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Short communication

Particle size distribution effect on catalytic conversion in a CSTR

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Abstract

The effect of the particle size distribution on catalytic conversion in a CSTR was studied by comparison with that obtained from an assumed single size. Differences were handled as an error analysis. Calculations were performed according to the following assumptions: first order reaction, spherical pellets with sizes distributed in agreement with gamma function, and the assumed single size value equal to the mean size in the distribution. At each test, major error was found in the region of large competition between reaction and mass transfer rates (Thiele modulus value from 1 to 4). Error increases as feedstock rate increases. Error magnitude as high as 30% were found within the set of parameters tested. To keep error in conversion calculations within 5%, particle size variation should be kept within 35% of the mean size value. To keep it within 1%, particle size variation should be kept within 15% of the mean size value.

Keywords: Thiele modulus; Gamma function; Catalytic conversion

1. Introduction

Estimates of reactor operation are necessary when new designs or modifications of the reactor are evaluated. The level of confidence of that design or modification depends on the quality of those estimates. When they are obtained from mathematical models representing the process within the reactor, the quality of these estimates is improved if more of the relevant features are taken into account. Thus, considering diesel hydrotreatment as an example, work has been invested in improvements on the definition of the set of reactions and their correspondent kinetics, from single reaction [1] to multiple ones [2]. Hydrodynamics of the kind of multiphase reactor used has been an important topic to be analyzed – from Larkins et al. [3] to Holub et al. [4] models. Influence of transport phenomena within the catalyst pellet has received a well deserved attention [5–7].

For the calculations, the catalyst is generally assumed as a certain amount of pellets with equal size. However, in real experiments, catalytic loads with a pellet size distribution are unavoidable, and therefore the observed process is the result of a distribution of contributions.

Careful experimental works [8–11] have allowed only narrow variations around the reported size. The parameters obtained from those works were evaluated assuming a single size particle in each experiment. The error associated to that assumption as a result of the imposed limits of distribution, has not been quantitatively evaluated.

The effect of the particle size in reactive catalytic systems has been studied only by Aris [12] and Sun and Grace [13,14]. Aris [12] treated the problem to determine the single particle size that represents the catalytic behavior of the real distribution of particle sizes. He reached the following conclusions: in the case of reaction control of the process rate in every pellet (Thiele modulus "Φ" < 0.1) any particle size could be used. A weighted harmonic average must be employed as the representative size in the case of mass transfer control in every pellet ($\Phi > 5$). Finally, any single particle size would lead to inaccurate estimations when the process is performed in the intermediate region ($0.1 < \Phi < 5$).

Sun and Grace [13,14] analyzed the effect of a distribution of particle sizes on experimental fluidized bed reactor performance. The two unimodal distributions treated there showed a larger conversion for the wider distribution, while keeping the same mean size value. Such result leads to think that the influence of the unavoidable variations in particle size on reactor performance deserve more attention.

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Nomenclature

A_p	pellet external area
b	parameter of the distribution function given in Eq. (10)
C	molar concentration
D	diffusivity
f	continuous density of distribution
g	single pellet contribution to reactor performance
k_f	mass transfer coefficient at the external surface
N	number of total particles
Q	volumetric flow rate
r_p	pellet radius (m)
U	global extensive like variable
V_{pj}	volume of pellet "j"
W_c	catalyst mass within the reactor
x	conversion, index variable in distribution function

Greek symbols

α	parameter of the distribution function given in Eq. (10)
α_j	Biot number
ε	pellet volumetric void fraction
μ	mean value
Ω	dimensionless parameter representing intraparticle mass transfer to input flow ratio
Φ	Thiele modulus
ρ_p	pellet density
σ^2	variance
υ	modified coefficient of variation
ζ	dimensionless radius introduced in Eq. (5)

In this work, an analysis of error was performed by comparing estimated conversions obtained considering a catalytic load where the set of particles shows: (1) one single size; (2) a distribution of particle sizes. Looking for a criterion to establish limits in errors associated to the calculations involved, the same idea is used to define size distribution limits in order to hold error magnitude within acceptable values.

