A Study of the Effect of Sample Size on the Analysis of Power Mixtures

L. E. MARC DE CHAZAL and YEN-CHI HUNG
University of Missouri, Columbia, Missouri

One of the greatest difficulties in the analysis of mixing operations for powders is that of specifying the degree of mixedness in a quantitative manner. This problem is studied for an idealized model. A precise index of the degree of mixing is found for this model, which holds promise of being useful for real mixtures. It is shown that samples of a single size provide all the necessary information. The effect of sample size is defined quantitatively, and a minimum sample size is recommended.

One of the greatest difficulties in the analysis of mixing operations is that of specifying the degree to which a mixture approaches complete mixing. To be useful, the index should be general, and should require a minimum number of samples.

Many investigators have attempted to define the degree of mixedness, and have met with varying degrees of success. The composition variance, used first by Lacey (*1*), has been demonstrated to be inadequate. Bosanquet (*2*), Valentin (*3*), Bourne (*4*), and many others have pointed out, with varying rigor, that composition variance is a function of sample size as well as of "degree of mixedness."

In 1964 Poole et al. (*5*) published work in which, for the first time, several sample sizes were used in an attempt to increase the amount of information obtained out of the experimental results. These investigators analyzed mixtures of powders, taking some ten samples at each of as many as eight sample sizes. They plotted the coefficient of variation vs. sample size on a logarithmic plot, and drew a straight line through the somewhat scattered points.

Their coefficient of variation is defined as

$$C = \frac{s}{m} \tag{1}$$

for the case in which an actual mix is studied. The equation for the coefficient of variation is the same as that for a random mix, except that, in that case, the authors compute the standard deviation by means of a modified form of the equation proposed by Stange (*6*).

Poole et al. concluded that the slope of the best straight line through the points on the aforementioned plot was an index—although not a formula—of the deviation from perfect mixing. Their method, however, has the drawback of requiring the analysis of a large number of samples without satisfying the need for a precise index of mixedness. It is evident from experimental work, for example, that of Poole et al. (*5*), that, at least for small sample sizes, the indices of mixing used to date are dependent on sample size. The important unanswered question is whether one can define a sample size that permits the use of an index of mixedness that no longer depends on sample size.

The problem may be stated as follows: If samples are very large, the variability of their composition may be completely overshadowed by that of the analytical method. If, on the other hand, the samples are small, their composition may be unrepresentative of the mixture from which they are taken. In the latter case, one may obtain an index of mixedness which depends more upon the size of the samples taken than upon the nature of the mixture. Between these two extremes, there may exist a range of sample sizes which will yield an index of mixedness not unduly biased by sample size. If so, can the lower limit of this range be defined?

The present study attempts to answer this question by studying the effect of sample size when an idealized sampling procedure is applied to an idealized mix. The solution is then extended to other types of mix models to show that the conclusions reached have some degree of generality.

MODEL FOR THE MIXTURE

While many types of poor mixing occur, one of the simplest to analyze mathematically has been proposed to Dukes (*7*). This model, which is adopted in the present study, represents mixtures as consisting of randomly distributed groups of either type of particles, each group containing p particles.

In this model *randomly distributed* means that the groups or clusters of the particles are distributed binomally throughout the volume of the total mixture. Let A be the type of particles under study. If X is the fraction of A clusters in the mixture, then in samples containing C clusters each, the variance of the fraction of A clusters in a sample would be

$$\sigma_p^2 = \frac{X(1-X)}{C}$$

If we have a perfectly random mixture in which X is the fraction of A particles, then in samples of N $(= C\ p)$ particles the fraction of A particles would have the variance $\sigma_R^2 = X(1-X)/N$. The ratio of the two variances is

$$\frac{\sigma_p^2}{\sigma_R^2} = \frac{X(1-X)}{(N/p)} \cdot \frac{N}{X(1-X)} = p \tag{2}$$

It would thus seem that if samples of N particles are taken from a mixture containing X percentage of A particles, the ratio of the actual variance of the sample percentages to the random variance should give a measure of mixedness. The advantage of this method is that the measure is (approximately at least) a simple number. The problem arises in that the sample size N is not in general a simple multiple of p and we would in practice need to be concerned about fractions of clusters being included in the sample. To meet this difficulty we assume an idealized method of sampling.

