

Modeling Micromixing Effects in a CSTR

CSTR, of all well behaved reactors, has the widest RTD i.e. $\bar{\sigma}^2 = 1$. This means that large differences in performance can exist between segregated flow and operations at maximum mixedness conditions.

The easiest thing to treat is the case of a premixed feed. A number of models exist. Among them some are based on population balances.

Let us consider the population balance description of a CSTR.

Consider that the fluid in the reactor can be represented by fluid elements of the same size but with different reactant concentrations. The fraction of the fluid in the system that has concentration of reactant A in the range between C_A and $C_A + dC_A$ at time t is $\psi(C_A, t)$. The probability density function of interest is a two place function $\psi(C_A, t)$. Here we assume that the fluid is premixed in the feed. If that was not the case, then for a reaction between A and B we would need a 3 place function $\psi(C_A, C_B, t)$. For the premixed case

$$\psi = \psi(C_A, t)$$

The general population balance equation is:

$$\frac{\partial \psi}{\partial t} + \frac{\partial(\psi R_A)}{\partial C_A} + \bar{D} - \bar{B} = \frac{1}{t}(\psi_{in} - \psi) \quad (1)$$

Define the moments of the p.d.f.

$$\mu_n = \int_{C_{A_m}}^{C_{A_M}} C^n \psi dC \quad \mu_0 = \int_{C_{A_m}}^{C_{A_M}} \psi dC = 1 \text{ by definition of } \psi$$

Acknowledge that the time rate of change of the property characterizing the p.d.f which is reactant concentration is the reaction rate i.e.

$$\frac{dC_A}{dt} = R_A$$

where R_A is the rate of generation of A by reaction (hence for a reactant it is negative).

Then consider obtaining the moments from the above partial differential equation.

$$\begin{aligned} \int_{C_{A_m}}^{C_{A_M}} \frac{\partial \psi}{\partial t} C^n dC &= \frac{d}{dt} \int_{C_{A_m}}^{C_{A_M}} C^n \psi dC - C_{A_M}^n \psi(C_{A_M}) \frac{dC_{A_M}}{dt} + C_{A_m}^n \psi(C_{A_m}) \frac{dC_{A_m}}{dt} \\ &= \frac{d\mu_n}{dt} \end{aligned}$$

$$\int_{C_{A_m}}^{C_{A_M}} C^n \frac{\partial(\psi R_A)}{\partial C} dC = C_{A_M}^n \psi(C_{A_M}) R_A(C_{A_M}) - C_{A_m}^n \psi(C_{A_m}) R_A(C_{A_m})$$

$$- n \int_{C_{A_m}}^{C_{A_M}} C^{n-1} R_A(C) \psi dC$$

$$\frac{1}{t} \int_{C_{A_m}}^{C_{A_M}} C^n (\psi_{in} - \psi) dC = \frac{1}{t} (\mu_{n_m} - \mu_n)$$

$$\bar{D} = \omega \psi(C_A) \int_{C_{A_m}}^{C_{A_M}} \psi(C') dC' = \omega \psi(C_A) \mu_0$$

$$\int_{C_{A_m}}^{C_{A_M}} C^n \bar{D} dC = \mu_0 \int_{C_{A_m}}^{C_{A_M}} \omega C^n \psi dC = \omega \mu_0 \int_{C_{A_m}}^{C_{A_M}} C^n \psi dC = \omega \mu_n \mu_0$$

If $\omega = \text{const}$, not function of C_A

$$\bar{B} = \omega \int_{C_{A_m}}^{C_{A_M}} \int_{C_{A_m}}^{C_{A_M}} \psi(C') \psi(C'') \delta\left(\frac{C'+C''}{2} - C\right) dC' dC''$$

$$\int_{C_{A_m}}^{C_{A_M}} C^n \bar{B} dC = \omega \int_{C_{A_m}}^{C_{A_M}} \int_{C_{A_m}}^{C_{A_M}} \psi(C') \psi(C'') dC' dC'' \int_{C_{A_m}}^{C_{A_M}} C^n \delta\left(\frac{C'+C''}{2} - C\right) dC$$

$$= \frac{1}{2^n} \omega \int_{C_{A_m}}^{C_{A_M}} C \int_{C_{A_m}}^{C_{A_M}} \psi(C') \psi(C'') (C' + C'')^n dC' dC''$$

