

# RESIDENCE TIME DISTRIBUTION MODEL FOR CONTINUOUS CRYSTALLIZERS

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The crystal size distribution in various continuous crystallizers is usually evaluated by the population balance model<sup>6,7)</sup>. The population balance model is most advantageous for treating cases with crystal breakage. When a crystallizer is imperfectly mixed, a multistage model with a population balance for each stage is usually employed<sup>1,7)</sup>. It is well known, however, that the residence time distribution of particles often cannot be fitted to a multistage model.

The concept of residence time distribution has been used to find the average population density for an imperfectly mixed crystallizer<sup>2)</sup> and the population density in a well-mixed crystallizer<sup>4)</sup>. In the second case, the probability, which is actually the internal residence time function, of survival of crystal in a crystallizer is correlated with crystal size and growth rate. Miyauchi<sup>5)</sup> has employed the concentration distribution of particles to evaluate the residence time distribution of the particles. In the two previous papers of this author<sup>9,10)</sup>, both residence time distribution and population balance models are employed to evaluate the activity distributions of catalysts in reactors and regenerators with feed catalysts of either uniform or nonuniform activity.

In this study, the concept of residence time distribution (RTD) is adopted to find the crystal size distribution (CSD) in continuous crystallizers whether they are well mixed or not. A simple relation between crystal size distribution and residence time distribution is derived first. Then, the application of this relation to an MSMR crystallizer is demonstrated. In the later part of this paper, the concept of residence time of crystal is extended to crystallizers with seeding and to multistage crystallizers.

## 1. Crystallizers without Seeding

In an isothermal continuous crystallizer without seeding, which undergoes no crystal breakage and is operated at steady state, the rate of nucleation equals that of crystals removed. Thus, the nuclei generated can be regarded as those flow in the crystallizer and will remain in the crystallizer according to a residence time distribution. The crystals with a size between  $L$  to

$L+dL$  are those having the residence time  $t$  to  $t+dt$ , so that the crystal size distribution function,  $n(L)$ , and the residence time distribution function,  $E(t)$ , are correlated by

$$n(L)dL = N_T E(t)dt \quad (1)$$

Upon rearrangement, it is obtained that

$$n(L) = N_T E(t)/G(L) \quad (2)$$

where the growth rate is defined as

$$G(L) = dL/dt \quad (3)$$

This simple relation can be used to find the CSD,  $n(L)$ , provided that  $E(t)$  and  $G(L)$  are known in advance. Note that the time variable  $t$  in  $E(t)$  should be eliminated by the relation between  $L$  and  $t$ , which is obtained by integrating Eq. (3).

In the modeling of an imperfectly mixed crystallizer, Abegg and Balakrishnan<sup>1)</sup> applied the concept of the tanks-in-series model and used the population balance model for each crystallization unit. They used the number of crystallization units to represent the degree of imperfect mixing by matching the values of coefficient of variation for the crystal size distribution. Larson and Wolff<sup>3)</sup> (or see Randolph and Larson<sup>6)</sup>) also studied multistage crystallizers, but did not mention the modelling of the crystallizer with imperfect mixing by multistage systems. Referring to Miyauchi's approach<sup>5)</sup>, Eq. (1) can also be used to evaluate the residence time distribution from the crystal size distribution

$$E(t) = G(L)n(L)/N_T \quad (4)$$

provided that  $L$  on the right-hand side is substituted by its expression in terms of  $t$  obtained from Eq. (3). This approach is a simple method of obtaining the residence time distribution when the growth rate kinetics,  $G(t)$ , is in a simple form and direct experiment to find the residence time distribution is inconvenient or impossible.

Although Eq. (2) may be employed for any continuous crystallizer to find the crystal size distribution whether the crystallizer is well mixed or not, here an MSMR crystallizer is treated by the residence time distribution model for the purpose of comparison with the population balance approach.