SAMPLING MODEL

It is postulated that the samples taken for analysis are

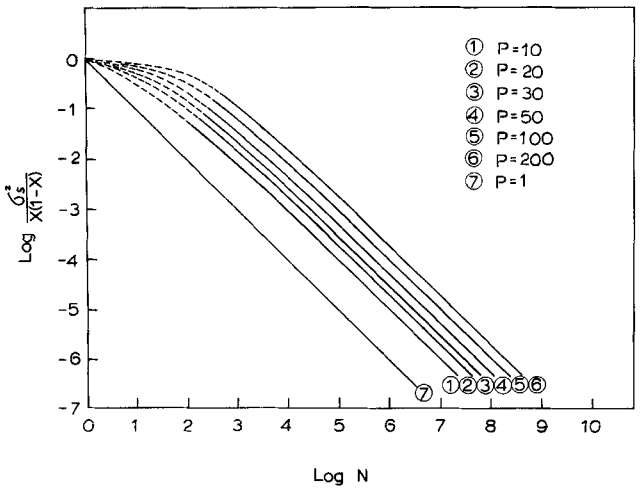

Fig. 1. Logarithmic plot of sample variance vs. sample size, showing the influence of cluster size.

spherical and each contain the exact number N of particles. The samples, which are taken from random points throughout the mixture, cut through the clusters near the sample surface so that the analysis is conducted on a sample containing untouched clusters in the inner portion, and partial clusters about its surface.

MATHEMATICAL TREATMENT

The mathematical analysis of the model is given below in abbreviated form. In general terms, the development is as follows:

1. For a sample size N, the probable number C'_p of complete clusters inside the sample was calculated assuming spherical clusters.
2. The probable number C_i of cut clusters, each with i particles remaining in the sample, was calculated for $i = 1 \ldots p$.
3. The variances of the numbers C_p and C_i were calculated.
4. The composition variance of the sample was calculated for one component of the mixture. This was done by accounting for the variability in both number and composition for each group of cut and uncut clusters. The resulting equation for the variance is given in Equation (3). A derivation of this equation is given at the end of the paper.

$$\sigma_s^2 = \frac{X(1-X)}{N^2}\left[\sum_{i=1}^{p} i^2 C_i + p^2\ C'_p\right] \qquad (3)$$

The influence of sample size on Equation (3) is readily demonstrated, since the relative importance of the term $\sum_{i=1}^{p} i^2 C_i$ to that of $p^2\, C'_p$ is roughly proportional to the ratio of surface to volume of the spherical sample—which ratio is inversely proportional to the sample radius.

It is clear that if the total number of particles in each sample is N, the following expression is true:

$$N = \sum_{i=1}^{p} iC_i + pC'_p \qquad (4)$$

If $p = 1$, that is, if one is dealing with a perfect mixture, Equation (4) reduces to $N = (1)C_1 + (1)C'_1$ which yields $(1)^2C_1 + (1)^2C'_1 = N$. We thus have for a perfect mixture in which $p = 1$:

$$\sum_{i=1}^{p} i^2 C_i + p^2 C'_p = (1)^2\, C_1 + (1)^2\, C'_1 = N \qquad (5)$$

Thus, for a completely random mixture, Equation (3) reduces to

$$\sigma_s^2 = \sigma_R^2 = \frac{X(1-X)}{N} \qquad (6)$$

which is the well-established equation for a perfect mixture, and thus Equation (3) reduces to a proper limit. The ratio σ_s^2/σ_R^2 can be obtained from Equations (3) and (6) as

$$\frac{\sigma_s^2}{\sigma_R^2} = \frac{\sum_{i=1}^{p} i^2 C_i + p^2 C'_p}{N} \qquad (7)$$

As the size N of the sample becomes large, the contribution of the surface clusters becomes progressively less. In fact, it is not difficult to demonstrate that

$$\lim_{N\to\infty} \frac{\sum_{i=1}^{p} i^2 C_i + p^2 C'_p}{N} = \frac{p^2 C'_p}{N} = Np/N = p \qquad (8)$$

Thus, Equation (7) approaches the form Equation (2) as a limit, and Equation (3) may be said to describe properly the physical model postulated.