$$= \frac{\omega}{2^n} \int_{C_{A_m}}^{C_{A_M}} \int_{C_{A_m}}^{C_{A_M}} \sum_{k=0}^n \binom{n}{k} C^{n-k} C''^k \psi(C') \psi(C'') dC' dC''$$

$$= \frac{\omega}{2^n} \sum_{k=0}^n \binom{n}{k} \int_{C_{A_m}}^{C_{A_M}} C^{n-k} \psi(C') dC' \int_{C_{A_m}}^{C_{A_M}} C''^k \psi(C'') dC''$$

$$= \frac{\omega}{2^n} \sum_{k=0}^n \binom{n}{k} \mu_{n-k} \mu_k \quad \text{where} \quad \binom{n}{k} = \frac{n!}{(n-k)!k!}$$

In the formulas below we anticipate the result that $\mu_0 = 1$.

$$\underline{n=0} \Rightarrow \omega \mu_0^2 = \omega$$

$$\underline{n=1} \Rightarrow \frac{\omega}{2} [\mu_1 \mu_0 + \mu_0 \mu_1] = \omega \mu_1 \mu_0 = \omega \mu_1$$

$$\begin{aligned} \underline{n=2} \Rightarrow \frac{\omega}{4} [\mu_2 \mu_0 + 2\mu_1^2 + \mu_0 \mu_2] &= \frac{\omega}{2} [\mu_1^2 + \mu_2] \\ &= \frac{\omega}{2} [\sigma^2 + 2\mu_1] = \omega \left[\frac{\sigma^2}{2} + \mu_1^2 \right] = 2\beta \left[\frac{\sigma^2}{2} + \mu_1^2 \right] \end{aligned}$$

$$\underline{n=3} \Rightarrow \frac{\omega}{4} [\mu_3 \mu_0 + 3\mu_2 \mu_1] = \frac{\omega}{4} [\mu_3 + 3\mu_2 \mu_1]$$

The following equations for the moments are obtained:

$$\frac{d\mu_n}{dt} - n \int_{C_{A_m}}^{C_{A_M}} C^{n-1} R_A(C) \psi(C) dC + \frac{\omega}{2^n} \sum_{k=0}^n \binom{n}{k} \mu_{n-k} \mu_k - \omega \mu_n \mu_0 = \frac{1}{t} (\mu_{n,in} - \mu_n) \quad n = 0, 1, \dots \quad (2)$$

For $n = 0$ we get:

$$\frac{d\mu_0}{dt} + \omega \mu_0^2 - \omega \mu_0^2 = \frac{1}{t} (\mu_{0,in} - \mu_0)$$

$$\frac{d\mu_0}{dt} = \frac{1}{t} (\mu_{0,in} - \mu_0)$$

$$t = 0 \quad \mu_0 = 1$$

Since $\mu_{0,in} = 1$, then it follows that $\mu_0 = 1$ always.

For $n = 1$ we get from eq (2):

$$\frac{d\mu_1}{dt} - \int_{C_{A_m}}^{C_{A_M}} R_A(C) \psi(C) dC + \omega \mu_1 \mu_0 - \omega \mu_1 \mu_0 = \frac{1}{t} (\mu_{1,in} - \mu_1)$$

$$\frac{d\bar{C}_A}{dt} = \int_{C_{A_m}}^{C_{A_M}} R_A(C) \psi(C) dC + \frac{1}{t} (\bar{C}_{A_o} - \bar{C}_A) \quad (3)$$

$$t = 0 \quad \bar{C}_A = \bar{C}_{A_i} \quad (3a)$$

Valid for: i) non-reactive tracer $R_A = 0$
 ii) transient reaction
 iii) steady state reactor with $\frac{d}{dt} \equiv 0$

1. Need to express $\int_{C_{A_m}}^{C_{A_M}} R_A(C) \psi(C) dC$ in terms of the moments and close the equation for the moments.

2. Need to relate β to experimental or theoretical descriptions of turbulence and micromixing in the system. First get equation for σ_c^2 (n=2).