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### EXAMPLE:

Consider that an MSMPR crystallizer with growth rate obeying McCabe's  $\Delta L$  law

$$dL/dt = G(L) = G_0 \quad (5)$$

from which one obtains

$$t = L/G_0 \quad (6)$$

Because the residence time distribution in an MSMPR crystallizer with a mean residence time of  $\tau$  is

$$E(t) = (1/\tau)e^{-t/\tau} \quad (7)$$

The use of Eq. (2) yields

$$n(L) = \frac{N_\tau}{G_0\tau} \exp\left(-\frac{L}{G_0\tau}\right) = n^0 \exp\left(-\frac{L}{G_0\tau}\right) \quad (8)$$

which is exactly the same as that derived from the population balance equation. Similarly, for the same crystallizer with growth rate in the form of  $G(L) = G_0(1 + \alpha L)^\beta$ , one can obtain

$$n(L) = \begin{cases} n^0(1 + \alpha L) \exp\{- (1 + 1/\alpha G_0\tau)\}, & \beta = 1 \\ n^0(1 + \alpha L)^{-\beta} \exp\left[-\frac{(1 + \alpha L)^{1-\beta} - 1}{\alpha(1-\beta)G_0\tau}\right], & \beta \neq 1 \end{cases} \quad (9)$$

When the residence time distribution approach is used for modified systems, i. e., those with fines dissolver and/or product classifier, the same crystal size distribution functions as those using the population balance model are obtained. It is noted that the residence time distribution model is as simple as the population balance model. However, as has been mentioned earlier, the residence time distribution model can be applied for crystallizers with nonideal mixing, whereas the population balance model can be used only for well-mixed crystallizers.

## 2. Crystallizers with Seeding

The crystals in a continuous-flow crystallizer with seeding can be divided into two groups: crystals grown from seeds and those grown from the nuclei generated by nucleation. Hence, the population density can be represented by

$$n(L) = n_s(L) + n_n(L) \quad (10)$$

The second term on the right-hand side can be evaluated by Eq. (2) while the first term can be regarded as the crystal size distribution function of a crystallizer with seeding but without nucleation.

The crystal size distribution function for such a crystallization system can be evaluated by considering the relation between the seeds in the feed stream and the crystals in the crystallizer.

The contribution of seeds with size between  $L$  to  $L + dL$  to the size distribution of crystals with size  $L$  is represented by

$$\frac{E(t)}{G(L)} n_f(L) dL$$

Since crystals with size  $L$  in a crystallizer are from those seeding crystals smaller than  $L$ , the crystal size distribution function in such a crystallizer is

$$n_n(L) = \int_0^L \frac{E(t)}{G(L')} n_f(L') dL' \quad (11)$$

As far as the functions  $E(t)$ ,  $G(L)$  and  $n_f(L)$  are known, the crystal size distribution can be predicted. It is also noted that this equation can be used for both ideal and nonideal mixing states.

For an MSMPR crystallizer, as an example, the term  $n_n(L)$  can be found by substituting the following equations into Eq. (11).

$$E(t) = (1/\tau)e^{-t/\tau}$$

$$G(L) = dL/dt = G_0$$

or

$$t = (L - L_f)/G_0$$

Here a constant growth rate is assumed. The result is

$$n_n(L) = \frac{1}{G_0\tau} e^{-L/G_0\tau} \int_0^L e^{L'/G_0\tau} n_f(L') dL' \quad (12)$$

For a feed of the following type:

$$n_f(L) = [u(0) - u(L_s)] n_f^0(-L/G_f\tau_f) \quad (13)$$

the crystal size distribution in an MSMPR crystallizer with seeding, by adding the term  $n_n(L)$ , is found to be:

$$n(L) = \begin{cases} \exp\left(-\frac{L}{G_0\tau}\right) \left[ \frac{n_f^0}{\lambda - 1} \left\{ 1 - \exp\left(-\frac{\lambda - 1}{G_0\tau} L\right) \right\} + n^0 \right], & L < L_s \\ \exp\left(-\frac{L}{G_0\tau}\right) \left[ \frac{n_f^0}{\lambda - 1} \left\{ 1 - \exp\left(-\frac{\lambda - 1}{G_0\tau} L_s\right) \right\} + n^0 \right], & L > L_s \end{cases} \quad (14)$$

## 3. Multistage Crystallizers

Multistage crystallizers with each stage being perfectly mixed have been theoretically studied by Larson and Wolff<sup>3)</sup> by using a population balance approach. Here, instead, the residence time distribution model is employed for such a system, although this approach can be used whether each stage is perfectly mixed or not.

