SYSTEM CONSTANT AND ITS SIGNIFICANCE IN INDUSTRIAL CRYSTALLISATION

Jaroslav NÝVLT* and Miroslav BROUL

Chemopetrol, Research Institute of Inorganic Chemistry, 400 60 Ústi nad Labem

Received September 12th, 1978

Dedicated to Professor E. Hála on the occassion of his 60th birthday.

Fundamental equations describing behaviour of the continuous stirred crystalliser in steady state include a system constant B, whose value strongly depends on selection of the size of initial crystals L_N. To avoid this dependence and to see that the equations be applicable for crystalliser design also in the case when the value L_N approaches zero, a general derivation of the dependence between the mean size of crystals $\bar{L}$ and specific output of the crystalliser $\dot{m}_c$ has been derived on basis of the numerical nucleation rate. The derived relations do not include the quantity L_N and they can be transformed by a simple arrangement to the published relations.

In one of our recent papers[1] a relation has been derived for calculation of the mean size of product crystals $\bar{L}$ from the perfectly stirred continuous MSMPR crystalliser, from a known concentration of suspension m_c, and the output of the crystalliser $\dot{m}_c$ in the form

$$\left(\frac{\bar{L} - L_N}{L_N}\right)^{1+3g/n} . f(z_N)^{g/n} = 3Bm_c^{1-cg/n}\dot{m}_c^{g/n-1} .$$

The proportionality constant B characterizing the given system, which in itself incorporates the kinetic constants of growth and nucleation, includes also quantity L_N. But if the size of initial crystals L_N approaches zero, the system constant B is approaching infinity and then the given form of equation is not applicable for crystalliser design. Beside this value L_N is usually determined by extrapolation of the crystal size distribution to the value $M(L) = 100\%$ which could be affected in the region of small L_N by a large error and the value of the system constant then significantly depends on the chosen value L_N. The aim of this study is to derive the fundamental equation for design of the continuous stirred crystalliser with the mixed product removal (MSMPR) so that the derived relations could be applied also to the case $L_N = 0$ and which would not include – if possible – this arbitrary quantity at all.

---

* Present address: Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 160 00 Prague 6.

THEORETICAL

The population density balance of crystals[2] for steady state of the MSMPR crystalliser, at the assumption that no new seed crystals are entering the crystalliser and that the rate of crystal growth is independent of their size and that the crystals are not subject to macroattrition, can be simplified to the familiar form

$$n(L) = n^0 \exp\left(-t/\bar{t}_1\right) . \qquad (1)$$

If the size of crystals is in general expressed as a function of their residence time in the crystalliser t

$$L = L_{\mathrm{N}} + \dot{L}t \qquad (2)$$

Eq. (*1*) can be rewritten into form

$$n(L) = n^0 \exp\left(-(L - L_{\mathrm{N}})/\dot{L}\bar{t}_1\right) . \qquad (3)$$

It was then derived[1] for the mass of crystals or for concentration of suspension

$$m_{\mathrm{c}} = \int_{L_{\mathrm{N}}}^{\infty} n(L)\, \alpha \varrho_{\mathrm{c}} L^3 \,\mathrm{d}L = 6\alpha\varrho_{\mathrm{c}}\, n^0 (\dot{L}\bar{t}_1)^4 \,.\, f(z_{\mathrm{N}}) , \qquad (4)$$

where

$$f(z_{\mathrm{N}}) = 1 + z_{\mathrm{N}} + z_{\mathrm{N}}^2/2 + z_{\mathrm{N}}^3/6 \qquad (5)$$

and

$$z_{\mathrm{N}} = \frac{L_{\mathrm{N}}}{\dot{L}\bar{t}_1} = \frac{3L_{\mathrm{N}}}{\bar{L} - L_{\mathrm{N}}} . \qquad (6)$$

The value of the population density of initial crystals n^0 can be expressed both from Eq. (*4*) and from the numerical nucleation rate $\dot{N}_{\mathrm{N}}$

$$\dot{N}_{\mathrm{N}} = n^0 \dot{L} = k'_{\mathrm{N}} m_{\mathrm{c}}^{\mathrm{c}}\, \Delta w^{\mathrm{n}} \qquad (7)$$

while the rate constant of the numerical and usually given mass nucleation rate is given by the relation

$$k_{\mathrm{N}} = k'_{\mathrm{N}} \alpha \varrho_{\mathrm{c}} L_{\mathrm{N}}^3 . \qquad (8)$$

