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Micro-Mixing in a Continuous Flow Reactor (Coalescence and Redispersion Models)

By

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For the fluid mixing which occurs in a continuous flow reactor, two different mechanisms must be considered. The one is macro-mixing resulting from the difference in residence time of outflowing fluid and the other is micro-mixing caused by the mass exchange between fluid elements.

In this paper new models for the micro-mixing are presented as follows: The incoming fluid is broken up into discrete fragments of equal volume which are small enough compared to the reactor size. A fragment of fluid comes into contact and coalescence with another $1/t_c$ times per unit time on an average, and is immediately rebroken into two fragments of equal volume. The concentration in the fragments becomes uniform at the instant of coalescence.

From the above assumptions, the basic design equations are derived, and for the ideal perfect macro-mixing reactor, the effect of micro-mixing on the conversion of zero, first, and second order reactions is considered. In the case of first order reactions the micro-mixing has no effect on the conversion. In the case of reactions of zero and second order, the conversion is calculated by equations (24), (36) and (30), (38), respectively. And the validity of these equations for second order reaction is discussed using a reaction which takes place in liquid droplets dispersed in an inert phase.

1. Introduction

For the fluid mixing which occurs in the continuous flow reactor, two different mechanisms must be considered; the one is the mixing resulting from the difference in residence time of outflowing fluid from the reactor, and the other is the mixing caused by the exchange of mass among fluid elements. The residence time distribution is originated from the statistical phenomenon, i.e., what is the discharging probability of a fluid element flowing out of a reactor when the inflowing fluid is broken up into a large number of elements with an equal volume. Therefore, the mass exchange among elements is neglected when only the mixing based on the residence time distribution is considered. The exchange of mass

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among elements, however, is one of the important factors for rate processes, such as chemical reactions and mass transfer in the continuous flow system. In this paper, the mixing based on the residence time distribution is called "macro-mixing" and that caused by mass exchange "micro-mixing".

Miyauchi³⁾ and Rietema⁵⁾ considered a chemical reaction taking place within droplets that are dispersed in a continuous phase, which has no effect on the reaction, in a perfect macro-mixing tank. They pointed out the following: For the reaction of an order lower than unity referring to the reactant in the dispersed phase, the interaction between dispersed droplets increases the overall conversion. The conversion of zero order reaction in the droplets of highest interaction is the same as that in batchwise operation or in a piston flow reactor. When the order of reaction is unity, this effect of interaction disappears. For the reaction of an order higher than unity, the effect of interaction appears again, but in the opposite way, so that interaction decreases the overall conversion. However, the results as mentioned above are only obtained in both extremes of micro-mixing, i.e., in the state of perfect intermingling or no interaction between droplets.

Danckwerts²⁾ also obtained the same conclusion for a continuous homogeneous reaction in a perfect macro-mixing tank. Danckwerts introduced the intensity of segregation, J , to express the intensity of micro-mixing. As Zwietering⁶⁾ pointed out, however, lower limiting value of J is not always zero but takes a value depending on the intensity of macro-mixing.

Nishimura and coworkers⁴⁾ introduced the concept of collision probability of the fluid elements and obtained approximate solution of second order reaction for the case where the collision probability is close to both the limiting values stated above.

Zwietering⁶⁾ considered a continuous flow reactor with side flow in the paper criticizing the Dankwerts' report²⁾.

In this paper, the authors propose models of coalescence and redispersion for micro-mixing, and estimate the effects of micro-mixing on the conversion in continuous flow reactor using this model.

2. Coalescence and redispersion model (I)

Let the case be considered where the reaction takes place in the dispersed droplets which are suspended in an inert continuous phase. The following assumptions are made;

- (1) The incoming fluid is broken up at the moment of introduction to discrete fragments of equal volume which are far smaller compared with reactor size.
- (2) A dispersed droplet coalesces with the surrounding droplets $1/t_c$ times per

unit time on an average and is immediately rebroken into two droplets of equal volume. The process of coalescence is represented by the following way; the incoming droplet coalesces for the first time after the lapse of time $t_c/2$ in the reactor and after that coalesces again at the interval of time, t_c . More than three droplets do not coalesce at the same time.

- (3) As soon as coalescence occurs, the concentration of reactant within droplets which are newly produced by the coalescence becomes uniform.
- (4) Density of the dispersed phase is constant regardless of the progress of reaction.

Fig. 1 shows the chain of the process of coalescence and redispersion of a representative droplet based on the above assumptions.

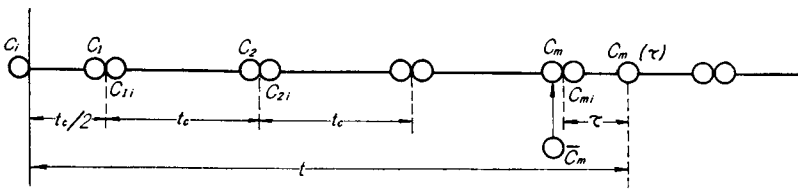


Fig. 1. Coalescence and redispersion process of a representative droplet in model (I).

