalyst samples, for example mostly small vs. mostly large particles. If sample induced incertitude is not acceptable, then next step can be either to change the reactor or to include a sieving/sorting operation in the catalyst preparation workflow. The second option not only corresponds to capital expenditure but also higher complexity and operating costs.

Is it possible to go further in downscaling below 100 grains, let's say 50 grains? It is our belief, that on the sampling point of view at least, the answer is yes. With such limited sample population, it is easy to perform a thorough check of all the catalyst pellets before loading the reactor: optical measurement of the size of each grain, optical check of color disparity ... Any outlier would be readily detected before the test. On the opposite, with such a limited number of particles, another emerging source of incertitude is the hydrodynamics that can affect drastically mass transfer, as it has been recently hinted using CFD (M. Rolland, 2013; Götz et al., 2015). We believe controlling the hydrodynamics (or modeling it) will be the major challenge toward to further downscaling.

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6 Appendix

6.1 Note about modeling with a cascade of continuous stirred tank reactors

A similar conclusion to that proposed in §3.1 can be obtained by splitting the reactor in a cascade of continuous stirred tank reactors (CSTR). In this case, assuming a 1st order kinetic and that the activity in each CSTR reactors is the average of the apparent activity of the particles in that reactor, the concentration evolution (Eq. 5) can be re-written as

$$\frac{C_{outlet,CSTR_i}}{C_{inlet,CSTR_i}} = \frac{1}{1 + k_{CSTR_i} \cdot \frac{V}{Q}}$$

Noticing that equation 5 after integration yields $\frac{C_{outlet,layer_i}}{C_{inlet,layer_i}} = \exp\left(-k_{layer_i} \cdot \frac{\Delta h}{u}\right)$ and remembering that in the limit of small reactors ($V/Q \ll 1$), a first order development gives $e^{-a} \approx 1 - a \approx \frac{1}{1 + a}$: CSTR cascade equations are similar to those of layers cascade.

6.2 Composite incertitude formula

The incertitude of $f(x, y)$, function of two independent random variables x and y , is given by

$$I_f = \sqrt{\left(\left.\frac{\partial f}{\partial x}\right|_x\right)^2 \cdot I_x^2 + \left(\left.\frac{\partial f}{\partial y}\right|_y\right)^2 \cdot I_y^2}$$

6.3 Special cases:

- 1) $f(x) = a \cdot x$ with a constant, then $I_f = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 \cdot I_x^2} = \sqrt{a^2 \cdot I_x^2} = a \cdot I_x$
- 2) $f(x_1, x_2) = x_1 + x_2$, with x_1 and x_2 random variables of identical incertitude I_x :

$$I_f = \sqrt{\left(\frac{\partial f}{\partial x_1}\right)^2 \cdot I_x^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 \cdot I_x^2} = \sqrt{(1)^2 \cdot I_x^2 + (1)^2 \cdot I_x^2} = I_x \sqrt{2}$$
- 3) Sum of N variables of identical incertitude I_x . By extension of case 2, $I_f = I_x \sqrt{N}$
- 4) Average of N variables of identical incertitude I_x . Combining case 1 and 3, we easily deduce that averaging N times a random variable reduces the incertitude by $\sqrt{N}$.

$$I_f = \frac{I_x \sqrt{N}}{N} = \frac{I_x}{\sqrt{N}}$$

6.4 Derivation of Equation 12

Starting from Equation 11: $\phi \gg 1$, $k_{reactor} = \frac{1}{M} \sum_{j=1}^M 6\sqrt{D_{eff}} \frac{\sqrt{k_{particle_j}}}{d_{p,particle_j}}$

Let us note f , the function: $f(k, d_p) = 6\sqrt{D_{eff}} \frac{\sqrt{k}}{d_p}$, f is the particle apparent activity. We used the letter f instead of k to make the derivation easier.