Further generalization of Equation (3) can be made if, instead of calculating σ_s^2, one calculates $\sigma_s^2/X(1-X)$. Thus

$$\frac{\sigma_s^2}{X(1-X)} = \frac{1}{N^2}\left[\sum_{i=1}^{p} i^2 C_i + p^2 C'_p\right] \qquad (9)$$

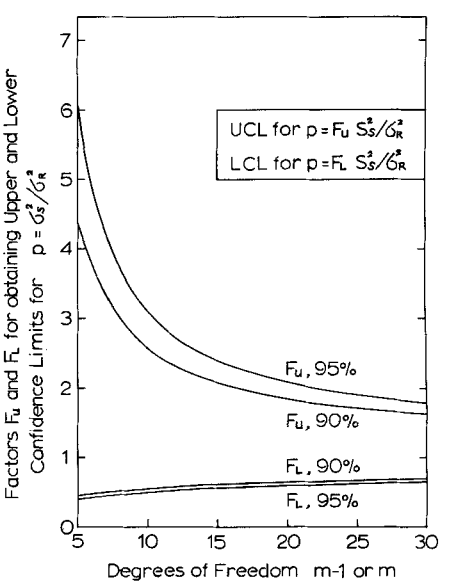

Fig. 2. Factors F_u and F_L for the upper and lower confidence limits for $p = \sigma_s^2/\sigma_R^2$ as a function of the degrees of freedom. These are also the limits of the ratio of the index p to estimate p_e, obtained by analyzing the m samples. The number of degrees of freedom is m if the mix composition is known, and m-1 if it is estimated from the analysis of the m samples.

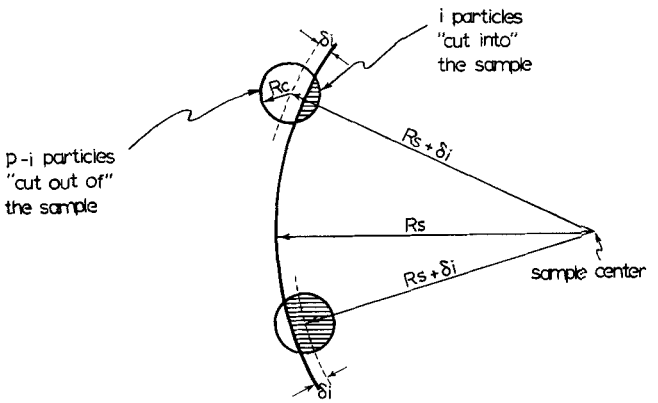

Fig. 3. Diagram showing the inclusion of partial clusters in a sample.

Since the right member of Equation (9) is independent of the composition X of the mixture, it follows that $\sigma_s^2/X(1-X)$ is a function only of the sample size N and the cluster size p.

Calculations were made of the dimensionless variance as a function of N for values of p ranging from 1 to 200. The results are reflected in the curves in Figure 1. These give us, as a function of the sample size N and cluster size p, the continuity correction $[1/(1-K)]$ that must be applied to the ratio of the actual variance to the random variance in order for it to yield the true measure of mixedness p.

DISCUSSION

For the type of mixture outlined above, it is thus sufficient, in order to characterize the mixture, to determine the experimental variance for samples of a single size. Given a sufficient number of samples, the value of p obtained from

$$p \simeq \frac{\sigma_s^2}{\sigma_R^2}\left(\frac{1}{1-K}\right) \qquad (10)$$

would provide an almost exact description of the mixture.

In practical cases, there exist a number of complicating factors. Additional errors which must be accounted for would be introduced by (1) variation of sample size about N, (2) variations in analytical technique, (3) concentration gradients in the mixture, and (4) other mix and sampling configurations. Furthermore, many other forms of poor mixing do exist, and mixes usually contain more than one size of solid.

These factors will complicate the characterization of a mixture. However, the propagation of error due to the additional sources 2 and 3 above has been described in several papers (for example, 8). The effect of source 1 depends on the value of K in Equation (10), and is somewhat complicated. For the value of N recommended in this paper, this source of error need not concern us.

In order to determine the effect of different types of mixing on the method presented above, two other types of mixing were checked.

The first of these mixes consists of randomly distributed sheets of unmixed particles. These sheets were assumed to be square monolayers with each side having a length $2\sqrt{p\ R_p}$, where R_p is the radius of an individual particle. For this mixture, Equation (10) gives the value p exactly if the sample size N is very large. However, the results for smaller samples are somewhat different: the correspondence between sample size and K is altered so that, for the same value K to be used, the sample size N needs to be about 2.4 times larger than that for the mixture of spherical clusters.