Consider the droplets which are flowing out a reactor in a steady state operation at a certain time. Of the outflowing droplets at a certain time, the fraction of the droplets with residence time between τ and $\tau + \Delta\tau$ which is shorter than $t_c/2$ is denoted by $f_0(\tau)\Delta\tau$, and the concentration of reactant in the representative droplet at time τ is denoted by $C_0(\tau)$. Expressing the volumetric flow rate of the dispersed phase by F , the rate of outflowing fluid with residence time between τ and $\tau + \Delta\tau$ is $Ff_0(\tau)\Delta\tau$, and the quantity of the reactant contained in $Ff_0(\tau)\Delta\tau$ is $FC_0(\tau)f_0(\tau)\Delta\tau$. Therefore, the outflowing rate of reactant carried by the representative droplets, which have a residence time shorter than $t_c/2$ and have no chance of coalescence is given as follows:

$$F \int_0^{t_c/2} C_0(\tau) f_0(\tau) d\tau \tag{1}$$

Of the droplets produced by the first coalescence and redispersion at time $t_c/2$, the fraction of the droplets staying further for time τ after that is denoted by $f_1(\tau)$ and the concentration of those by $C_1(\tau)$. Since the fraction of the droplets in the reactor with residence time longer than $t_c/2$, at a certain moment, is $1 - \int_0^{t_c/2} f_0(\tau) d\tau$, the outflowing rate of the dispersed phase with residence time between $\frac{1}{2}t_c + \tau$ and $\frac{1}{2}t_c + \tau + \Delta\tau$ (the latter is shorter than $3t_c/2$) is given as follows:

$$F \left\{ 1 - \int_0^{t_c/2} f_0(\tau) d\tau \right\} f_1(\tau) d\tau$$

The outflowing rate of reactant carried by the droplets which flow out after only one coalescence and redispersion is given as follows:

$$F \left\{ 1 - \int_0^{t_c/2} f_0(\tau) d\tau \right\} \int_0^{t_c} C_1(\tau) f_1(\tau) d\tau \quad (2)$$

Since $f_1(\tau)$ is the fraction of droplets staying in the reactor for an additional time τ after the first coalescence and redispersion among those which have been staying in the reactor for more than $t_c/2$, the following equation is obtained:

$$\left\{ 1 - \int_0^{t_c/2} f_0(\tau) d\tau \right\} f_1(\tau) = f_0 \left(\frac{1}{2} t_c + \tau \right) \quad (3)$$

Accordingly, equation (2) is written as follows:

$$F \int_0^{t_c} C_1(\tau) f_0 \left(\frac{1}{2} t_c + \tau \right) d\tau \quad (2')$$

Consider the droplets produced by m -th coalescence and redispersion. The fraction of the droplets staying further for time τ after that and the concentration of reactant in those droplets are denoted by $f_m(\tau)$ and $C_m(\tau)$, respectively.

The outflowing rate of the reactant carried by the representative droplets which flow out of the reactor after the repetition of m -times of coalescence and redispersion is given by the following equation:

$$\begin{aligned} & F \left\{ 1 - \int_0^{t_c/2} f_0(\tau) d\tau \right\} \left[\prod_{m=1}^{m-1} \left\{ 1 - \int_0^{t_c} f_m(\tau) d\tau \right\} \right] \int_0^{t_c} C_m(\tau) f_m(\tau) d\tau \\ & = F \int_0^{t_c} C_m(\tau) f_0 \left\{ \left(m - \frac{1}{2} \right) t_c + \tau \right\} d\tau \end{aligned} \quad (4)$$

The dispersed phase flowing out of the reactor at a certain moment must be the sum of all representative droplets which have repeated the multifarious times of coalescence and redispersion. Therefore, the average concentration of the dispersed phase, \bar{C}_o , flowing out of the reactor is given as follows:

$$\bar{C}_o = \int_0^{t_c/2} C_0(\tau) f_0(\tau) d\tau + \sum_{m=1}^{\infty} \int_0^{t_c} C_m(\tau) f_0 \left\{ \left(m - \frac{1}{2} \right) t_c + \tau \right\} d\tau \quad (5)$$

Since $\left(m - \frac{1}{2} \right) t_c + \tau$ is the residence time of the representative droplet in the reactor and $f_0 \left\{ \left(m - \frac{1}{2} \right) t_c + \tau \right\}$ is the fraction with residence time, $\left(m - \frac{1}{2} \right) t_c + \tau$, of the dispersed phase that is flowing in at time zero, the terms $\left(m - \frac{1}{2} \right) t_c + \tau$ and $f_0 \left\{ \left(m - \frac{1}{2} \right) t_c + \tau \right\}$ may be expressed by t and $f(t)$, respectively. Accordingly, equation (5) is written as follows.

$$\bar{C}_o = \int_0^{t_c/2} C_o(t) f(t) dt + \sum_{m=1}^{\infty} \int_{(m-1/2)t_c}^{(m+1/2)t_c} C_m \left\{ t - \left(m - \frac{1}{2} \right) t_c \right\} f(t) dt \quad (5)$$

or

$$\bar{C}_o = \int_0^{\infty} C(t) f(t) dt \quad (6)$$

Equation (6) means that the concentration of reactant flowing out of a continuous flow reactor should be estimated by integrating the product of concentration function $C(t)$ and residence time distribution function $f(t)$. $f(t)$ is obtained only when the macro-mixing is considered, but function $C(t)$ should be estimated by considering the micro-mixing as well.

