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# STOCHASTIC MODEL OF FIRST ORDER CHEMICAL REACTIONS TAKING PLACE IN PARTICLES

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Experimental observation had been made in the 1950s, that the application of the fluidisation method increases the formation rate and homogeneity of the iron oxide red product. Results of the interpretation of this observation by the recently developed mathematical models had been presented. The interpretation is based on the stochastic treatment of the virtual rate constant due to the random temperature differences of the particles at heating processes. The stochastic model is derived from the first order kinetic equations assuming uniform distribution for the rate constant and includes the momentum equations. Discussion of the model is described for different sets of parameters.

**Keywords:** stochastic model, particle dispersion processes, iron oxide red production, conversion rate, product homogeneity, momentum equation, particulate system

## Introduction

During the years of the '50s, an intensive research was lead by Prof. K. Polinszky, to study the properties of inorganic pigments and their production methods. This had been summarised elsewhere [1].

A group of inorganic pigments are produced by heat treatment of solid particles. For example:

- minium, from lead oxide,
- chromium oxide green, from potassium dichromate,
- iron oxide red from iron oxide black and yellow and from ferrous sulphate heptahydrate.

At that time one of the authors, T. Blickle, dealt with mathematical modelling and the application of fluidisation, respectively. As it was experienced, in a fluidised bed the conversion rate was higher than that in a rotating kiln, or in a steady layer. It was impossible to explain these phenomena by the available mathematical models.

The mathematical models of particle dispersion processes, including stochastic processes as well, had been studied in the recent and past decades [2-7]. Here we present the results of the interpretation of observations, gained by the recently developed mathematical model.

It is a crucial question what result can be obtained, if we treat the virtual rate constant as a stochastic parameter, due to the random temperature differences of the particles in thermal processes? The models of the first order processes are presented in the following:

## Stochastic Model

The kinetic equations:

$$\frac{dc_j^*}{dt} = -k_j c_j^* \tag{1}$$

$$c_j(0) - c_j(t) = -\lambda[c_j^*(0) - c_j^*(t)] \tag{2}$$

where $c_j^*$ is the concentration of the initial component, $c_j$ is the concentration of the final component in the $j^{th}$ particle, $\lambda$ is the stochiometric factor.

The virtual rate constant, $k$, is a stochastic variable with the probability density function, $B(k)$ and its $k_j$ values are assigned randomly to the $j^{th}$ particle by drawing according to this density function, i.e. $k_j$ is a realisation of $k$. In the moment of the start, the concentration frequency density function of the particles in the system is given by:

$$n\left[c(0), c^*(0), 0\right] \tag{3}$$

From *Eqs.(1)* and *(2)*, the transition functions can be obtained:

$$c_j^*(t) = c_j^*(0)e^{-k_j t} \tag{4}$$

$$c_j(t) = c_j(0) + \lambda c_j^*(0)(1 - e^{-k_j t}) \tag{5}$$

Density function $n\left[c(0), c^*(0), 0\right]$ and *Eqs.(4)* and *(5)* yield the following model of the integral transformation equation:

$$n\left[c(t), c^*(t), t\right] = \int_{k_m}^{k_M} n\begin{bmatrix} c(t) - \lambda c^*(t)(e^{kt} - 1), \\ c^*(t)e^{kt}, 0 \end{bmatrix} \cdot e^{kt} B(k)dk \tag{6}$$

The momentum equation is:

$$M_J(t) = \int_0^1 \int_0^1 c^J(t) n[c(t), c^*(t), t] dc(t) dc^*(t) \tag{7}$$

Using the *Eq.(6)*, one can get:

$$M_J(t) = \int_0^1 \int_0^1 \int_{k_m}^{k_M} c^J(t) n\begin{bmatrix} c(t) - \lambda c^*(t)(e^{kt} - 1), \\ c^*(t)e^{kt}, 0 \end{bmatrix} \cdot e^{kt} B(k)dk dc(t) dc^*(t) \tag{8}$$

By applying *Eqs.(4)* and *(5)*, and after transformation:

$$M_J(t) = \int_0^1 \int_0^1 \int_{k_m}^{k_M} [c(0) + c^*(0)\lambda(1 - e^{-kt})]^J \cdot n[c(0), c^*(0), 0] B(k) dk dc(0) dc^*(0) \tag{9}$$