The second type of mix consists of a random mixture of spherical clusters containing p particles each. In this case, unlike the main model discussed in this paper, it is assumed that the clusters have undergone some degree of mixing, so that they have compositions W, Y, or Z such that the overall composition remains X. In this case, Equation (10) will yield a constant of value less than p. This number p depends on the values of W, Y, Z and on their associated expectations. As a limit, as all three compositions approach X, the calculated value of p goes to unity. The difference between the calculated value of p and the cluster size is a reflection of the greater degree of mixing that occurs in this model that in the unmixed cluster model. The relationship between sample size and K, however, is identical to that for the unmixed cluster model.

The method of study of the two mixtures above was entirely analogous to that presented in this paper. Accordingly, they are not discussed further.

The influence of sample shape on Equation (10) comes from the change in the ratio of sample surface to sample volume. The greater the surface-to-volume ratio, the worse the results will be. Thus, cubic samples must be twice as large as spherical samples in order to achieve the same degree of accuracy as reflected by the value of K.

Since the value of K is not uniquely a function of sample size, the minimum sample used should be such that the value of K in Equation (10) may be neglected. According to Figure 1, the minimum number of particles in each sample should be about ten thousand. Under those circumstances, Equation (2) becomes directly applicable with acceptable accuracy.

The reliability of the estimate of p given by S_s^2/σ_R^2 depends on the number of m samples taken. If one assumes that the sample compositions X_i are normally distributed about the mix composition X, then the 0.95 and 0.90 confidence limits for S_s^2/σ_s^2, which is approximately the true value of p, can be derived from Figure 2. These limits can be obtained by multiplying the value of S_s^2/σ_R^2 derived in a given experiment by the values given by the upper and lower lines on the chart. For $S_s^2/\sigma_R^2 = 3$, for example, and $m = 21$, 0.95 confidence limits for p would be UCL $= 3(2.1) = 6.3$ and LCL $= 3(0.6) = 1.8$. The values used in Figure 2 are obtained from the chi-squared distribution, available in most texts on statistical analysis.

The number of samples used in any given case will depend on how wide a confidence interval is deemed acceptable. Figure 2 can be used to assist in selecting the number of samples appropriate to the occasion.

CONCLUSIONS

It may now be stated that an index of mixing such as the one given in Equation (2) is dependent on the shape and size of the samples taken, and on the nature of the unmixedness of the mixture. However, if the samples are approximately spherical or cubic in shape, and if the mixture is not grossly poor, samples containing some ten thousand particles will yield, by use of Equation (2), an index of mixing nearly independent of sample size.

The extent to which the index p diverges from unity represents possible improvements that may be achieved by better mixing. Thus, Equation (2) can serve to assess the need to make improvements in mixer design and operation.

It may further be stated that small samples, that is, samples containing much less than one thousand particles, may give deceptively good results. Under those circumstances, the analysis may fail to reveal the full extent of poor mixing.

NOTATION

C = coefficient of variation in Poole, Taylor, and Wall model
C_i = probable number of cut clusters in a sample that contains i particles
C'_p = probable number of uncut clusters in a sample
K = error involved in assuming that $p = \sigma_s^2/\sigma_R^2$
L = weight factor as defined in Equation (15)
m = mean composition of mixture in Poole, Taylor, and Wall model
N = number of particles in a sample
p = number of particles in a cluster or index of mixing
p_e = estimate of the index of mixing obtained from a finite number of samples
R_c = radius of the spherical clusters
R_s = sample radius
R_p = radius of individual particles
S = estimate of standard deviation in Poole, Taylor, and Wall model.
S^2_s = estimate of variance of the model mixture
w = weight factor in Equation (12)
X = overall composition of the mix

Greek Letters

α = weight factor as defined in Equation (17)
δ_i = distance between the sample center and the center of a "cut" cluster minus the sample radius
σ_{ci}^2 = variance of the quantity C_i
σ_i^2 = number variance of the component in i cut clusters
σ_{iX}^2 = composition variance of the component in the i cut clusters
σ_R^2 = composition variance of a perfect mixture
σ_s^2 = composition variance of the model mixture obtained from a finite sample size.
σ_u^2 = number variance of the component in interior clusters

LITERATURE CITED

1. Lacey, P. M. C., *J. Appl. Chem.*, **4**, 257 (1954).
2. Bosanquet, C. H., *Trans. Inst. Chem. Engrs.*, **37**, 62, (1959).
3. Valentin, F. H. H., *Chem. Proc. Eng.*, **24**, 181 (1965).
4. Bourne, J. R., *Chem. Eng.*, **43**, CE 198 (1965).
5. Poole, K. R., R. F. Taylor, and G. P. Wall, *Trans. Inst. Chem. Engrs.*, **42**, T305 (1964).
6. Stange, K., *Chem. Eng. Technol.*, **35**, 580 (1963).
7. Dukes, J. A., *Intern. Chem. Eng.*, 521 (1951).
8. Berthof, W. M., "ASTM Special Technical Publication No. 114," p. 46 (1951).