$C_m(\tau)$ is a function of rate constant, k , initial concentration of droplet produced newly by m -th coalescence and redispersion, C_{mi} , and reaction time, τ .

$$C_m(\tau) = g(C_{mi}, k, \tau) \quad (7)$$

Substituting t_c for τ in equation (7), the concentration just before $(m+1)$ -th coalescence, C_{m+1} , is given:

$$C_m(t_c) = C_{m+1} = g(C_{mi}, k, t_c) \quad (8)$$

The concentration of droplets produced by m -th coalescence and redispersion, C_{mi} , is given by the following equation according to the assumptions (2) and (3):

$$C_{mi} = \frac{1}{2} (C_m + \bar{C}_m) \quad (9)$$

where, C_m is the concentration just before m -th coalescence and \bar{C}_m is the mean concentration of all droplets which have the possibility to coalesce with the representative droplet. According to assumption (2), the coalescence and redispersion between droplets occurs instantaneously so that the disappearance of reactant at this moment may be negligible. Therefore, the sum of the quantity of reactant exchanged between droplets at the moment of coalescence and redispersion must be zero in total and so the following relation is derived.

$$\sum_{m=1}^{\infty} \left[\left\{ \sum_{m=1}^m (C_m - \bar{C}_m) \right\} \int_{(m-1/2)t_c}^{(m+1/2)t_c} f(t) dt \right] = 0 \quad (10)$$

Using the relations which have been derived as mentioned above, the effect of micro-mixing in a continuous flow reactor may be estimated in the case where the fluid flows out with arbitrary residence time distribution. However, the evaluation of \bar{C}_m is difficult, because it is generally a function of position in the reactor and intensity of macro-mixing.

Let the case be considered where the reactor is operated in perfect macro-mixing state.

Though the concentration of each droplet is different in the perfect macro-mixing reactor operated in a steady state, the time average concentration of dispersed droplets is independent of the position in the reactor.

\bar{C}_m is strictly the mean concentration of all droplets which may coalesce with a representative droplet. However, from assumption (1), there exist so many droplets which have an opportunity to coalesce with the droplet that \bar{C}_m is approximated to a mean value of all droplets including the representative droplet. In other word, \bar{C}_m may be considered to be independent of the position in a perfect macro-mixing reactor and of the number of times of coalescence and redispersion.

$$\bar{C}_m = \bar{C} = \text{constant} \quad (11)$$

The distribution of residence time in perfect macro-mixing reactor is given as follows:

$$f(t) = \frac{1}{\theta} e^{-t/\theta} = \frac{1}{\theta} e^{-\phi} \quad (12)$$

where, θ is the mean residence time and ϕ is equal to t/θ . Substituting the relations of equations (11) and (12) for \bar{C}_m and $f(t)$ in equation (10) respectively, the following relations is obtained:

$$\bar{C} = \frac{1 - e^{-\phi_c}}{e^{-\phi_c}} \sum_{m=1}^{\infty} C_m e^{-m\phi_c} \quad (10')$$

where,

$$\phi_c = t_c/\theta.$$

Equation (9) and (5) become equation (9') and (5'') respectively.

$$C_{mi} = \frac{1}{2} (C_m + \bar{C}) \quad (9')$$

$$\begin{aligned} \bar{C}_o = & \int_0^{\phi_c/2} C_o(\tau) e^{-\phi} d\phi \\ & + \sum_{m=1}^{\infty} \left\{ e^{-(m-1/2)\phi_c} \int_0^{\phi_c} C_m(\tau) e^{-\phi} d\phi \right\} \end{aligned} \quad (5'')$$

(1) Application to the rate processes of first order

As an example of first order processes, let the extraction be considered in which transfer of solute takes place from dispersed phase to continuous phase. In this case, the rate equation is expressed by $-dC/dt = Ka(C - C^*)$. When the continuous phase is perfectly mixed in the scale of macro- as well as micro-mixing, the concentration of solute in the continuous phase and the equilibrium concentration in the dispersed phase, C^* , are held constant in a steady state. Therefore, the relation of equation (7) is expressed as follows using the rate equation.

$$\frac{C_m(\tau) - C^*}{C_{mi} - C^*} = e^{-Ka\tau} \quad (13)$$

Substituting t_c for τ in the above equation and using equation (9), the following difference equation is obtained:

$$C_{m+1} - C^* = \alpha_1(C_m - C^*) + \alpha_1(\bar{C} - C^*) \quad (14)$$

where, $\alpha_1 = \frac{1}{2} e^{-Kat_c}$.

