RESULTS AND DISCUSSION

A comparison of the efficiency of the elimination procedure with other solutions for examples 1 to 5 is shown in Table 1. Significant improvements are noted for each problem, except example 3, which was not heavily constrained. The computational effort was reduced by factors of 5 to 20 over the best results reported previously. Greatest improvement was achieved, as expected, for those solutions which lie near an inequality constraint.

Perfect reliability was achieved in each of the solutions, that is, all fifty runs converged to the optimum. In each case, the variable eliminated from a constraint equation was simply that variable which resulted in the simplest equations for solution. Even better efficiency might result with different variable selection. Elimination was accomplished when the search reached 1 to 5% of the constraint value. For constraint values of 0, variable elimination was made when the constraint value was 0.05.

In cases where the optimum lies near more than one constraint, it may not be possible to solve the resulting equations to eliminate all variables. This was found to be the case for example 2, which bordered on two constraints. However, elimination of just one variable, in this case, resulted in a significant improvement in efficiency.

A comparison of the solution of example 6 with that of Gisvold and Moe (1972) is given in Table 2. To reach the optimum of this problem, the search must proceed down a tunnel formed by four constraining equations. Thus, elimination of several variables simultaneously was necessary. Elimination was achieved when the search reached 5% of any of the constraints.

As noted, the elimination method, with the adaptive random search, resulted in a substantial reduction in the computational effort in solving this problem. A better optimum was also located. It should be noted that this problem is mixed integer. No special programming is necessary to apply the adaptive random search to this type of problem.

SUMMARY AND CONCLUSIONS

The variable elimination method can be readily applied to several different types of optimization problems. The procedure significantly improves the efficiency of problems with difficult explicit constraints. Perfect reliability was achieved in reaching the optimum of each example. This method should be quite useful in solving problems in which the inequality constraints are explicit and solvable for at least one variable.

LITERATURE CITED

Beveridge, G. S. G., and R. S. Schechter, Optimization Theory

and Practice, p. 483, McGraw-Hill, New York (1970).
Gaines, L. D., and J. L. Gaddy, "Process Optimization by Flow-sheet Optimization," Ind. Eng. Chem. Process Design Develop., 15, No. 1, 206 (1976).

Gisvold, K. M., and J. Moe, "A Method for Nonlinear Mixed-Integer Programming and Its Application to Design Problems," J. Eng. Ind., 94, 353 (1972).
Gould, F. J., "Nonlinear Pricing: Applications to Concave Programming," Operations Res., 19, 1026 (1971).
Heuckroth, M. W., L. D. Gaines, and J. L. Gaddy, "An Examination of the Adaptive Random Search," AIChE J., 22, No. 4, 744 (1976).

No. 4, 744 (1976).
Keefer, D. L., "Simpat: Self-Bounding Direct Search Method for Optimization," Ind. Eng. Chem. Process Design Develop., **12,** 92 (1973).

Luus, R., and T. H. I. Jaakola, "Optimization by Direct Search and Systematic Reduction of the Size of Search Region," AIChÉ J., 19, 760 (1973).

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Determination of Birth and Growth Rate of Secondary Nuclei: SSBCR Crystallizer

HONG H. LEE

Department of Chemical Engineering University of Florida Gainesville, Florida 32611

Although the secondary nucleation is well known and has been extensively studied (Clontz and McCabe, 1971; Cise and Randolph, 1972; Strickland-Constable, 1972; Ottens and de Jong, 1973; Sung et al., 1973; Bauer et al., 1974; Garside and Jancic, 1976), many aspects of the phenomenon are still quite uncertain, especially in the area of growth of secondary nuclei. Perhaps the uncertainties stem in part from lack of experimental and analytical methods for the determination of birth and growth rate of secondary nuclei which would be equivalent in their effectiveness to the MSMPR methods pioneered by Randolph and Larson (1962, 1971) and proven powerful for the studies of primary crystallization.

It is known that McCabe's ΔL law does not necessarily hold for the growth of secondary nuclei. Therefore, the population balance of MSMPR can not be used for the determination of birth and growth rate of secondary nuclei unless certain assumptions (Randolph and Cise, 1972)

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are made. To overcome this difficulty, Garside and Jancie (1976) formed secondary nuclei in an MSMPR crystallizer and then grew the nuclei in a stirred batch crystallizer, effectively eliminating birth rate in the population balance. A differential method was used to obtain growth rate from experimental data.