For n = 2, we get from eq (2):

$$\frac{d\mu_2}{dt} - 2 \int_{C_{Am}}^{C_{AM}} C R_A(C) \psi(C) dC + \frac{\omega}{2} [\mu_2 + \mu_1^2] - \omega \mu_2 = \frac{1}{t} [\mu_{2,in} - \mu_2]$$

But $\mu_2 = \sigma^2 + \mu_1^2$

$$\begin{aligned} \frac{d\sigma^2}{dt} + 2\mu_1 \frac{d\mu_1}{dt} - 2 \int_{C_{Am}}^{C_{AM}} C R(C) \psi(C) dC - \omega \left(\frac{\sigma^2}{2} + \mu_1^2 \right) \\ + \omega (\sigma^2 + \mu_1^2) = \frac{1}{t} [\sigma_{in}^2 + \mu_{1,in}^2 - \sigma^2 - \mu_1^2] \end{aligned}$$

$$\begin{aligned} \frac{d\sigma^2}{dt} = 2 \int_{C_{Am}}^{C_{AM}} C R(C) \psi(C) dC - 2\mu_1 \int_{C_{Am}}^{C_{AM}} R(C) \psi(C) dC + \frac{\omega}{2} \sigma^2 \\ - 2\mu_1 (\mu_{1,in} - \mu_1) = \frac{1}{t} [\sigma_{in}^2 - \sigma^2 + (\mu_{1,in}^2 - \mu_1^2)] \end{aligned}$$

Now let $2\beta = \omega$ and obtain the final equation for evolution of the variance of concentration fluctuations.

$$\frac{d\sigma^2}{dt} = 2 \int_{C_{Am}}^{C_{AM}} (C - \bar{C}_A) R(C) \psi(C) dC - \beta \sigma^2 + \frac{1}{t} [\sigma_{in}^2 - \sigma^2 + (\bar{C}_{A_o} - \bar{C}_A)^2] \quad (4)$$

$$t = 0 \quad \sigma^2 = \sigma_i^2 \quad (4')$$

Based on the population balance for a perfectly mixed vessel of $V = \text{const}$ on a global scale i.e

$$\bar{\psi} = \psi_{out}$$

where

$$\bar{\psi}(C_A) dC_A = \text{fraction of fluid elements of concentration between } C_A \text{ and } C_A + dC_A$$

we arrive to the following two equations for the mean

$$\bar{C}_A = \int C_A \bar{\psi}(C_A) dC_A$$

and the variance

$$\sigma_c^2 = \int (C_A - \bar{C}_A)^2 \bar{\psi}(C_A) dC_A = \int C_A^2 \bar{\psi}(C_A) dC_A - \bar{C}_A^2$$

$$\frac{d\bar{C}_A}{dt} = \int R_A \bar{\psi}(C_A) dC_A + \frac{1}{t} (\bar{C}_{A0} - \bar{C}_A) \quad (3)$$

$$\frac{d\sigma_c^2}{dt} = 2 \int (C_A - \bar{C}_A) R_A \bar{\psi}(C_A) dC_A + \frac{1}{t} \left[\sigma_{co}^2 - \sigma_c^2 + (\bar{C}_{A0} - \bar{C}_A)^2 \right] - \beta \sigma_c^2 \quad (4)$$

where $\frac{dC_A}{dt} = R_A$ and $\sigma_{co}^2 = \sigma_{in}^2$

Consider first a reactor at steady state and a first order process $R_A = -k_1 C_A$

$$0 = -k_1 \int C_A \bar{\psi}(C_A) dC_A + \frac{1}{t} (\bar{C}_{A0} - \bar{C}_A)$$

assume also no concentration fluctuations in the inlet line $\bar{C}_{A0} = C_{A0}$, $\sigma_{co}^2 = 0$

We get

$$0 = -k_1 \bar{C}_A + \frac{1}{t} (C_{A0} - \bar{C}_A) \quad (3a)$$

which is the formula for a perfectly mixed CSTR. Moreover from eq (4)

$$0 = -2k_1 \int (C_A - \bar{C}_A) C_A \bar{\psi}(C_A) dC_A + \frac{1}{t} \left[-\sigma_c^2 + (C_{A0} - \bar{C}_A)^2 \right] - \beta \sigma_c^2 \quad (4a)$$

$$\bar{\sigma}_c^2 = \left(\frac{\sigma_c}{\bar{C}_A} \right)^2 = \frac{(k_1 \bar{t})^2}{1 + \beta \bar{t} + 2k_1 \bar{t}} \quad \bar{\sigma}_c^2 = \frac{Da_1^2}{1 + \beta \bar{t} + 2Da_1}$$

The mean value of the concentration \bar{C}_A in unaffected by concentration fluctuations, we know that first order process is independent of micromixing, but the variance of concentration fluctuations is affected by the Damkohler number for the reaction. At fixed collision frequency β the concentration fluctuations increase with increase in $Da_1 = k_1 \bar{t}$.