Solving equation (14), C_m is given as follows:

$$C_m - C^* = \frac{\alpha_1 - \alpha_1^m}{1 - \alpha_1} (\bar{C} - C^*) + \alpha_1^{m-1} e^{-Kat_c/2} (C_i - C^*) \quad (15)$$

Combining equation (15) and equation (10'), the following relation is obtained:

$$\frac{\bar{C} - C^*}{C_i - C^*} = \frac{(1 - e^{-\phi_c}) e^{-Kat_c/2}}{1 - 2\alpha_1 e^{-\phi_c}} \quad (16)$$

From equations (9'), (13) and (15), $C_m(\tau)$ is derived as follows:

$$\frac{C_m(\tau) - C^*}{C_i - C^*} = \frac{e^{-Ka(\tau + t_c/2)}}{2} \left\{ \frac{(1 - e^{-\phi_c})(1 - \alpha_1^m)}{(1 - 2\alpha_1 e^{-\phi_c})(1 - \alpha_1)} + \alpha_1^{m-1} \right\} \quad (17)$$

Calculating \bar{C}_o using equations (5''), (16) and (17), the following relation is obtained:

$$\frac{\bar{C}_o - C^*}{C_i - C^*} = \frac{1}{1 + Ka\theta} \quad (18)$$

This relation is identical with the one obtained without considering micro-mixing. For an irreversible first order reaction with reaction rate $-dC/dt = k_1 C$, equation (18) becomes as follows:

$$\frac{\bar{C}_o}{C_i} = \frac{1}{1 + k_1\theta} \quad (18')$$

This is the same result which has already been reported by Miyauchi³⁾ and Rietema⁵⁾, so that micro-mixing has no effect on the conversion of first order reaction.

(2) Application to zero order reactions

For zero order reactions in which reaction rate is given as $-dC/dt = k_0$, equation (7) has the form of equation (19).

$$C_m(\tau) = C_{mi} - k_0\tau \quad (19)$$

Substituting equation (9') for C_{mi} in the above equation and then t_c for τ , the following difference equation is obtained:

$$C_{m+1} = \frac{1}{2} (C_m + \bar{C}) - k_0 t_c \quad (20)$$

Solution of equation (20) is given as follows:

$$C_m = \frac{C_i}{2^{m-1}} + \left(1 - \frac{1}{2^{m-1}}\right) \bar{C} + k_0 t_c \left(\frac{3}{2^m} - 2\right) \quad (21)$$

The case should be considered in zero order reaction where the concentration of reactant reaches zero after the progress of a certain reaction time. Consider the case where the concentration of reactant in the representative droplet in the chain shown by Fig. 1 reaches zero for the first time after time τ_0 in succession to n -th coalescence and redispersion.

In this case,

$$C_{n+1} = C_{n+2} = \dots = 0$$

and

$$C_{n+1i} = C_{n+2i} = \dots = \bar{C}/2$$

Therefore, equation (10') is written as follows.

$$\sum_{m=1}^{\infty} (C_m - \bar{C}) e^{-(m-1)\phi_c} - \bar{C} \sum_{m=n}^{\infty} e^{-m\phi_c} = 0 \quad (22)$$

Substituting equation (21) for C_m in equation (22), equation (23) is obtained:

$$\bar{C} = \frac{\beta_0 C_i + 2k_0 t_c \left(\frac{3}{4} \beta_0 - \alpha_0\right)}{\beta_0 - \alpha_0 + \{1/(1 - e^{-\phi_c})\}} \quad (23)$$

where, $\alpha_0 = (1 - e^{-n\phi_c}) / (1 - e^{-\phi_c})$, and $\beta_0 = \left\{1 - \left(\frac{1}{2} e^{-\phi_c}\right)^n\right\} / \left\{1 - \frac{1}{2} e^{-\phi_c}\right\}$. Then equation (5'') can be reduced to the form:

$$\begin{aligned} \bar{C}_0 &= \int_0^{\phi_c/2} C_0(\tau) e^{-\phi} d\phi + \sum_{m=1}^{n-1} e^{-(m-1/2)\phi_c} \int_0^{\phi_c} C_m(\tau) e^{-\phi} d\phi \\ &\quad + e^{-(n-1/2)\phi_c} \int_0^{\phi_0} C_n(\tau) e^{-\phi} d\phi + \sum_{m=n+1}^{\infty} e^{-(m-1/2)\phi_c} \int_0^{\phi'} \left(\frac{1}{2} \bar{C} - k_0 \tau\right) e^{-\phi} d\phi \\ &= (C_i - k_0 \theta) (1 - e^{-\phi_c/2}) + (k_0 \theta \phi_c / 2) e^{-\phi_c/2} \\ &\quad + \sum_{m=1}^{n-1} e^{-(m-1/2)\phi_c} \{(1 - e^{-\phi_c}) (C_{mi} - k_0 \theta) + k_0 \theta \phi_c e^{-\phi_c}\} \\ &\quad + e^{-(n-1/2)\phi_c} \{(1 - e^{-\phi_0}) (C_{ni} - k_0 \theta) + k_0 \theta \phi_0 e^{-\phi_0}\} \\ &\quad + \sum_{m=n+1}^{\infty} e^{-(m-1/2)\phi_c} \left\{(1 - e^{-\phi'}) \left(\frac{1}{2} \bar{C} - k_0 \theta\right) + k_0 \theta \phi' e^{-\phi'}\right\} \end{aligned} \quad (24)$$

where, $\phi_0 = \tau_0 / \theta$ and $\phi' = \bar{C} / 2k_0 \theta$.