2. Methodology

Particle size distributions can be handled as percent mass, frequency or number of particles of a size interval [15]. In this work, number of particles was used. This number was evaluated from average values, load mass, and pellet density according to the following equation:

$$N = \frac{W_C}{\rho_p V_p|_{\bar{r}_p}} \frac{V_p|_{\bar{r}_p}}{V_{p,AV}} \tag{1}$$

An extensive type variable "U" obtained from the set of pellets is evaluated as the sum of contributions of each pellet. If the system contains a huge number of particles showing a distribution of sizes that can be represented by a continuous function, the variable "U" could be evaluated as

$$U = \frac{W_C}{\rho_p V_p|_{\bar{r}_p}} \frac{V_p|_{\bar{r}_p}}{V_{p,AV}} \int_{r_{p,min}}^{r_{p,max}} u\, f(x)\mathrm{d}x = \frac{W_C}{\rho_p V_p|_{\bar{r}_p}} \frac{\int_{r_{p,min}}^{r_{p,max}} u\, f(x)\mathrm{d}x}{\int_{r_{p,min}}^{r_{p,max}} \frac{V_p}{V_p|_{\bar{r}_p}} f(x)\mathrm{d}x} \tag{2}$$

It can be noted that, when pellet density is constant a continuous density of distribution based on mass of pellets "f_w" can be related with density of distribution based on number of pellets "f" through the expression

$$f_w(\varsigma) = \frac{V_p|_\varsigma f(\varsigma)}{\int_{r_{p,min}}^{r_{p,max}} V_p|_x f(x)\mathrm{d}x} \tag{3}$$

In Eq. (2), the substitution of "f" by "f_w" must be accompanied with the substitution of the property per pellet "u" by the product of the property per mass unit "$\hat{u}$" and the pellet mass. Thus, the analyzed variable "U" should not be different one way or another.

2.1. Balance equations

In order to facilitate calculations, a load of spherical catalytic particles promoting a single irreversible first order reaction was assumed. From the solution for such diffusion–reaction problem, the contribution of each particle to reactor performance is

$$A_{p\,j} k_{f\,j}(C_f - C_{p\,j}) = 4\pi r_{p\,j} \varepsilon D_{ef} C_f \frac{\frac{\Phi_j}{\tanh(\Phi_j)} - 1}{\frac{\Phi_j}{\tanh(\Phi_j)^{-1}} + 1} \tag{4}$$

A dimensionless radius with unitary mean value was defined as

$$\zeta_j = \frac{r_{p\,j}}{\bar{r}_p} \tag{5}$$

From Eqs. (4) and (5), the contribution of each pellet can be handled through a variable "g" defined as

$$g(\zeta_j, \bar{\Phi}) = \zeta_j \frac{\frac{\zeta_j\bar{\Phi}}{\tanh(\zeta_j\bar{\Phi})} - 1}{\frac{\zeta_j\bar{\Phi}}{\tanh(\zeta_j\bar{\Phi})^{-1}} + 1} \tag{6}$$

In order to isolate the particle size distribution effect from that of external gradient of temperature or mass concentration, a steady state CSTR was selected. Therefore, conversion would be evaluated as

$$x = 1 - \frac{1}{1 + \Omega \frac{\int_{\zeta_{min}}^{\zeta_{max}} g(x,\bar{\Phi}) f(x)\mathrm{d}x}{\int_{\zeta_{min}}^{\zeta_{max}} \frac{V_p}{V_p|_{\bar{r}_p}} f(x)\mathrm{d}x}} \tag{7}$$

where the parameter Ω was defined as

$$\Omega = \frac{4\pi\varepsilon D_{ef} \bar{r}_p}{Q} \frac{W_C}{\rho_p V_p|_{\bar{r}_p}} \tag{8}$$

The commonly assumed case of a single pellet radius, equal to the mean value, leads to the estimate conversion

$$x^* = 1 - \frac{1}{1 + \Omega g(1, \Phi)} \tag{9}$$

2.2. Distribution function

The particle size distribution was assumed described by the gamma function [16], given as

$$f(\zeta) = \frac{1}{b^\alpha \Gamma(\alpha)}(\zeta - \zeta_{\min})^{\alpha-1} \exp\left(-\frac{\zeta - \zeta_{\min}}{b}\right) \tag{10}$$