At fixed Da_1 , an increase in β reduces $\bar{\sigma}_c^2$.

Now consider a 2nd order process in a reactor at steady state

$$0 = -k_2 \int C_A^2 \bar{\psi}(C_A) dC_A + \frac{1}{t} (C_{A0} - \bar{C}_A) \quad (3b)$$

$$0 = -2k_2 \int (C_A - \bar{C}_A) C_A^2 \bar{\psi}(C_A) dC_A + \frac{1}{t} \left[0 - \sigma_c^2 + (C_{A0} - \bar{C}_A)^2 \right] - \beta \sigma_c^2 \quad (4b)$$

This yields (1st equation)

$$-k_2(\sigma_c^2 + \bar{C}_A^2) + \frac{1}{\bar{t}}(C_{Ao} - \bar{C}_A) = 0$$

or

$$\bar{t} = \frac{C_{Ao} - \bar{C}_A}{k_2(\bar{C}_A^2 + \sigma_c^2)} \quad (3c)$$

$$Da_2 = \frac{1 - \bar{C}_A / C_{Ao}}{(\bar{C}_A / C_{Ao})^2 + \sigma_c^2 / C_{Ao}^2}$$

Since

$$\bar{C}_A = \frac{-1 + \sqrt{1 + 4k_2\bar{t}(C_{Ao} - k_2\sigma_c^2\bar{t})}}{2k_2\bar{t}}$$

Clearly

$$\bar{C}_{A\sigma^2=0} > \bar{C}_{A\sigma^2 \neq 0}$$

$$\bar{C}_{A_{\max \text{ mix}}} > \bar{C}_{A_{\text{partial aegregation}}}$$

$$X_{A_{\max \text{ max}}} \leq X_{\text{partial sequence}}$$

Reactor performance clearly depends now on concentration fluctuations. We cannot obtain \bar{C}_A without knowing σ_c^2 . However, solution of eq (4b) now requires the third moment of the $\bar{\psi}(C_A)$ density function. Thus, we encounter the problem of closure, i.e we would need then one more equation for the third moment but this would introduce additional moments, etc. Two approaches are possible:

i) we can assume the form of $\bar{\psi}(C_A)$ and calculate the required third moment from this form.

or

ii) assume that concentration fluctuations are symmetric and therefore the third central moment (skewness) of the $\bar{\psi}(C_A)$ is zero, i.e: $\int (C_A - \bar{C}_A)^3 \bar{\psi}(C_A) dC_A = 0$

This implies (if we define $\mu_n = \int C_A^n \bar{\psi}(C_A) dC_A$ and $\mu_1 = \bar{C}_A, \mu_2 = \sigma_c^2 + \bar{C}_A^2$) that

$$\mu_3 - 3\mu_2\bar{C}_A + 3\bar{C}_A^3 - \bar{C}_A^3 = \mu_3 - 3\mu_2\bar{C}_A - 2\bar{C}_A^3 = 0$$

$$\text{Hence } \mu_3 = 3\mu_2\bar{C}_A + 2\bar{C}_A^3$$

Therefore we get

$$\int (C_A - \bar{C}_A) C_A^2 \bar{\psi}(C_A) dC_A = \mu_3 - \bar{C}_A \mu_2 = 3\mu_2 \bar{C}_A - 2\bar{C}_A^3 - \bar{C}_A \mu_2$$

$$= 2\bar{C}_A \mu_2 - 2\bar{C}_A^3 = 2\bar{C}_A \sigma_c^2$$

This yields

$$\left(k_2 \bar{t} \bar{C}_A\right)^2 \left[\left(\frac{\sigma_c}{\bar{C}_A} \right)^2 + 1 \right]^2 = \left(\frac{\sigma_c}{\bar{C}_A} \right)^2 (4k_2 \bar{t} \bar{C}_A + \beta \bar{t} + 1) \quad (4c)$$

Now eqs (3c) and (4c) must be solved simultaneously for \bar{C}_A and σ_c^2 provided of course β is given and kinetic constant k_2 is known.