The term τ_0 is given as follows, from equation (19).

$$\tau_0 = C_{ni} / k_0 = (C_n + \bar{C}) / 2k_0 \quad (25)$$

Applying equation (21) at $m=n$ and substituting the relation into equation (25), the following equation is derived.

$$n = \left(\log \frac{C_i + \frac{3}{2} k_0 t_c - \bar{C}}{k_0 \tau + k_0 t_c - \bar{C}} \right) / \log 2 \quad (26)$$

The value, n , in equation (26) must be zero or a positive integer and τ_0 must satisfy the following relation ;

$$\bar{C}/2k_0 < \tau_0 < t_c$$

When k_0 , C_i , θ and t_c are given, \bar{C}_o is calculated by equation (24), using values of n and \bar{C} which are determined by trial and error.

(3) Application to second order reactions

For second order reactions in which rate equation is expressed by $-dC/dt = k_2C^2$, equation (7) has the form :

$$C_m(\tau) = C_{mi}/(1+k_2C_{mi}\tau) \tag{27}$$

Applying the above equation at $\tau=t_c$ and using equation (9'), the following difference equation is obtained :

$$C_{m+1}C_m + \left(\frac{2}{k_2t_c} + \bar{C}\right)C_{m+1} - \frac{1}{k_2t_c}C_m = \frac{1}{k_2t_c}\bar{C} \tag{28}$$

The solution of this difference equation in Riccati type is given as follows :

$$C_m = \frac{\bar{C}}{2\bar{R}_2}(f_{\bar{R}_2} - \bar{R}_2 - 1) + \frac{1}{\left[1/\left\{\frac{C_i}{1 + \frac{1}{2}R_{2i}} - \frac{\bar{C}}{2\bar{R}_2}(f_{\bar{R}_2} - \bar{R}_2 - 1)\right\} + \frac{\bar{R}_2}{f_{\bar{R}_2}\bar{C}}\right] \left(\frac{3+f_{\bar{R}_2}+\bar{R}_2}{3-f_{\bar{R}_2}+\bar{R}_2}\right)^{m-1} - \frac{\bar{R}_2}{\bar{C}f_{\bar{R}_2}}} \tag{29}$$

where, $R_{2i} = k_2C_it_c$, $\bar{R}_2 = k_2\bar{C}t_c$ and $f_{\bar{R}_2} = (\bar{R}_2^2 + 6\bar{R}_2 + 1)^{1/2}$.

When k_2 , C_i , θ and t_c are given, C_m and \bar{C} can be calculated by trial and error using equations (10') and (29). From the values obtained as mentioned above, \bar{C}_o is obtained by the following equation :

$$\bar{C}_o = \frac{C_i}{\bar{R}_2} e^{1/\bar{R}_2} \left[E_i \left\{ -\left(\frac{1}{\bar{R}_2} + \frac{\phi_c}{2}\right) \right\} - E_i \left(-\frac{1}{\bar{R}_2} \right) \right] + \sum_{m=1}^{\infty} \frac{C_{mi}}{\bar{R}_{2mi}} e^{-(m-1/2)\phi_c + (1/\bar{R}_{2mi})} \left[E_i \left\{ -\left(\frac{1}{\bar{R}_{2mi}} + \frac{\phi_c}{2}\right) \right\} - E_i \left(-\frac{1}{\bar{R}_{2mi}} \right) \right] \tag{30}$$

where, $R_2 = k_2C_i\theta$, $R_{2mi} = k_2C_{mi}\theta$ and $-E_i(-y) = \int_y^{\infty} (e^{-x}/x) dx$.

3. Coalescence and redispersion model (II)

Let the case be considered where the reaction takes place in the dispersed phase which is suspended in an inert phase in a perfect macro-mixing reactor, and the following assumption (2') is made, instead of the assumption (2) in the previous section 2.

- (2) The incoming droplets coalesce in the reactor at the constant rate of $1/t_c$ times per unit time and redisperse instantaneously. More than three droplets do not coalesce at the same time.

Consider a representative droplet with the concentration of reactant $C(t)$ at any time t . The concentration change of this droplet occurring between t and $t + \Delta t$ is denoted by $\Delta C(t)$. When Δt is small enough, the representative droplet may coalesce and redisperse only once at most within the time interval, Δt . When the droplet does not coalesce, the concentration change will be as follows:

$$-\Delta C(t) = r\{C(t)\} \Delta t$$

where, $r\{C(t)\}$ is the rate of reaction.

When the droplet coalesces and redisperses once, the concentration change is given as follows:

$$-\Delta C(t) = r\{C(t)\} \Delta \tau + \frac{C(t) - r\{C(t)\} \Delta \tau - \bar{C}}{2} + r\left[\frac{C(t) - r\{C(t)\} \Delta \tau + \bar{C}}{2}\right] (\Delta t - \Delta \tau)$$

where, $\Delta \tau$ is the time interval from time t to that at which one coalescence occurs, and \bar{C} is the average concentration of the droplets which have an opportunity to coalesce with the representative droplet.