Assuming that the distribution of $k$ values are uniform in the range of $k_m$ - $k_M$:

$$\bar{k} = \frac{k_m + k_M}{2}, \ \Delta k = k_M - k_m, \ \sigma_k = \frac{\Delta k}{\sqrt{12}}, \ \hat{\sigma}_k = \frac{\sigma_k}{\bar{k}}$$

Values $k_m$ and $k_M$ are the lower and upper limits of a uniform distribution, $\bar{k}$ is the average value of the uniformly distributed virtual rate constant, $\Delta k$ is the width and $\sigma_k$ is the standard deviation of its range, while $\hat{\sigma}_k$ is the coefficient of variation (relative standard deviation) of the uniformly distributed virtual rate constant.

$$\bar{c}(t) = \bar{c}(0) + \lambda \overline{c^*}(0)\left(1 - e^{-\bar{k}t} \frac{\sinh \frac{\Delta kt}{2}}{\frac{\Delta kt}{2}}\right) \tag{10}$$

$$\sigma^2(t) = \sigma^2(0) + \sigma^{*2}(0)\lambda^2\left(1 - 2e^{-\bar{k}t} \frac{\sinh \frac{\Delta kt}{2}}{\frac{\Delta kt}{2}}\right) + \lambda^2 \overline{c^*}^2(0)e^{-2\bar{k}t}\left[\frac{\sinh \Delta kt}{\Delta kt} - \left(\frac{\sinh \frac{\Delta kt}{2}}{\frac{\Delta kt}{2}}\right)^2\right] \tag{11}$$

Until now it was assumed, that the values of $k_j$, which had been drawn at $t = 0$ stay unchanged during the entire process. However, in many cases there are such effects in the system which make it necessary to draw again periodically, after each $\Theta$. Here, when the elapsed time, $\tau$ between two drawings is $0 < \tau \leq \Theta$ and $t$ time is:

$$t = l \cdot \Theta + \tau \tag{12}$$

where $l$ is the number of drawing.

If $\bar{c}(0) = 0$ and $\tau \neq 0$, then:

$$\bar{c}(t) = \lambda \overline{c^*}(0)\left[1 - e^{-\bar{k}t}\left(\frac{\sinh \bar{k}\Theta \frac{\sqrt{12}\hat{\sigma}_k}{2}}{\bar{k}\Theta \frac{\sqrt{12}\hat{\sigma}_k}{2}}\right)^l \cdot \left(\frac{\sinh \bar{k}\tau \frac{\sqrt{12}\hat{\sigma}_k}{2}}{\bar{k}\tau \frac{\sqrt{12}\hat{\sigma}_k}{2}}\right)\right] \tag{13}$$

If $\bar{c}(0) = 0$ and $\tau = 0$, then:

$$\bar{c}(t) = \lambda \overline{c^*}(0)\left[1 - e^{-\bar{k}t}\left(\frac{\sinh \bar{k}\Theta \frac{\sqrt{12}\hat{\sigma}_k}{2}}{\bar{k}\Theta \frac{\sqrt{12}\hat{\sigma}_k}{2}}\right)^l\right] \tag{13a}$$

If $\sigma^2(0) = \sigma^{*2}(0) = 0$ and $\tau \neq 0$, then:

$$\sigma^2(t) = \lambda^2 \overline{c^*}^2(0)e^{-2\bar{k}t} \cdot \left[\left(\frac{\sinh \bar{k}\Theta\sqrt{12}\hat{\sigma}_k}{\bar{k}\Theta\sqrt{12}\hat{\sigma}_k}\right)^l \frac{\sinh \bar{k}\tau\sqrt{12}\hat{\sigma}_k}{\bar{k}\tau\sqrt{12}\hat{\sigma}_k} - \left(\frac{\sinh \bar{k}\Theta \frac{\sqrt{12}}{2}\hat{\sigma}_k}{\bar{k}\Theta \frac{\sqrt{12}}{2}\hat{\sigma}_k}\right)^{2l}\left(\frac{\sinh \bar{k}\tau \frac{\sqrt{12}}{2}\hat{\sigma}_k}{\bar{k}\tau \frac{\sqrt{12}}{2}\hat{\sigma}_k}\right)^2\right] \tag{14}$$

If $\sigma^2(0) = \sigma^{*2}(0) = 0$ and $\tau = 0$, then:

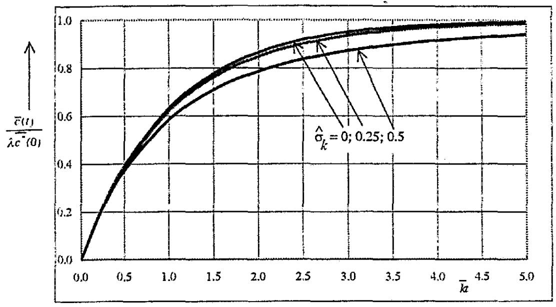

*Fig.1* Plot of conversion against time, at different relative ranges of the virtual rate constant

$$\sigma^2(t) = \lambda^2 \overline{c^*}^2(0) e^{-2\bar{k}t} \left[ \left( \frac{\sinh \bar{k}\Theta\sqrt{12}\hat{\sigma}_k}{\bar{k}\Theta\sqrt{12}\hat{\sigma}_k} \right)^l - \left( \frac{\sinh \bar{k}\Theta \frac{\sqrt{12}}{2} \hat{\sigma}_k}{\bar{k}\Theta \frac{\sqrt{12}}{2} \hat{\sigma}_k} \right)^{2l} \right] \tag{14a}$$

Because $\lim_{x \to 0} \frac{\sinh x}{x} = 1$ if $\tau$ and $\Theta$ converges to 0, while $t$ is constant:

$$\bar{c}(t) = \lambda \overline{c^*}(0)\left[1 - e^{-\bar{k}t}\right] \tag{15}$$

$$\sigma^2(t) = 0 \tag{16}$$

## Discussion of the Stochastic Model

*Eqs.(13a)* and *(14a)* are used.

Case1

$\tau = 0$; $l = 1$; $\bar{c}(0) = 0$ (in this case $t = \Theta$ ). While discussing the function $\frac{\bar{c}(t)}{\lambda \overline{c}^*(0)} \div \bar{k}t$ let $\hat{\sigma}_k$ be 0; 0.25; 0.5. (See *Fig.1.*)

Case2

$\tau = 0$; $l = 1$, $\bar{c}(0) = 0$, $\sigma^2(0) = \sigma^{*2}(0) = 0$. Here we discuss $\hat{\sigma}(t) = \frac{\sigma(t)}{\bar{c}(t)} \div \bar{k}t$ relationship, if $\hat{\sigma}_k = 0.25; 0.5$. (*Fig.2.*)

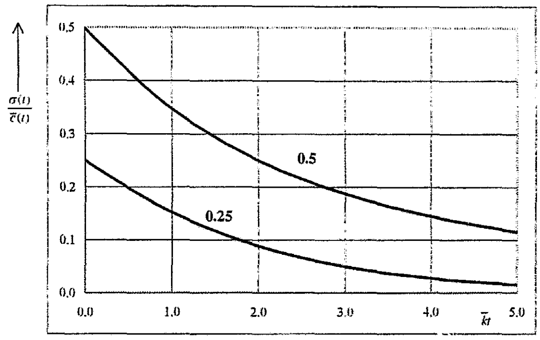

*Fig.2* Plot of relative concentration variance against time, at different relative ranges of the virtual rate constant

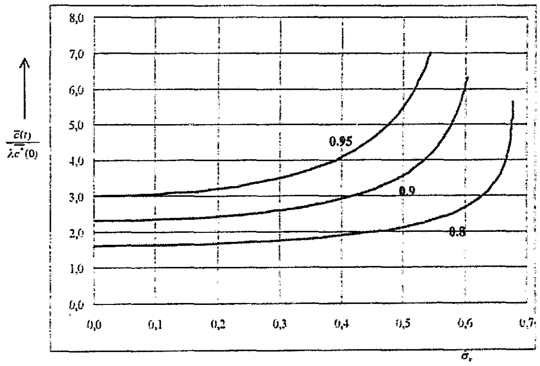

*Fig.3* Plot of conversion against the relative range of the virtual rate constant, at different times

Case3

Here the $\frac{\bar{c}(t)}{\lambda \overline{c}^*(0)}$ is studied at different (0.8, 0.9, 0.95) values of the necessary time $t$ (if $\tau = 0$, $l = 1$, $\bar{c}(0) = 0$) as a function of $\hat{\sigma}_k$. (See *Fig.3.*)