Manuscript received May 2, 1966; revision received May 26, 1967; paper accepted May 29, 1967. Paper presented at AIChE Atlantic City meeting.

APPENDIX: DERIVATION OF THE EQUATION FOR THE SAMPLE VARIANCE

Consider a sample containing N particles. It will contain clusters which were entirely within the surface of the sample, and partial clusters which were cut through by the surface of the sample. In terms of a large number of samples, one can expect that each possible type of cut will appear with a given frequency. Then

$$N = 1 \cdot C_1 + 2 \cdot C_2 + \ldots + i \cdot C_i + \ldots + p \cdot C_p + p \cdot C'_p = \sum_{i=1}^{p} i \cdot C_i + p \cdot C'_p \quad (11)$$

To simplify the problem of evaluating the expectation values C_i, it is desirable to make certain simplifying assumptions that are best understood with the help of Fig. 3.

Assume that all clusters are essentially spherical. Then, as shown in Figure 3, the clusters that are cut to leave i particles in the sample will all be located with centers at a distance $R_s + \delta_i$ from the center of the sample. As shown in Figure 3, δ_i may be either positive or negative. Also, if the radius R_s of the sample is large compared with the radius R_c of the cluster, δ_i will be zero when $i = p/2$.

Given the premise that clusters are located randomly, and that the center of the sample has equal probability of being located in any differential volume, the value of the expectation C_i is proportional to the square of the distance between the sample center and cluster center or

$$C_i = w(R_s + \delta_i)^2 \quad (12)$$

Then, by division, if p is even

$$\frac{C_i}{C_{p/2}} = \frac{(R_s + \delta_i)^2}{R_s^2} \quad (13)$$

and hence

$$w = \frac{C_{p/2}}{R_s^2} \quad (14)$$

Since p may be odd, Equation (12) is best rewritten in the form

$$C_i = \frac{L}{R_s^2}(R_s + \delta_i)^2 \quad (15)$$

where

$$L = C_{p/2} \text{ for } p \text{ even}$$

$$L = \frac{C_{p+1}}{2} \text{ for } p \text{ odd}$$

The relationship between i and the associated δ_i is geometrical. The derivation, although simple, is tedious, and results in the following equation

$$\delta_i = -2 R_C \cos\left[\frac{1}{3}\cos^{-1}\left(\frac{2i}{p} - 1\right) + \frac{\pi}{3}\right] \quad (16)$$

where

$$0 \leq \left|\cos^{-1}\left(\frac{2i}{p} - 1\right)\right| \leq \pi$$

Similarly, the value of L may be derived by solving the combined geometrical and probabilistic models. The value of L obtained is

$$L = \frac{\pi}{1.6\alpha}\left(\frac{R_s}{R_c}\right)^2 \quad (17)$$

where

$\alpha = 0.5\,(p + 2)$ when p is even
$\alpha = 0.5\,(p + 1)$ when p is odd

Substituting Equations (16) and (17) in Equation (15), one gets

$$Ci \simeq \frac{\pi}{1.6\alpha}\left\{\frac{R_s}{R_c} - 2\cos\left[\frac{1}{3}\cos^{-1}\left(\frac{2i}{p} - 1\right) + \frac{\pi}{3}\right]\right\}^2 \quad (18)$$

Substituting this equation into Equation (11) allows one to solve for C'_p, with the following result:

$$C'_p \simeq \frac{\pi}{6}\left(\frac{R_s}{R_c}\right)^3 - \frac{\pi}{1.6\alpha}\left(\frac{R_p}{R_c}\right)^3 \sum_{i=1}^{p} \left\{\left[\frac{R_s}{R_c} - 2\cos\left\langle\frac{1}{3}\cos^{-1}\left(\frac{2i}{p} - 1\right) + \frac{\pi}{3}\right\rangle\right]^2 \cdot i\right\} \quad (19)$$

where R_p is the radius of individual particles; hence, allowing for void space, one obtains

$$N \simeq \frac{\pi}{6} p \left(\frac{R_s}{R_c}\right)^3 + \frac{\pi}{1.6\alpha}\left[1 - p\left(\frac{R_p}{R_c}\right)^3\right] \sum_{i=1}^{p} \left\{\left[\frac{R_s}{R_c} - 2\cos\left\langle \frac{1}{3}\cos^{-1}\left(\frac{2i}{p} - 1\right) + \frac{\pi}{3}\right\rangle\right]^2 \cdot i\right\} \quad (20)$$

The expected values C_i and C'_p are mean values, given an infinite number of samples. Variations about these numbers will exist. Furthermore, the composition of the sample will be affected by the variability in the composition of the clusters in the sample.