The statistical number of times, i.e., the probability of coalescence and redispersion in time interval Δt is $(1/t_c) \Delta t$, and the probability not to be subjected to coalescence is $\{1 - (1/t_c) \Delta t\}$ from the assumption (2'). Therefore, the expected value of $\Delta C(t)$ is given as follows, by neglecting the second order infinitesimal terms.

$$-\Delta C(t) = r\{C(t)\} \Delta t + \frac{C(t) - \bar{C}}{2t_c} \Delta t$$

or

$$-\frac{dC(t)}{dt} = r\{C(t)\} + \frac{C(t) - \bar{C}}{2t_c} \quad (31)$$

The sum of the quantity of reactant exchanged between droplets at the moment of coalescence and redispersion must be zero in total, and the following equation is obtained in this model (II), referring to equation (12).

$$\int_0^\infty e^{-\phi} \left[\int_0^t \{C(t) - \bar{C}\} dt \right] d\phi = 0 \quad (32)$$

The above equation can be rewritten as follows, using equation (6) and (12).

$$\bar{C} = \bar{C}_o = \text{average concentration of all droplets in the reactor.} \quad (32')$$

Substituting equation (32') into equation (31), equation (32) can be reduced to the form:

$$-\frac{dC(t)}{dt} = r\{C(t)\} + \frac{C(t) - \bar{C}_o}{2t_c} \quad (33)$$

The average concentration of reactant in the dispersed phase flowing out of the perfect macro-mixing reactor is evaluated by substituting the solution of equation (33) for $C(t)$ in equation (6) together with the relation of $f(t) = (1/\theta)e^{-t/\theta}$.

(1) **Application to first order reactions** [$r\{C(t)\} = k_1C(t)$]

Solving equation (33) for first order reactions under the initial condition of $C(0) = C_i$, the following equation is obtained.

$$C(t) = \left(C_i - \frac{\bar{C}_o}{1 + 2k_1t_c} \right) e^{-(2k_1t_c + 1)t/2t_c} + \frac{1}{1 + 2k_1t_c} \bar{C}_o \quad (34)$$

Substituting equation (12) and (34) for $f(t)$ and $C(t)$ in equation (6), \bar{C}_o is given as follows:

$$\frac{\bar{C}_o}{C_i} = \frac{1}{1 + k_1\theta} \quad (18')$$

This result coincides with the one which is obtained by the application of model (I).

(2) **Application to zero order reactions** [$r\{C(t)\} = k_o$]

Solving equation (33) for zero order reactions under the condition of $C(0) = C_i$, the following equation is obtained:

$$C(t) = (C_i + 2k_o t_c - \bar{C}_o) e^{-t/2t_c} - (2k_o t_c - \bar{C}_o) \quad (35)$$

In equation (35), $C(t)$ becomes zero in the range of $t > t_0 = 2t_c \ln(C_i + 2k_o t_c - \bar{C}_o) / (2k_o t_c - \bar{C}_o)$, when $\bar{C}_o < 2k_o t_c$. The mean concentration of reactant in outflowing fluid, \bar{C}_o is calculated by the following equation.

$$\begin{aligned} \bar{C}_o &= \int_0^{t_0/\theta} C(t) e^{-\phi} d\phi \\ &= (C_i + 2k_o \theta \phi_c - \bar{C}_o) \frac{2\phi_c}{1 + 2\phi_c} \left\{ 1 - \left(\frac{C_i + 2k_o \theta \phi_c - \bar{C}_o}{2k_o \theta \phi_c - \bar{C}_o} \right)^{-(1+2\phi_c)} \right\} \\ &\quad - (2k_o \theta \phi_c - \bar{C}_o) \left\{ 1 - \left(\frac{C_i + 2k_o \theta \phi_c - \bar{C}_o}{2k_o \theta \phi_c - \bar{C}_o} \right)^{-2\phi_c} \right\} \end{aligned} \quad (36)$$

(3) **Application to second order reactions** [$r\{C(t)\} = k_2C(t)^2$]

Solving equation (33) for second order reactions under the condition of $C(0) = C_i$, $C(t)$ is given as follows:

$$C(t) = C_i - \frac{1 - e^{-2ak_2t}}{(1/A) - (1/B)e^{-2ak_2t}} \quad (37)$$

where,

$$a = \left\{ \frac{1}{2k_2\theta\phi_c} \left(\bar{C}_o + \frac{1}{8k_2\theta\phi_c} \right) \right\}^{1/2}$$

$$A = C_i + (1/4k_2\theta\phi_c) - a$$

$$B = C_i + (1/4k_2\theta\phi_c) + a$$

Substituting equation (12) and (37) for $f(t)$ and $C(t)$ in equation (6), the following equation is obtained:

$$\frac{\bar{C}_o}{C_i} = 1 - \frac{A}{2aR_2} \sum_{j=0}^{\infty} \frac{(A/B)^j}{\{j + (C_i/2aR_2)\} \{j+1 + (C_i/2aR_2)\}} \quad (38)$$

The infinite series in the right hand side of equation (38) is convergent.

4. Discussion

The process of coalescence and redispersion is a sort of continuous process of probability. Therefore, the variation of the time at which a representative droplet may coalesce and redisperse again after the previous coalescence and redispersion follows a continuous distribution function of probability. This distribution function is considered to depend on the properties of the reaction system and operating conditions, and it is very difficult to determine the function experimentally or theoretically.

The authors considered two extreme cases, i.e., model (I) and (II), where a representative droplet coalesces and redisperses with the surrounding droplets by $1/t_c$ times per unit time on an average. In model (I), the distribution function is expressed by delta function and in model (II), the function is expressed by a uniform distribution of $1/t_c$ in the range of $0 < t < t_c$.

Figs. 2 and 3 show the effect of micro-mixing in a perfect macro-mixing reactor for zero and second order reaction respectively.