The unknown supersaturation Δw in Eq. (*7*) can be then expressed by the linear crystal growth rate

$$\dot{L} = (k_{\mathrm{G}}\beta/3\alpha\varrho_{\mathrm{c}})\, \Delta w^{\mathrm{g}} = k'_{\mathrm{G}}\, \Delta w^{\mathrm{g}} \qquad (9)$$

so that

$$n^0 \dot{L} = k'_N \, m_c^c (\dot{L}/k'_G)^{n/g} \tag{10}$$

and the resulting relation for the population density of initial crystals or for the nuclei population density is

$$n^0 = k'_N k'^{-n/g-1}_G m_c^c \tag{11}$$

If we consider the definition of mean size of crystals $\bar{L}$

$$\bar{L} = L_N + 3\dot{L}\bar{t}_1 \tag{12}$$

and if we substitute the corresponding relations from Eqs (*11*) and (*12*) into Eq. (*4*) we obtain

$$m_c = 6\alpha\varrho_c k'_N k'^{-n/g}_G \, m_c^c \, f(z_N) \,.\, 3^{-3-n/g} (\bar{L} - L_N)^{3+n/g} \, \bar{t}_1^{1-n/g} \tag{13}$$

and after arrangement and substitution

$$\dot{m}_c = m_c/\bar{t}_1 \tag{14}$$

$$(\bar{L} - L_N)^{1+3g/n} \,.\, f(z_N)^{g/n} = 3B_N m_c^{1-cg/n} \dot{m}_c^{g/n-1} \tag{15}$$

where

$$B_N = \frac{4 \cdot 5^{g/n} k'_G}{(\alpha\varrho_c k'_N)^{g/n}} \tag{16}$$

or

$$B_N = \frac{4 \cdot 5^{g/n} \dot{L} m_c^{cg/n}}{(\alpha\varrho_c \dot{N}_N)^{g/n}} \tag{17}$$

DISCUSSION

If we compare Eq. (*15*) with the earlier relation quoted in the introductory part of this study we can see that they are identical and that between the system constants B and B_N holds the relation

$$B_N = B \,.\, L_N^{1+3g/n} \,. \tag{18}$$

The advantage of the derived relation (*15*) is also in its suitability for $L_N \to 0$ when it takes the form

$$\bar{L}^{1+3g/n} = 3B_N m_c^{1-cg/n} \dot{m}_c^{g/n-1} \,. \tag{19}$$

When considering the analogy of Eq. (*14*) we can obtain relations also for description of the batch crystalliser[3] which in our case have the form

$$(\bar{L} - L_{\mathrm{N}})^{1+3g/n} . f(z_{\mathrm{N}})^{g/n} = 3B_{\mathrm{N}} m_{\mathrm{c}}^{(1-c)g/n} t_{\mathrm{c}}^{1-g/n} \tag{20}$$

or

$$\bar{L}^{1+3g/n} = 3B_{\mathrm{N}} m_{\mathrm{c}}^{(1-c)g/n} t_{\mathrm{c}}^{1-g/n} . \tag{21}$$

It remains to repeat how it is possible to determine the values of individual constants from the model crystallisation experiments. The first series of experiments is performed in the continuous crystalliser so that the concentration of suspension is kept constant *i.e.* with constant composition of the feed and constant temperature in the crystalliser but with the significantly different flow rate. If using the batch crystalliser, just the time of batch t_{c} should be changed. For individual experiments the distribution of product crystal sizes is evaluated[4] *i.e.* the screen size L is plotted in dependence on the dimensionless residence time of crystals

$$z = \frac{L - L_{\mathrm{N}}}{\dot{L}\bar{t}_1} = 3\,\frac{L - L_{\mathrm{N}}}{\bar{L} - L_{\mathrm{N}}} \tag{22}$$

or on to it corresponding oversize fractions

$$M(L) = 100(1 + z + z^2/2 + z^3/6)\exp(-z) \tag{23}$$

and from the plot the values $\bar{L}$ and L_{N} are determined. Linearisation is performed by the least square method so that L_{N} should be $L_{\mathrm{N}} \geqq 0$. From these values the linear crystal growth rate is determined

$$\dot{L} = \frac{\bar{L} - L_{\mathrm{N}}}{3\bar{t}_1} \quad \text{resp.} \quad \dot{L} = \frac{\bar{L} - L_{\mathrm{N}}}{3t_{\mathrm{c}}} \tag{24}$$

and by use of the arranged relation (*4*) the numerical nucleation rate is obtained

$$\dot{N}_{\mathrm{N}} = 27m_{\mathrm{c}}\dot{L}/[2\alpha\varrho_{\mathrm{c}}(\bar{L} - L_{\mathrm{N}})^4 f(z_{\mathrm{N}})] \tag{25}$$

Further the value of the exponent g/n is determined again by the least square method from the relation derived from Eq (*15*) where for $f(z_{\mathrm{N}}) \rightarrow 1$ holds

$$\frac{1 - g/n}{1 + 3g/n} = \frac{\Delta \log(\bar{L} - L_{\mathrm{N}})}{\Delta \log \dot{m}_{\mathrm{c}}} \tag{26}$$

So obtained values from individual experiments are then substituted into Eq. (*17*) at the assumption $c = 0$.