Consider a single component of the mixture having an overall concentration X in the mixture. Then, the expected number of particles of the component in the sample contributed by the i-cut is

$$N_i = i \cdot C_i \cdot X$$

with variance

$$\sigma_i^2 = \sigma^2 (i \cdot C_i \cdot X) = (i \cdot C_i)^2 \sigma_{iX}^2 + (i \cdot X)^2 \sigma_{ci}^2 \quad (21)$$

The variance σ_{iX}^2 is obtained from the binomial distribution as though the mixture consisted of clusters of i particles each, and as though C_i such clusters were picked. Thus

$$\sigma_{iX}^2 = \frac{X(1-X)}{C_i} \quad (22)$$

For the whole sample, if the number N of particles in the sample is assumed invariant, the composition variance is given by the followning expression:

$$\sigma_s^2 = \frac{\sum_{i=1}^{p} \sigma_i^2 + \sigma_u^2}{N^2} \quad (23)$$

If one substitutes Equations (21) and (22) into Equation (23), one gets

$$\sigma_s^2 = \frac{1}{N^2}\left\{\sum_{i=1}^{p} [i^2 \cdot C_i X(1-X) + i^2 X^2 \sigma_{ci}^2] + C'_p \cdot p^2 X(1-X) + X^2 p^2 \sigma_{cp'}^2\right\} \quad (24)$$

When N is sufficiently large that $\sigma_{cp'}^2$ is small compared with C'_p, or when X is small, Equation (24) can be simplified. Since N is constant

$$\sum_{i=1}^{p} i^2 \sigma_{ci}^2 = -p^2 \sigma_{cp'}^2 \quad (25)$$

then, for $X^2 p^2 \sigma_{cp}^2$ negligible, one gets

$$\sigma_s^2 = \frac{X(1-X)}{N^2}\left[\sum_{i=1}^{p} C_i \cdot i^2 + C'_p \cdot p^2\right] \quad (3)$$

or, in terms of Equations (18) and (19)

$$\sigma_s^2 = \frac{X(1-X)}{N^2}\left\{\sum_{i=1}^{p}\left[\frac{i^2\pi}{1.6\alpha}\left(\frac{R_s}{R_c} - \beta\right)^2\right] + p^2\left[\frac{\pi}{6}\left(\frac{R_s}{R_c}\right)^3 - \frac{\pi}{1.6\alpha}\left(\frac{R_p}{R_c}\right)^3 \sum_{i=1}^{p}\left(\frac{R_s}{R_c} - \beta\right)^2 i\right]\right\} \quad (26)$$

where

$$\beta = 2\cos\left[\frac{1}{3}\cos^{-1}\left(\frac{2i}{p} - 1\right) + \frac{\pi}{3}\right]$$

Equation (26) was used to calculate the values of σ_s^2/σ_R^2 used in Figure 1. As can be seen from that plot a sample size of one to ten thousand particles is an acceptable lower limit for use of Equation (2) unless mixing is very poor. Samples much smaller than that will reflect a pseudo mixing effect of sampling to a degree which may be unacceptably large.

Dynamic Optimization with Constraints from Wiener's Techniques

R. H. LUECKE and M. L. MCGUIRE

University of Oklahoma, Norman, Oklahoma

Most process optimization techniques under development in recent years were obtained as fallout from military and communications applications. Interest in these methods within the chemical and process industries has been stimulated in part by competitive and other economic pressures to reduce operating costs. However, these optimization techniques usually require extensive modification before they are suited to most process industry problems.

This paper describes the development of design equations for composite feedback-feedforward process controllers based on a technique originated by Wiener (*12*) for studies in communications engineering. Controllers based on these equations were subsequently applied to various analog simulations as well as to a physical experimental laboratory system. The results of the applications are de-

R. H. Luecke is with Monsanto Company, St. Louis, Missouri.