The solid line is the values calculated by model (I), and the dotted line is the one by model (II). Similar results are also obtained under the other conditions

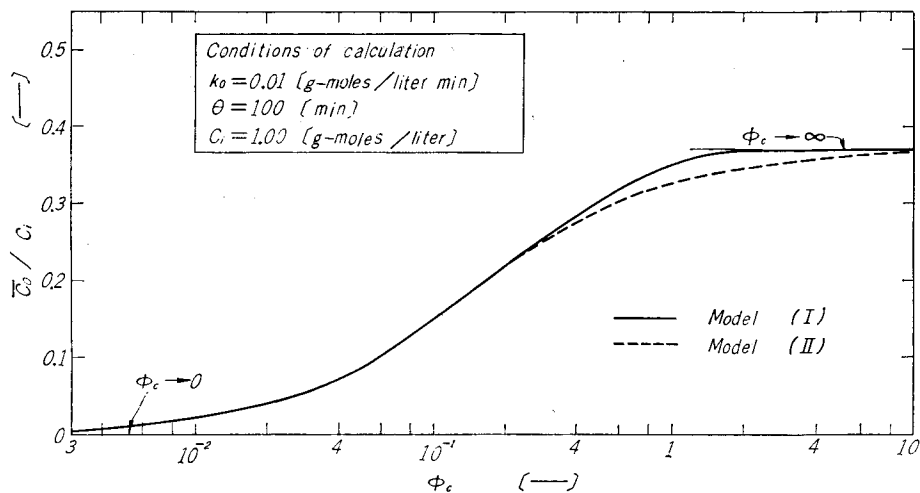


Fig. 2. Illustration of effect of micro-mixing on conversion for zero order reaction.

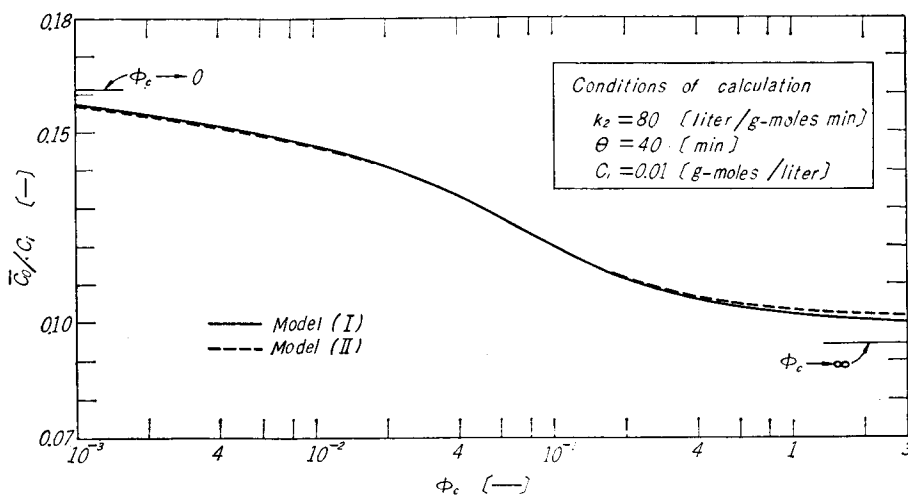
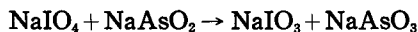


Fig. 3. Illustration of effect of micro-mixing on conversion for second order reaction.

of k , θ and C_i . The values of conversion calculated by model (I) agree well with those of model (II). In other word, there is little or no difference for the values of conversion from the difference in the form of distribution function, and the effect of coalescence and redispersion on conversion is evaluated only by the rate of coalescence and redispersion, $1/t_c$.

The conversion for zero order reactions in the range of $t_c > 2C_i/k_0$ almost agrees with that in the case where no coalescence takes place, and the conversion for maximum interaction is obtained in the range of $t_c < \frac{1}{2} \{(C_i/k_0) - \theta\}$. For the conversion of second order reaction, the effect of micro-mixing is generally marked in the range of $10^{-3} < t_c/\theta < 1$.

Fig. 4 shows the relation between \bar{C}_o/C_i and θ for second order reaction. The experimental results¹⁾ which are obtained by the authors are plotted in this diagram. The dimensions of the reactor used in this experiments are shown in Fig. 5. In the reactor, the following second order reaction takes place in the water phase which is dispersed in a continuous phase of octanol.



The reaction rate constant, k_2 is 80 liter/g-moles min. at 60.0°C under the condition of pH=6.6 in the water phase. These reactants, products and water have negligible solubility in octanol. The initial concentration of both reactants were fixed to 0.01 g-moles/liter and the reaction proceeded at 60.0°C.

By the tracer response method, the dispersed phase was verified to be in a perfect macro-mixing state.