We perform another series of experiments at the constant flow rate or constant batch time t_c but with differing concentration of the initial solution *i.e.* with different concentration of suspension m_c. From these experiments are determined the values $\dot{N}_N$ and $\dot{L}$ in a similar way and they are again substituted into Eq. (*17*) at the assumption $c = 0$. Now we check the dependence of the so computed constant B_N on concentration of suspension m_c. The slope of straight line in the plot $\log (B_N)_{c=0}$ *vs* $\log m_c$ corresponds to the value cg/n so that from it we can easily determine the value of c. The basical assumption for the described determination of constants c and g/n is availability of sufficiently reliable experimental data at considerably differing parameters in the series of experiments. Otherwise, the computation is very inaccurate and in the extreme case it is better to use the value of g/n calculated from individual kinetic measurements (dependence of $\dot{L}$ on supersaturation[5], evaluation of the width of metastable region[6], and for the exponent c to assess the values $c = 0$ (primary nucleation, secondary nucleation with the mechanism of adsorption layer), $c = 1$ (interaction crystal–crystalliser) or $c = 2$ (interaction crystal–crystal)[7].

LIST OF SYMBOLS

B	system constant based on the mass nucleation rate ($\mathrm{kg}^{(c-1)g/n}\ \mathrm{kg}_0^{(1-c)g/n}\ \mathrm{s}^{g/n-1}$)
B_N	system constant based on the numerical nucleation rate ($\mathrm{m}^{1+3g/n}\ \mathrm{kg}^{(c-1)g/n}\ \mathrm{s}^{g/n-1}$)
c	exponent of secondary nucleation
$f(z_N)$	function defined by Eq. (*5*)
g	order of kinetic growth equation of crystals
k_G	rate constant of growth ($\mathrm{m}^{-2}\ \mathrm{kg}_0^{g}\ \mathrm{kg}^{1-g}\ \mathrm{s}^{-1}$)
k'_G	rate constant of growth ($\mathrm{m}\ \mathrm{kg}_0^{g}\ \mathrm{kg}^{-g}\ \mathrm{s}^{-1}$)
k_N	kinetic constant of nucleation rate ($\mathrm{kg}_0^{n+c-1}\ \mathrm{kg}^{1-c-n}\ \mathrm{s}^{-1}$)
k'_N	kinetic constant of numerical nucleation rate ($\mathrm{kg}_0^{n+c-1}\ \mathrm{kg}^{-c-n}\ \mathrm{s}^{-1}$)
L	size of crystals (m)
L_N	size of initial crystals (m)
$\bar{L}$	mean size of crystals (m)
$\dot{L}$	linear crystal growth rate ($\mathrm{m\ s}^{-1}$)
m_c	concentration of suspension ($\mathrm{kg/kg_0}$)
$\dot{m}_c$	specific output of the crystalliser ($\mathrm{kg\ kg_0^{-1}\ s^{-1}}$)
$M(L)$	oversize fraction (mass %)
n	order of nucleation equation
$n(L)$	population density of crystals ($\mathrm{kg_0^{-1}\ m^{-1}}$)
n^0	population density of initial crystals ($\mathrm{kg_0^{-1}\ m^{-1}}$)
$\dot{N}_N$	numerical nucleation rate ($\mathrm{kg_0^{-1}\ s^{-1}}$)
t	time (s)
$\bar{t}_l$	mean residence time of solution in crystalliser (s)
t_c	time of batch (s)
Δw	supersaturation ($\mathrm{kg/kg_0}$)
z	dimensionless residence time of crystals

z_N	dimensionless initial size of crystals
α	volume shape factor
β	surface shape factor
ϱ_c	density of crystals (kg m^{-3})

The symbol kg_0 denotes the unit amount of free solvent.

REFERENCES

1. Nývlt J., Broul M.: This Journal *41*, 536 (1976).
2. Randolph A. D., Larson M. A.: *The Theory of Particulate Processes*. Academic Press, New York 1971.
3. Nývlt J., Kočová H., Černý M.: This Journal *38*, 3199 (1973).
4. Nývlt J.: Chem. Prům. *18*, 579 (1968).
5. Kočová H., Nývlt J., Kočí J.: Chem. Prům. *17*, 477 (1967).
6. Procházka S., Sůra J., Nývlt J.: Chem. Listy *71*, 1086 (1977).
7. Asselbergs C., de Jong E. J.: Presented at the Annual Meeting of the Working Party on Crystallisation in the European Federation of Chemical Engineering, Boekelo (The Netherlands) 1972.

Translated by M. Rylek.