A modified coefficient of variation (MCV) was used, defined as

$$\upsilon = \frac{\sigma}{\mu - \zeta_{\min}} \tag{11}$$

This MCV is equal to the coefficient of variation [17] when the minimum radius is equal to zero. For a given mean and MCV value, the distribution parameters are

$$\alpha = \frac{1}{\upsilon^2} \tag{12}$$

and

$$b = \upsilon^2(\mu - \zeta_{\min}) \tag{13}$$

The volume quotient average appearing in Eq. (7) was evaluated in the next way

$$\int_{\zeta_{\min}}^{\infty} \frac{V_p}{V_p|\bar{r}_p} f(\zeta)\mathrm{d}\zeta = b^3(\alpha+2)(\alpha+1)\alpha + 3\zeta_{\min} b^2(\alpha+1)\alpha + 3\zeta_{\min}^2 b\alpha + \zeta_{\min}^3 \tag{14}$$

Calculations were done in two steps. In the first one, conversions were evaluated from Eq. (7) considering different distributions defined by mean value and MCV, and from Eq. (9) considering single size equal to the distributions mean value. In this step any control on particle size was assumed absent. Thus, minimum particle size would have a negligible value, here handled as zero. MCV used were $\upsilon = 1/n$, $n = 2$–5. Three orders of magnitude were tested for the parameter Ω, meaning three different input flow rate values "Q". Ω values were 10 (low Q), 1 (intermediate Q) and 0.1 (high Q). Average Thiele modulus values from reaction rate control to mass transfer rate control were used. Considering that the best estimate for conversion is provided when the particle size distribution is used, the error produced by an assumed unique size value was evaluated through the next expression

$$\%\,\text{Error} = \frac{x - x^*}{x} \times 100 \tag{15}$$

The objective of this step was to know the significance of the error that could be reached.

In the second step, a control on particle size (sieving for example) was assumed. Variations around the mean particle size were tested in order to limit the maximum error to acceptable levels. MCV and Ω values leading to maximum error in the first step were fixed in the second one. $\zeta_{\min}$ was handled as the limit of variation. Two possible limits for acceptable error were considered: 1% and 5%.

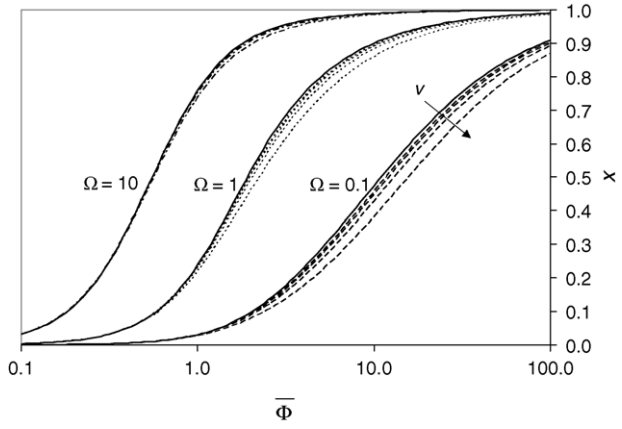

Fig. 1. Conversion vs. mean Thiele modulus. Arrow shows the direction of increasing modified coefficient of variation "υ".

3. Results

Conversion versus mean Thiele modulus evaluated in the first step is shown in Fig. 1. It can be seen that as Ω decreases (input flow rate increases) the differences among conversions at each MCV value are more notable. For each distribution tested, the major error was always located in the region of large competition between mass transfer and reaction rate, as it can be seen in Fig. 2. With the parameter values tested, the maximum error (30.9%) was obtained when Ω was equal to 0.1 (high input flow rate) and MCV is equal to 1/2. Curve "a" in Fig. 2 shows the maximum error found in the first step, and its significance is evident.