Although based on an ideal (exponential) RTD this is now a one parameter micromixing model for a CSTR with imperfect mixing on molecular level. The parameter is β . How can β be obtained?

1. If we could measure concentration variations around the mean in a steady state reactor then σ_c^2 would be given directly and we could calculate \bar{C}_A from eq (3b) and β from eq (4b). However, in that case we would also know \bar{C}_A by direct measurement and this would not be a useful predictive method but could be used to test the theory. It is not easy to measure concentration variations on a small scale in an exit line of a reactor or in the reactor itself. Methods for this need to be developed.
2. We could perform a tracer study. Suppose we introduce a step input of tracer $C_oH(t)$. Then $\psi_o = \delta(C - C_o)$ and the tracer is non reactive so that $R = 0$.

Then the equations for the first moment and the variance become:

$$\frac{d\bar{C}}{dt} = \frac{1}{\bar{t}}(C_o - \bar{C}) \quad (3d)$$

$$\frac{d\sigma_c^2}{dt} = \frac{1}{\bar{t}}[-\sigma_c^2 + (C_o - \bar{C})^2] - \beta\sigma_c^2 \quad (4d)$$

$$\bar{C} = C_o(1 - e^{-t/\bar{t}})$$

$$\sigma_c^2 = C_o^2 e^{-t/\bar{t}} \frac{e^{-t/\bar{t}} - e^{-\beta \bar{t}(t/\bar{t})}}{\beta \bar{t} - 1}$$

$$\beta \bar{t} \rightarrow \infty \quad \sigma_c^2 = 0 \quad \text{perfect mixing}$$

$$\text{Take } \frac{d\sigma_c^2}{dt} = 0 \Rightarrow t_{\max}$$

$$t_{\max} = \bar{t} \frac{\ln\left(\frac{\beta \bar{t} + 1}{2}\right)}{\beta \bar{t} - 1} \quad (5)$$

If one could accurately measure σ_c^2 vs t then one could experimentally determine the time, t_{\max} , at which σ_c^2 is maximal. From t_{\max} and eq (5) the value of β can be calculated.

If the flow through the tank does not contribute much to its hydrodynamic behavior (large \bar{t} , high RPM, large Re, well baffled system) then a batch tracer experiment is easier to perform i.e introduce $m_T \delta(t)$ of tracer in a vessel with no net flow in or out i.e $\bar{t} \rightarrow \infty$.

Then

$$\frac{d\bar{C}}{dt} = 0 \quad (3e)$$

$$\frac{d\sigma_c^2}{dt} = -\beta\sigma_c^2 \quad (4e)$$

$$t = 0 \quad \bar{C} = \frac{m_T}{V} \quad ; \quad \sigma_c^2(0) \\ \uparrow \text{unknown}$$

$$\ln \sigma_c^2 = \ln \sigma_{c0}^2 - \beta t \quad (6)$$

A semilogarithmic plot of $\ln \sigma_c^2$ vs t should yield a straight line with a slope of $-\beta$.

Evangelista, J.J., Shinnar, R. and S. Katz, AIChE J., 15, 843-853 (1969), from which the above treatment is taken, try to relate β to the degree of segregation J of Danckwerts by

$$J = 1 - \frac{VAR(\alpha_t)}{VAR(\alpha)} = \frac{1}{1 + \beta \bar{t}} \quad (7)$$

The question still remains how to measure concentration variations on a small scale in the outflow. One should also prove that the ones in the outflow have the same variance as the fluctuations in the vessel. Scattering of light due to gradients in refractive index, fiber optics and colored tracers, micro-conductivity cells have all been suggested. The student should consult the turbulence literature for possible experimental tools.

Another approach is to assume that fluctuations on small time scale are related to space fluctuations at a given time. A fast responding instrument records values of C over $\Delta t = \varepsilon$ interval and finds \bar{C} and σ_c^2 for the interval. The question then arises on how to show that the values obtained are independent of ε over a range of $\varepsilon(0, \varepsilon_0)$ and that the space and time variations are correlated. Statistical methods need to be consulted.

3. The final approach is to calculate β from turbulence theory or more specifically the theory of isotropic turbulence. To do that we need to digress and review briefly some key concepts of turbulent mixing.