An experimental method of a single-seeded batch crystallizer with an in situ Coulter counter can be combined with the analytical method of population balance (Randolph and Larson, 1971) to obtain the birth and growth rate of secondary nuclei. Consider a single-seeded, stirred batch crystallizer. If the seed crystal is removed from the crystallizer at time $t = t_r$ and the secondary nuclei formed are allowed to grow, the population balance yields

$$\frac{\partial}{\partial t} n(t, L) + \frac{\partial}{\partial L} G(L) n(t, L) = b_n(L; t \leq t_r, L \geq L_c)$$
(1)

Integrating Equation (1) with respect to time, we have

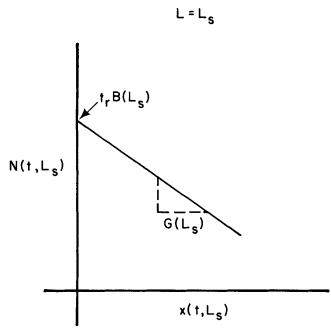


Fig. 1. Determination of growth rate and cumulative birth rate.

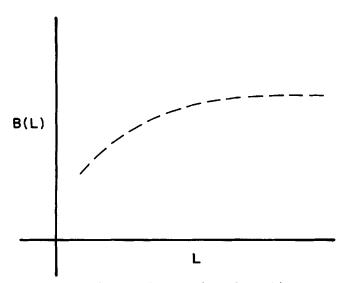


Fig. 3a. Cumulative birth rate of secondary nuclei.

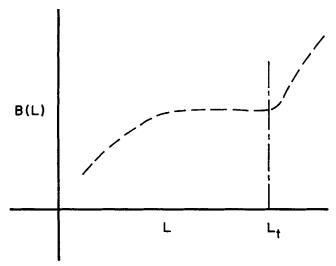


Fig. 3b. Determination of threshold size.

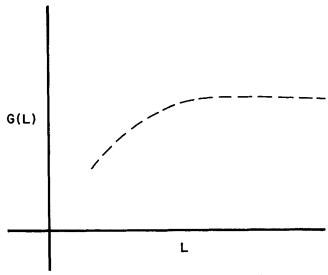


Fig. 2. Growth rate of secondary nuclei.

$$n(t,L) + \frac{d}{dL} \left(G \int_0^t n \, dt \right) = b_n t_r \quad t \ge t_r \quad (2)$$

where n(0, L) = 0 since no nucleus is present at the start of an experiment. Integrating again this time with respect to size, we have

$$\int_0^L n(t,\zeta)d\zeta + G(L) \int_0^t n(\tau,L)d\tau = t_\tau \int_0^L b_n(\zeta)d\zeta$$
(3)

since the critical size for the net birth of nuclei, $L_c > 0$ and therefore n(t,0) = 0. The first term in Equation (3) is the total cumulative number of crystals with size up to L, denoted as N(t,L), and the right-hand side of the equation is the total cumulative number of nuclei born with size up to L, denoted as B(L). Rearranging Equations (3), we have

$$N(t, L) = -G(L) x(t, L) + t_r B(L)$$
 (4)

where

$$x(t,L) = \int_0^t n(\tau,L)d\tau$$

For a given value of the crystal size L_s , Equation (4) is a straight line with a slope of $G(L_s)$ and an intercept of $t_rB(L_s)$ as shown in Figure 1. Repeating the same procedures as in Figure 1 over the entire range of the crystal size of interest, we would obtain the results in Figure 2 for the growth rate of secondary nuclei and those in Figure 3a for the cumulative birth rate with respect to size.

Comparison of a single-seeded, stirred batch crystallization with removal of the seed after $t = t_r$ (SSBCR crystallizer) with the MSMPR crystallizer reveals some interesting points. Steady state MSMPR crystallizer results yield a straight line as in Figure 1, with its slope yielding the size independent growth rate and its intercept the size independent birth rate when the logarithms of size distribution are plotted against size. In the case of the SSBCR crystallizer, a plot as in Figure 1 necessarily yields a point in the growth rate vs. size relationship, and such a plot has to be made for each size selected to obtain a growth curve as a function of size. A fundamental difference between the two methods could be in defining the birth rate. In the steady state MSMPR analysis, the birth rate is defined as $n(0, L; L \rightarrow 0)$. In the case of the SSBCR analysis, the net birth rate is defined in terms of nuclei with size greater than or equal to the critical size. This, in turn, relies on the

survival theory (Lal et al., 1969) that for a given saturation, a nucleus has to have a size greater than the critical size to survive. Size dependent birth rate in the SSBCR analysis recognizes that secondary nucleation dominated by contact nucleation (Clontz and McCabe, 1971) may not necessarily generate nuclei of equal size.