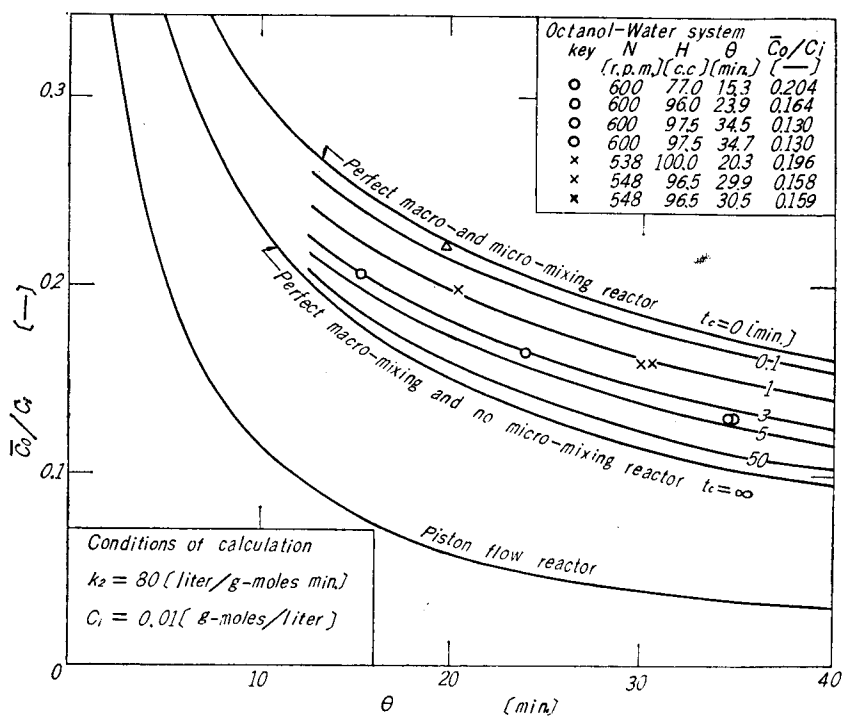
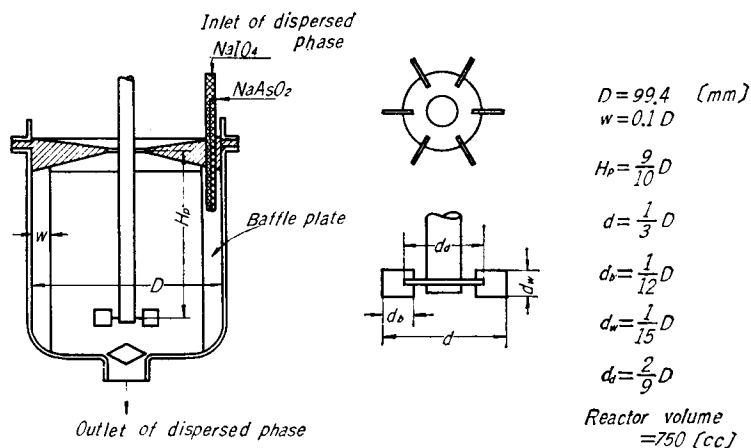
Fig. 4. Relation between \bar{C}_0/C_i , θ and t_c for second order reaction.

Fig. 5. Experimental apparatus.

The symbols, ○ and × in Fig. 4 show the experimental results of the octanol-water system, and that of △ shows the experimental result which was obtained in a homogeneous flow reactor to verify that the conversion of the homogeneous reaction coincided with the one in the state of perfect micro-mixing.

In Fig. 4, the experimental points lie along the curves calculated with constant values of t_c , when the agitator speed, N , and hold-up volume of dispersed phase, H , are held nearly constant.

According to the experimental results, t_c is independent of the average residence time under the operating conditions of constant values for N and H . It may be clear that the process of coalescence and redispersion in the liquid-liquid agitation vessel can be explained well by the models mentioned in this paper.

In this paper, rate processes in droplets which are dispersed in an inert phase are considered for convenience. When the conversion of a reaction proceeding in a homogeneous flow reactor is effected by the micro-mixing and also the concept of fluid elements or fragments can be used for the fluid, these models may be applied for this system working in a steady state, considering coalescence and redispersion between fluid elements.

Nomenclature

C_i	: Concentration of reactant in entering stream	[g-moles/cm ³]
C_{m_i}	: Concentration of reactant just after the m -th interaction (coalescence and redispersion)	[g-moles/cm ³]
C_m	: Concentration of reactant just before the m -th interaction	[g-moles/cm ³]
\bar{C}_m	: Average concentration of reactant in the fluid elements which are able to coalesce with a representative element at the m -th interaction	[g-moles/cm ³]
\bar{C}_o	: Average concentration of reactant in exhaust stream	[g-moles/cm ³]
$C(t)$: Concentration of reactant at time t .	[g-moles/cm ³]
$C_m(\tau)$: Concentration of reactant after time τ from the m -th interaction	[g-moles/cm ³]
F	: Volumetric flow rate	[cm ³ /sec]
$f(t)$: Residence time distribution function of fluid elements	[sec ⁻¹]
$f_m(\tau)$: Residence time distribution function of fluid elements which are generated by m -th interaction	[sec ⁻¹]
k_n	: Reaction rate constant for n -th order reaction	[C ¹⁻ⁿ /sec]
R_n	: Modulus of reaction rate for n -th order reaction	[—]
t	: Time	[sec]
t_c	: Average time interval between interactions	[sec]
θ	: Average residence time	[sec]
τ	: Time after redispersion in model (I)	[sec]
$\phi=t/\theta$: Reduced time	[—]
$\phi_c=t_c/\theta$: Micro-mixing parameter	[—]

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