In the second step, to simulate a control on particle size distribution, the minimum radius was varied keeping the same MCV value. Fig. 3 shows the distributions obtained when minimum radius was increased looking for error percent smaller than 1% (the steepest distribution) and 5% (the next). For the last one, variation around mean radius value should be smaller than 35%. To get error smaller than 1%, radius variation should be smaller

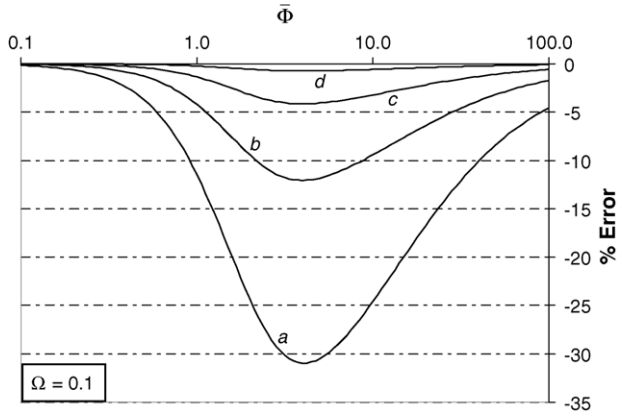

Fig. 2. Conversion error percent vs. mean Thiele modulus, at high input flow rate and modified coefficient of variation $\upsilon = 1/2$. Minimum radius "$\zeta_{\min}$" in each curve are: (a) zero; (b) 0.4; (c) 0.65; (d) 0.85.

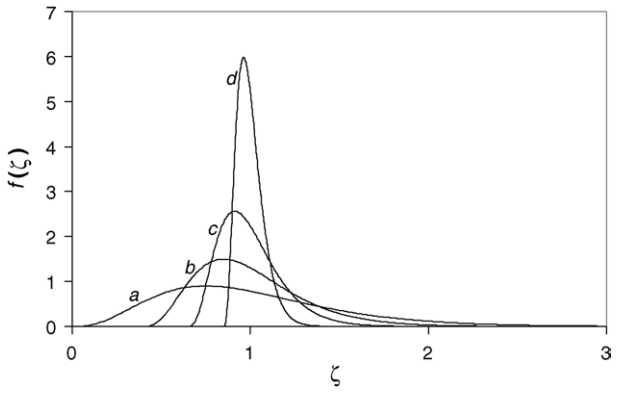

Fig. 3. Particle size distributions at modified coefficient of variation $\upsilon = 1/2$ and high input flow rate. Minimum radius "ζ_{min}" in each curve are: (a) zero; (b) 0.4; (c) 0.65; (d) 0.85.

than 15%. Fig. 2 shows error versus mean Thiele modulus value corresponding to each distribution in Fig. 3.

4. Discussion

Analysis of processes through mathematical models allows isolation of effects from particular features than real experiments hardly could, or could not, disassociate. In this way the relevance of each effect can be evaluated. The reaction–diffusion process within each particle contributes to the observed reactor performance. Each contribution depends on particle size. To isolate that effect, ideal mixing and no thermal effects were considered; avoiding additional variations due to regions of different concentration and temperature resulted from zones of different load of catalyst, as they would be seen in some real experimental units [12,13].

As a practical case, H-oil in petroleum industry could be approximately described by this model, considering the type of mixing and huge number of particles.

Results show agreement with Aris' analysis [12] in the limit cases ($\Phi < 0.1$ and $\Phi > 5$) providing in addition, a quantitative evaluation of differences detected in reactor performance. Contact time showed to have a significant influence in the difference magnitudes. Although limited to the set of assumptions taken in this work (first order single reaction, spherical particles, gamma distribution), a quantitative estimation of the limits allowable in distribution of sizes to keep error within acceptable levels was obtained. Therefore, it could be used as a criterion for planning experimental studies.

5. Conclusions

(1) In a stirred reactor, when the estimated conversions are obtained considering the size of the particle equal to the mean of particle sizes, the resulted values are higher than those obtained considering a distribution of particle sizes.
(2) Error in estimate conversion increases as input flow rate is increased.
(3) Major error is located in the region of large competition between reaction and mass transfer rates. Significant errors, as high as 30%, are possible in that region.
(4) Under the tested distribution function and parameter values, to set conversion error smaller than 5%, radius variation should be kept around 35% of the average value. If error conversions smaller than 1% are desired, radius variations should be kept around 15% of the average value.

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