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Fractional order modelling of zero length column desorption response for adsorbents with variable particle sizes

Short Communication

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Abstract: This manuscript analyses the data generated by a Zero Length Column (ZLC) diffusion experimental set-up, for 1,3 Di-isopropyl benzene in a 100% alumina matrix with variable particle size. The time evolution of the phenomena resembles those of fractional order systems, namely those with a fast initial transient followed by long and slow tails. The experimental measurements are best fitted with the Harris model revealing a power law behavior.

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1. Introduction

Fluid catalytic cracking (FCC) catalysts are used in the petrochemical industry to split heavy oils into valuable smaller hydrocarbon molecules [1, 2]. It is known that the cracking reactions are mainly the diffusion controlled type.

Thus, the measurement of diffusivity values of hydrocarbons in FCC catalysts is important not only to evaluate the diffusion controlled rate for the cracking reaction, but also to design the FCC reactor.

The cracking reactions mainly involve Zeolite crystals, consisting of micropores (diameter, $d_p < 20$ Å). In most cases, the molecular size of the heavy hydrocarbon is much larger than the pore opening of zeolite crystals. So the heavy hydrocarbon cannot penetrate the zeolite cage which contains around 97% of the active sites for the cracking reaction [3]. Usually zeolites crystals are embedded

in an amorphous matrix allowing the larger molecule to be cracked into smaller ones which can then penetrate inside the zeolite cage. Typically an alumina–silica matrix (macroporous, $d_p > 50$ Å) is adopted to bind the zeolites which mainly consist of 80% Al_2O_3 and 20% SiO_2 [4]. It is also important to know the diffusivity value of the heavy hydrocarbon through the alumina matrix because it represents the molecular highway to transport reactant and products to and from the zeolite micropores.

The Zero Length Column (ZLC) technique is a simple and well established method to measure the diffusivity value of hydrocarbons in zeolites, achieved by analysing the desorption curve for a particular sorbet (i.e. hydrocarbons). This experimental method and the mathematical model for ZLC were developed by Eic and Ruthven [5] for linear adsorption isotherms of hydrocarbons in zeolites. More recently the mathematical model was improved to include the effects of the presence of external film resistance [6], interstitial fluid holdup [7], incomplete saturation [8], and non linear adsorption [9]. In all proposed models the particle size was assumed to be constant. Moreover, the diffusivity values of the hydrocarbons in solids were derived from the well established solution of the Fickian type diffusion equation [6]. The corresponding chart consists of a straight line in a semi–log plot of normalized sorbent concentration versus time and its slope represents the diffusivity value (D) divided by the square of the particle radius (R). The ability of the ZLC technique to measure diffusivity in variable size distributed particles is still an open question. The effect of variable particle size will induce a tailoring effect in the ZLC desorption response curve as desorption is a function of mass loading in the solid. The theory of the calculation of diffusivity value for variable size distribution was first developed by Ruthven and Loughlin [10] for the gravimetric analysis method. Duncan and Möller [11] proposed a model for ZLC experiments with variable particle size using a Fast Fourier transformation technique and taking into consideration the standard deviation of the particle size distribution. Analysing the ZLC response curve using this model causes the diffusional time constant ($\frac{D}{R^2}$) to be under predicted and the adsorption related parameter over predicted. Loos et al. [12] also modelled the effect of crystal size upon the ZLC desorption response curve by summing up the desorption curve for different size ranges, weighting their volume fraction according to the model developed by Ruthven and Loughlin [10] for the gravimetric method. Thus, an appropriate model should be developed to extract the correct value of diffusivity taking consideration of the variable particle size effect.

Recently, fractional dynamics started to be applied intensively to properly treat data from several disciplines [13–21]. Thus, in this paper we suggest a fractional order model which better fits experimental results containing the memory effect. We explain that the investigated data points were generated from a ZLC diffusion experimental setup for 1,3 Di-isopropyl benzene in 100% alumina matrix with variable particle size, whose mean diameter (d_m) and standard deviation (S_D) are 116.7 and 68.9 μm measured on a normal distribution basis and 105.6 and 1.9 μm measured on the basis of log normal distribution.

The organization of the manuscript is as follows. Section 2 reviews briefly the diffusion equation for a spherical particle. Section 3 is devoted to the experimental details. Section 4 presents the Harris model and its application to the fitting of the investigated data. Finally, section 5 outlines the main conclusions.

