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

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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.

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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: the 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.

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 100, 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. 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

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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 depends 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 (Fig. 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 (Fig. 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.

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.

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

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 the 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:

$$k_{apparent} = \eta \;\; k \tag{1}$$

$$\eta = \frac{1}{\phi}\left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi}\right) \tag{2}$$

$$\phi = \frac{d_p}{6}\sqrt{\frac{k}{D_{eff}}} \tag{3}$$

The reactor apparent kinetic constant, $k_{reactor}$, is computed as follows. Let us 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 layer[1].

$$k_{layer\_i} = \frac{1}{M_i}\sum_{j=1}^{M_i} k_{apparent,particle\_j} \tag{4}$$

[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.