The quantity N(t, L) can be easily obtained by use of a Coulter counter so long as the smallest size it can measure is less than the critical size. It has been shown (Cise and Randolph, 1972) that a Coulter counter can be used to measure the size of small particles down to 1 μ m range. However, the inability to measure the size of small particles could become the limiting factor. In such a case, Equation (2) should be integrated from L to $L = \infty$ to

$$\int_{L}^{\infty} n(t,\zeta)d\zeta - G(L) \int_{0}^{t} n(\tau,L)d\tau = t_{\tau} \int_{L}^{\infty} b_{n}(\zeta)d\zeta$$
(5)

since $n(t, \infty) = 0$. This is to say that for all practical purposes, the number of crystals with infinite size is zero in any experiment. Equation (5) can be rewritten in terms of the cumulative number of oversize crystals, and we have

$$\overline{N}(t,L) = G(L)x(t,L) + t_r \overline{B}(L)$$
 (6)

Equation (6) is again a straight line with a slope of $G(L_s)$ and an intercept of $t_r \overline{B}(L_s)$ for a given size, L_s , when \overline{N} is plotted against x. Therefore, either Equation (6) or Equation (4) can be used for the determination of growth rate and cumulative birth rate of secondary nuclei. Birth rate can be obtained by differentiating the cumulative birth rate with respect to size.

It has been tacitly assumed that the duration of an experiment is not long enough for the secondary crystals to become the source of secondary nuclei. In this regard, it is notable that an estimate of the threshold size above which the secondary crystals themselves become the source of secondary nuclei can be made by simply allowing the secondary nuclei to grow and then utilizing the results of Figure 3a. The size in Figure 3b at which the cumulative birth rate breaks away from a plateau it reached (L_t in Figure 3b) would then become the threshold size.

NOTATION

= birth rate

= net birth rate, b - d

B(L) =cumulative birth rate, $\int_0^L b_n(\zeta) d\zeta$

 $\overline{B}(L) = \text{cumulative oversize birth rate, } \int_{L}^{\infty} b_n(\zeta) d\zeta$

= death rate

G(L) = linear growth rate, dL/dt= characteristic size of a crystal

 L_c = critical size L_t = threshold size

= threshold size n(t, L) = number of crystals with size L

N(t, L) = cumulative number of crystals with size up to

$$L,\,\int_0^L\,n(t,\,\zeta)\,d\zeta$$

 $\overline{N}(t, L) = \text{cumulative number of oversize crystals,}$ $\int_0^\infty n(t, \zeta) d\zeta$

$$\int_0^\infty n(t,\zeta)\,d\zeta$$

= time at which a seed crystal is removed from a

$$x(t,L) = \int_0^t n(t,L) dt$$

LITERATURE CITED

Bauer, L. G., M. A. Larson, and V. J. Dallons, "Contact Nucleation of MgSO₄ · 7H₂O in a Continuous MSMPR Crystallizer," Chem. Eng. Sci., 29, 1253 (1974).

Cise, M. D., and A. D. Randolph, "Secondary Nucleation of Potassium Sulfate in a Continuous-Flow, Seeded Crystallizer,

AIChE Symposium Ser. No. 121, 68, 42 (1972) Clontz, N. A., and W. L. McCabe, "Contact Nucleation of Magnesium Sulfate Heptahydrate," Chem. Eng. Progr. Symposium Ser. No. 110, 67, 6 (1971).
Carside, J., and S. J. Jancic, "Growth and Dissolution of

Potash Alum Crystals in the Subsieve Size Range," AIChE J.,

Lal, D. P., R. E. A. Mason, and R. F. Strickland-Constable, "Collison Breeding of Crystal Nuclei," J. Crystal Growth, **5**, 1 (1969)

Ottens, E. P. K., and E. J. de Jong, "A Model for Secondary Nucleation in a Stirred Vessel Cooling Crystallizer," Ind.

Eng. Chem. Fundamentals, 12, 179 (1973).
Randolph, A. D., and M. D. Cise, "Nucleation Kinetics of the Potassium Sulfate-Water System," AIChE J., 18, 806 (1972). —, and M. A. Larson, Theory of Particulate Processes, Academic Press, New York (1971).

"Transient and Steady State Size Distributions in

Continuous Mixed Suspension Crystallizer," AIChE J., 8, 639

Strickland-Coustable, R. F., "The Breeding of Crystal Nuclei A Review of the Subject," AIChE Symposium Ser. No. 121, 68, 1 (1972).

Sung, C. Y., J. Estrin, and G. R. Youngquist, "Secondary Nucleation of Magnesium Sulfate by Fluid Shear," AIChE J., 19, 957 (1973).

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The Effect of pH on Continuous High-Temperature | Short-Time Sterilization of Liquid Foods

K. R. DAVEY, S. H. LIN, AND D. G. WOOD

Department of Chemical Engineering University of Melbourne Parkville, Victoria 3052 Australia

Thermal sterilization of liquid foods for preservation is an important operation in the food industries. High-temperature/short-time (HTST) processing is gaining increasing applications because of the improved product quality (Pfeifer and Vojnovich, 1952; Holdsworth, 1969). Furthermore, the continuous process permits greater control of the processing temperature and exposure time than is possible with the batch process. A major disadvantage of the

Correspondence concerning this note should be addressed to S. H. Lin, Department of Chemical Engineering, Polytechnic Institute of New York, Brooklyn, New York 11201.

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