2. A mathematical model of the ZLC

The diffusion equation for a spherical particle is given by the Ficks second law:

$$\frac{\partial q}{\partial t} = D \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right), \tag{1}$$

where $q = Kc$ represents the sorbet concentration in solids, K denotes the Henry's adsorption coefficient, c is the gas phase sorbet concentration, r corresponds to the radial coordinate and D denotes the diffusivity.

For uniform spherical adsorbent particles under linear equilibrium conditions the response curve can be expressed as derived by Crank [22]:

$$\frac{c}{c_o} = 2L \sum_{n=1}^{\infty} \frac{\exp \left(-\frac{\beta_n^2 Dt}{R^2} \right)}{\beta_n^2 + L(L-1)}, \tag{2}$$

where c_0 yields the initial gas phase sorbet concentration and β_n are the roots of the transcendental equation [22]:

$$\beta_n \cot \beta_n + L - 1 = 0, \tag{3}$$

with

$$L = \frac{1}{3} \frac{F R^2}{K V_s D}, \tag{4}$$

where F denotes the purge flow rate, R is the solid particle radius and V_s represents the solid volume.

As time increases the Eq. (1) reduces to a simple exponential decay curve since only the first term of the summation is significant, namely:

$$\frac{c}{c_o} = \frac{2L}{\beta_1^2 + L(L-1)} \exp \left(-\frac{\beta_1^2 Dt}{R^2} \right), \tag{5}$$

where β_1 is the first root of the transcendental Eq. (3). Under these conditions, $\frac{D}{R^2}$ and L can be determined directly from the slope and intercept of the semi logarithmic plot of $\frac{c}{c_o}$ versus t. This is known as long time (LT) analysis. This model depicts a straight line at long time with uniform particle size distribution (radius, R = fixed) and cannot handle the particle size effect.

3. Experimental details

The ZLC is a tiny volume reactor made of a $\frac{1}{4}''$ stainless steel coupler. A very small weight of adsorbent particles (1 $\sim$ 10 mg) was kept inside the reactor and its open ends were sealed with (20 μm pore diameter) sintered disks. A small amount of adsorbent will minimize the intrusion of thermal effects and extra particle resistance to mass transfer. The ZLC cell was kept inside an oven. To provide isothermal conditions, both the carrier and purge gas flowed through a 2 meter long tube inside the oven before it entered the ZLC cell. The carrier gas contained a low concentration of 1,3 Di-isopropyl benzene in helium. Two gas streams, (gas flow was controlled using a mass flow controller from OMEGA inc), were mixed to prepare the career gas. One was a high velocity stream (100 cc/min pure He) and the other , a low velocity helium stream (10–20 cc/min) passing through a 1,3 Di-isopropyl benzene liquid bath to get saturated with 1,3 Di-isopropyl benzene at the liquid bath temperature. These two streams were mixed with a tee and continued to the ZLC cell. At the beginning of the experiment, the adsorbent in the ZLC cell was saturated with 1,3 Di-isopropyl benzene by the carrier gas and at time zero the carrier gas line was changed to purge gas (pure Helium gas only and with the same velocity of the carrier gas). Desorption of 1,3 Di-isopropyl benzene was detected with time by using a Flame Ionization detector (FID). A plotter was used to record the data points. The normalized concentration y versus time t, for the set of tested temperatures T, can be seen in Figure 1.

4. Description by means of the Harris model

We have verified that after dissipating the initial transient the plots approximately follow a power law. This is in contrast with the classical exponentially decreasing curves that occur with integer models. It is possible to find a regression of this part of the trace, however it seems preferable to obtain a fitting expression for all points. Therefore, several models where tested in order to fit to the experimental data by adopting the nonlinear
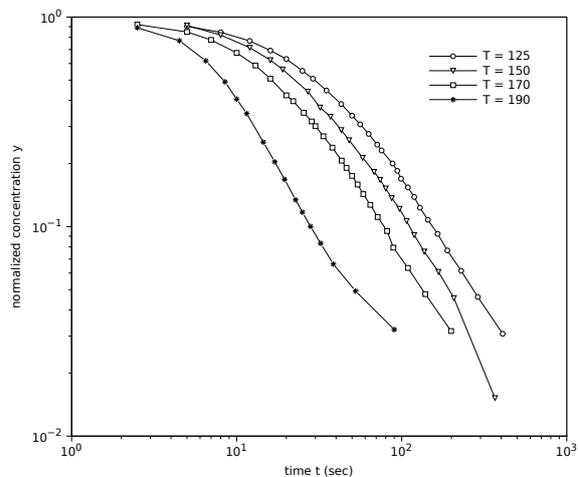
Figure 1. Normalised concentration y versus time t for temperatures $T = 125 \,(°C)$, $T = 150 \,(°C)$, $T = 170 \,(°C)$ and $T = 190 \,(°C)$.