The crystallization system considered here is a three-stage crystallizer in which the growth of crystals obeys McCabe's  $\Delta L$  law. No seed is added to the first stage, so the crystals are generated from nucleation. The crystals in the second and third stages are from the preceding unit and nucleation. Hence the crystal size distribution in the first stage is found to be

$$n_1(L) = n_1^0 \exp(-L/G_1\tau) \quad (15)$$

by referring to Eq. (8). Since the effluent crystals from the first stage are the feed to the second stage, the crystal size distribution can be derived by the same

approach as that in the last section (Eq. (14)) to be

$$n_2(L) = \left( n_2^0 + \frac{\mu n_1^0}{1-\mu} \right) \exp\left(-\frac{\mu L}{G_1 \tau}\right) - \frac{\mu n_1^0}{1-\mu} \exp\left(-\frac{L}{G_1 \tau}\right) \quad (16)$$

Similarly, for the third stage,

$$n_3(L) = n_3^0 \exp\left(-\frac{L}{G_1 \mu}\right) + \left[ \frac{\nu}{\mu-\nu} n_2^0 + \frac{\mu\nu}{(1-\mu)(\mu-\nu)} n_1^0 \right] \times \left[ 1 - \exp\left(-\frac{\mu L}{G_1 \tau}\right) \right] - \frac{\mu\nu n_1^0}{(1-\mu)(1-\nu)} \left[ 1 - \exp\left(-\frac{L}{G_1 \tau}\right) \right] \quad (17)$$

If only the first stage generates the nuclei, then

$$n_3(L) = \frac{\mu\nu n_1^0}{1-\mu} \left\{ \frac{1}{\mu-\nu} \left[ 1 - \exp\left(-\frac{\mu L}{G_1 \tau}\right) \right] - \frac{1}{1-\nu} \left[ 1 - \exp\left(-\frac{L}{G_1 \tau}\right) \right] \right\} \quad (18)$$

## Conclusions

From the derivations of this study, it is seen that the residence time distribution approach can be applied to a crystallizer with or without seeding and to a multistage crystallizer. This model gives the same results as the population balance model.

However, the residence time distribution model can be employed to evaluate crystal size distributions in continuous crystallization systems with imperfect mixing, while the current method of treating such systems is to represent the crystallizer by a tanks-in-series model and then to apply the population balance for each tank.

## Nomenclature

$E(t)$	= residence time distribution function
$G$	= growth rate of crystals
$G_i$	= growth rate of crystals in the $i$ -th stage
$G_0$	= constant growth rate of crystals
$L$	= crystal size
$L_f$	= size of feed crystal
$L_s$	= largest size of feed crystals
$N_T$	= total number of crystals per unit volume of suspension

$n(L)$	= crystal size distribution (population density) function
$n_f(L)$	= crystal size distribution of the feed crystals
$n_i(L)$	= crystal size distribution in the $i$ -th stage
$n_n(L)$	= population density function contributed by nucleation
$n_s(L)$	= population density function contributed by seeding
$n^0$	= population density of nuclei
$n_f^0$	= population density of nuclei in the feed stream
$n_i^0$	= population density of nuclei in the $i$ -th stage
$Q$	= volumetric feed and discharge rate
$t$	= time
$V$	= total volume of suspension
$\lambda$	= $G_0 \tau / G_f \tau_f$
$\mu$	= $G_1 / G_2$
$\nu$	= $G_1 / G_3$
$\tau$	= mean drawdown time of crystallizer, $\tau = V/Q$

## <Subscripts>

$f$	= feed
$T$	= total

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