$k_{reactor}$ is the average of a composite random variable f .

$$k_{reactor} = \frac{1}{M} \sum_{j=1}^M f(k_{particle_j}, d_{p,particle_j})$$

$$I = \frac{1}{\sqrt{M}} I_f$$

Using the formula:

$$I_f = \sqrt{\left(\left. \frac{\partial f}{\partial d_p} \right|_{\bar{d}_p} \right)^2 I_{d_p}^2 + \left(\left. \frac{\partial f}{\partial k} \right|_{\bar{k}} \right)^2 I_k^2}$$

$$\frac{\partial f}{\partial d_p} = -6\sqrt{D_{eff}} \frac{\sqrt{\bar{k}}}{d_p^2} = -\frac{f(k, d_p)}{d_p}$$

$$\frac{\partial f}{\partial k} = \frac{6\sqrt{D_{eff}}}{2.d_p.\sqrt{k}} = \frac{1}{2} \frac{f(k, d_p)}{k}$$

$$I_f = \sqrt{\left(-\frac{f(\bar{k}, \bar{d}_p)}{\bar{d}_p} \right)^2 I_{d_p}^2 + \left(\frac{1}{2} \frac{f(\bar{k}, \bar{d}_p)}{\bar{k}} \right)^2 I_k^2}$$

$$I_f = \left| f(\bar{k}, \bar{d}_p) \right| \sqrt{\left(\frac{I_{d_p}}{\bar{d}_p} \right)^2 + \frac{1}{4} \left(\frac{I_k}{\bar{k}} \right)^2}$$

Hence the conclusion:

$$\phi \gg 1, I = \frac{\bar{k}}{\sqrt{M}} \sqrt{\left(\frac{I_{d_p}}{\bar{d}_p} \right)^2 + \frac{1}{4} \left(\frac{I_k}{\bar{k}} \right)^2}$$

6.5 Derivation of Equation 21 for large Thiele moduli

Let us start with Eq. 20 : $\phi \gg 1$, $\eta = \frac{1}{\phi}$ with $\phi = \frac{V}{S} \cdot \sqrt{\frac{k}{D_{eff}}}$ and $\frac{V}{S} = \frac{d.L}{2.d + 4.L}$ (Eq. 19)

The apparent kinetic constant at reactor level is given by Eq. 8 which can be written in that case:

$$k_{reactor} = \frac{1}{M} \sum_{j=1}^M \frac{S_{particle_j}}{V_{particle_j}} \cdot \sqrt{D_{eff} \cdot k_{particle_j}}$$

$$k_{reactor} = \frac{1}{M} \sum_{j=1}^M \frac{2.d + 4.L_{particle_j}}{d.L_{particle_j}} \cdot \sqrt{D_{eff} \cdot k_{particle_j}}$$

We assumed that the diameter d is not a random variable.

Let us define the apparent kinetic function g:

$$g(k, L) = \frac{2.d + 4.L}{d.L} \cdot \sqrt{k.D_{eff}}$$

$$k_{reactor} = \frac{1}{M} \sum_{j=1}^M g(k_{particle_j}, L_{particle_j})$$

Thus

$$I = \frac{1}{\sqrt{M}} I_g$$

I_g is estimated using the formula: $I_g = \sqrt{\left(\left.\frac{\partial g}{\partial L}\right|_{\bar{L}}\right)^2 I_L^2 + \left(\left.\frac{\partial g}{\partial k}\right|_{\bar{k}}\right)^2 I_k^2}$

$$\frac{\partial g}{\partial L} = \sqrt{k \cdot D_{eff}} \left(-\frac{2}{L^2}\right) = -\frac{2}{L^2} g(k, L) \frac{V}{S}$$

$$\frac{\partial g}{\partial k} = \frac{2d + 4L}{dL} \sqrt{D_{eff}} \frac{1}{2\sqrt{k}} = \frac{1}{2} \frac{g(k, L)}{k}$$

$$I_g = \sqrt{\left(-\frac{2}{L^2} g(\bar{k}, \bar{L}) \frac{\bar{V}}{\bar{S}}\right)^2 I_L^2 + \left(\frac{1}{2} \frac{g(\bar{k}, \bar{L})}{\bar{k}}\right)^2 I_k^2}$$

$$I_g = \left|g(\bar{k}, \bar{L})\right| \sqrt{4 \frac{\left(\frac{V}{S}\right)^2}{L^2} \left(\frac{I_L}{L}\right)^2 + \frac{1}{4} \left(\frac{I_k}{\bar{k}}\right)^2}$$

Hence the conclusion:

$$\phi \gg 1, I = \frac{\bar{k}}{\sqrt{M}} \sqrt{4 \frac{\left(\frac{V}{S}\right)^2}{L^2} \left(\frac{I_L}{L}\right)^2 + \frac{1}{4} \left(\frac{I_k}{\bar{k}}\right)^2}$$

7 References

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