Case4

We studied $\bar{c}$ and $\sigma^2(t)$ at different $l$ values. Let $\tau = 0$; and for example $\bar{k}t = 1$, $\sqrt{12}\hat{\sigma} = 2$. *Eq.(13a)* is then:

$$\bar{c}(t) = \lambda \overline{c^*}(0)\left[1 - e^{-1}\left(\sinh \frac{1}{l}\right)^l\right] \tag{17}$$

and *Eq.(14a)*:

$$\sigma^2(t) = \lambda^2 \overline{c^*}^2(0) e^{-2} \left[ \left( \frac{\sinh \frac{2}{l}}{\frac{2}{l}} \right)^l - \left( \frac{\sinh \frac{2}{l}}{\frac{2}{l}} \right)^{2l} \right] \tag{18}$$

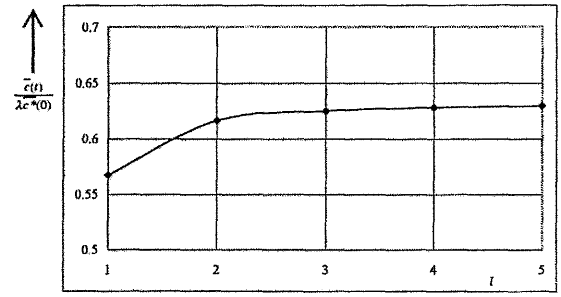

*Fig.4* Plot of conversion against the number of drawings

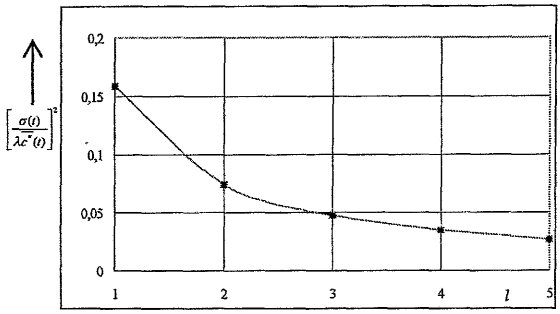

*Fig.5* Plot of concentration variance against the number of drawings

*Fig.4* shows the $\frac{\overline{c}(t)}{\lambda \overline{c}^*(0)} \div l$ relationship according to *Eq.(17)*, while the $\left[\frac{\sigma(t)}{\lambda \overline{c}^*(t)}\right]^2 \div l$ function according to *Eq.(18)* is plotted in *Fig.5*.

## Conclusions

On the basis of the above discussions it could be concluded:

i. The conversion time and the relative standard deviation of the product concentration are increasing as the relative standard deviation of the virtual rate constant increases. (*Fig.1*, *Fig.2* and *Fig.3*.)
ii. At a given $\theta$ as $l$ increases the conversion increases and the variance decreases. (*Fig.4* and *Fig.5*.)
iii. In steady layer system $\tau \to 0$ and $l = 1$; in rotating kiln when $\theta$ is a given value: $l = \frac{t}{\theta}$ (that is the time of one revolution) and σ is less then in a steady layer; while in fluidised layer $\theta \to 0$, $l \to \infty$ and $\sigma \to 0$.
iv. These all, in our opinion, support the experimental observation: at the ferric oxide red production the fluidisation increased the rate of conversion and the homogeneity of the product.

## Summary

It is an experimental observation made in the years of the '50s, that the application of the fluidisation method has increased the formation rate and homogeneity of the iron oxide red product. It could be explained by the models developed later that, the virtual rate constant is a stochastic variable due to the variation of the temperature in the fluidised bed. This stochastic model showed the most important tendencies as well.

## REFERENCES

1. POLINSZKY K.: Further examinations on the chemistry and technology of iron oxide pigments. (in Hungarian) Veszprém, 1960
2. BLICKLE T., MIHÁLYKÓ C. and LAKATOS B.: Mathematical models of particle dispersion systems and their processes.(in Hungarian). Proceedings of the Conference of Technical Chemistry Days, Veszprém, 7-13, 2000
3. BLICKLE T., MIHÁLYKÓ C. and LAKATOS B.: Stochastic and deterministic models of processes taking place in operation units (in Hungarian) Proceedings of the Conference of Technical Chemistry Days, Veszprém, 25-30, 2001
4. CHEN X. -Q. and Pereira J. C. F.: International Journal of Heat and Mass Transfer, *1997*, 40, 1727-1741
5. MARCHISIO D. L., BARRESI A. A. and GARBERO M.: AICHE Journal, *2002*, 48, 2039-2050
6. HILL P. J. and NG K. M.: Chem. Eng. Sci., *2002*, 57, 2125-2138
7. JONES A. G., HOSTOMSKY. J. and WACHI. S.: Chem. Eng. Comm., *1996*, 146, 105-130