Marquardt–Levenberg optimization [23, 24]. The Harris model [25, 26] was found to lead to a very good fit for all cases and, therefore, has been subsequently adopted. The Harris model is defined by the expression:

$$y(t) = \frac{1}{a + bt^\alpha},\qquad (6)$$

where $\{a, b, \alpha\}$ are parameters (that depend on the temperature T) to be determined, t denotes the time and y represents the normalized concentration.

It should be noted that other models did also provide a good numerical fit for some temperatures, but that the Harris model accomplished best results when considering all cases.

Table 1 presents the values of the three parameters together with the correlation coefficient (ρ). The figures demonstrate very good correlation. We also observe that a is very close to 1.0 and that the values of the other two parameters vary with temperature. Furthermore, it was verified numerically that, if we "normalize" the time variable so that the range of measured values falls into the interval between zero and one, then the parameters a and α remain invariant but b increases several orders of magnitude. Therefore, we conclude that α is the most important parameter that describes the the fractional order dynamics of the phenomenon.

Figure 2 depicts the variation of the three parameters versus temperature. In this case we observe that a clear relationship is more difficult to reach.

Besides the numerical fitting details, expression (6) demonstrates that the time responses have a power law behavior, characteristic of fractional order systems. While

Table 1. Parameters of the Harris model for the tested temperatures T.

T (°C)	125	150	170	190
a	1.0047716	0.9902946	1.0036169	1.0001506
b	0.0113998	0.0128535	0.0184412	0.0201651
α	1.3157845	1.3949092	1.4216989	1.8460826
ρ	0.9999347	0.9998371	0.9998847	0.9994520
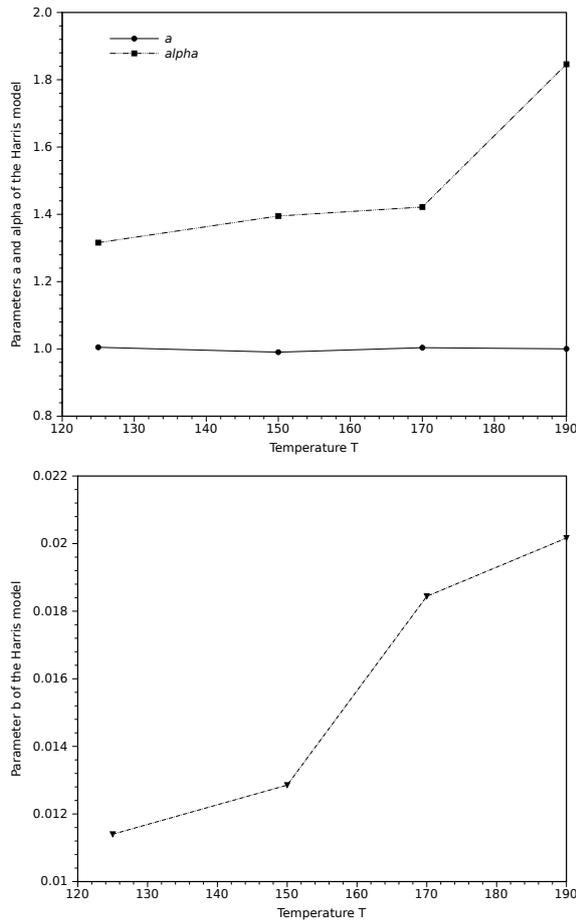
Figure 2. Parameters $\{a, b, \alpha\}$ of the Harris model versus temperature T (°C).

the numerical model fitting procedure may be open for discussion, since it is an experimental technique and other heuristic expressions can emerge, the long tails in the time response are doubtless a symptom of the fractional dynamics. Therefore, methods that demonstrate, in a more formal way, the fractional nature of the phenomenon addressed here remain to be developed.

5. Conclusions

We know that the standard classical mathematical models do not work adequately in several cases where power laws are reported. As a result some alternative modelling tools should be introduced to explain more accurately the experimental data.

In this manuscript we reported the existence of the power law in the data points generated from a ZLC diffusion experimental set-up for 1,3 Di-isopropyl benzene in 100% alumina matrix with variable particle size by using the Harris model. While the fitting of the responses over time is very good, the parameters b and c are shown to have a non-linear dependence on temperature T which needs to be analysed further. Therefore, this study is merely the first step in properly understanding the power law effect and the existence of the non-local phenomena which are present in the investigated process.

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