APPENDIX B

LIQUID DISPERSION DATA ANALYSIS

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LIQUID MIXING DATA ANALYSIS PROGRAM

A modified method of moments involving approximation of the RTD curves by a log-normal distribution has been selected to process the liquid mixing data. This method starts with calculations of the total area under the RTD curve and the percentage of cumulated area as a function of time. These percentage-cumulated areas are then plotted against sampling time on logarithmic probability paper and fit by a straight line to smooth the raw, experimental data points. The Peclet number (or the dispersion coefficient) is calculated from the mean (the first moment) and the variance (the second moment) of the RTD curves according to an axial dispersion model.

Axial Dispersion Model

To calculate the liquid Peclet number and the dispersion coefficient, a dispersed plug flow axial mixing model is assumed. In dimensionless form, the basic differential equation representing this dispersion model is

$$\frac{\partial c}{\partial \theta} = \left(\frac{D_1}{U_z L}\right)\frac{\partial^2 c}{\partial z^2} - \frac{\partial c}{\partial z} \tag{B-1}$$

where C = Sulfur concentration, ppm.
θ = Sampling time, $T \cdot U_z/L$, dimensionless.
D_1 = Liquid dispersion coefficient, cm^2/sec.
U_z = Average linear liquid velocity, cm/sec.
L = Distance between measuring points, cm.
Z = Axial position, z/L, dimensionless.

Solutions to the Dispersion Model

If a perfect input pulse is assumed, the analytical solution to Equation 1 (Levenspiel and Smith, B-4) is

$$C = \frac{Q}{A\sqrt{4\pi\theta D_1/U_z L}} \ exp \left[\frac{-(1-\theta)^2}{4\theta D_1/U_z L}\right] \tag{B-2}$$

where Q = Amount of tracer injected into the system.
A = Cross-sectional area of the reactor.

D_1 can be estimated by least squares using Equation 2 and the concentration-time data.

In practice, it is impossible to introduce an ideal input pulse of the tracer into the system. In order to eliminate the necessity for a perfect input pulse, the technique of detecting tracer concentration at two downstream positions is employed.

As shown by many investigators (Aris [B-1]; Bischoff and Levenspiel [B-2]; Levenspiel and Smith [B-4]; Sater and Levenspiel [B-7]), the axial dispersion coefficient can be calculated from the first and second moments of the RTD curves at two positions. The first and second moments of the RTD curves are given by

$$\mu_i = \frac{\int_0^\infty c_i \cdot T \, dT}{\int_0^\infty c_i \, dT} \tag{B-3}$$

$$\sigma_{\theta_i}^2 = \frac{\int_0^\infty c_i \cdot T^2 \, dT}{\int_0^\infty c_i \, dT} - \mu_i^2 \tag{B-4}$$

where i = 1 and 2.
    T = Real time, sec.

Since the first moment of the RTD curve is the mean of that curve, the average residence time of the tracer can be calculated by taking the difference of the first moments of the RTD curves:

$$T_m = \mu_2 - \mu_1 \tag{B-5}$$

The second moments of the RTD curves are a measure of the spread of the RTD curves, and the difference of the second moments is a measure of the amount of axial mixing occurring between the two measuring points. This relationship has been derived analytically by Levenspiel and Smith (B-4):

$$(\Delta\sigma_\theta)^2 = (\sigma_{\theta 2})^2 - (\sigma_{\theta 1})^2 = 2/Pe + 8 \ (1/Pe)^2 \tag{B-6}$$

Aris (B-1) has shown that for a one-shot injection of tracer with the RTD being measured at two downstream positions, the above equation can be approximated adequately by

$$(\Delta\sigma_\theta)^2 = 2/Pe \tag{B-7}$$

In this method, however, the tail of the RTD curve can cause significant error in the calculation of Pe. Ostergaard and Michelsen (B-6) introduced a method involving the Laplace transform of the axial dispersion model and evaluation of a linear transfer function. The authors claim that this method gives more consistent results than the method of moments, regardless of the severity of the tailing and the terminal point of the tail.

The transfer function for a linear system is described by

$$F(s) = \frac{C_2(s)}{C_1(s)} = \frac{\int_0^\infty C_2(T) \exp(-ST)dt / \int_0^\infty C_2(T)dT}{\int_0^\infty C_1(T) \exp(-ST)dt / \int_0^\infty C_1(T)dT} \qquad \text{(B-8)}$$

The axial dispersion model after the Laplace transformation is

$$F(s) = \exp\left\{\frac{P_e}{Z} [1 - (1 + \frac{4S\,T_m}{P_e})^{1/2}]\right\} \qquad \text{(B-9)}$$

After rearranging, the above equation becomes

$$\left[\log\left(\frac{1}{F(s)}\right)\right]^{-1} = T_m S \left[\log\left(\frac{1}{F(s)}\right)\right]^{-2} - \frac{1}{P_e} \qquad \text{(B-10)}$$

A plot of $(1/F[s])^{-1}$ versus $S[\log(1/F[s])]^{-2}$ should yield a straight line. The Peclet number and the mean residence time can then be calculated from the intercept and slope, respectively.

This method was evaluated by processing several sets of liquid mixing data, and the results were unsatisfactory. One of the problems associated with using the Laplace transfer function for estimating dispersion parameters is the range of the Laplace operator, s. Hopkins, et al., (B-3) studied this effect and showed that for small values of s, the transfer function becomes insensitive to variation in the parameter $s \cdot T_m$. Therefore, small errors in the transfer function will greatly affect the resulting values of slope and intercept. For large values of s, the initial part of the tail is too heavily weighted to give accurate evaluation of the transfer function.

Selected Method of Solution

Due to unsatisfactory results produced by using the Laplace transfer function, a modified method of the moments was used to process the liquid mixing data. This modified method of moments, involving approximation of the RTD curves by a log-normal distribution, has been selected to process the liquid-phase mixing data. The method requires plotting the cumulative percentage (per cent total area) against the corresponding sampling time (t) on the logarithmic probability paper (Levenspiel and Smith [B-4]). Data smoothing, including determination of the cut-off point of the tail, was done by drawing a straight line which best fit the data points up to about 98% total area on the logarithmic probability paper. An example plot is shown in Figure B-1.

Because the cumulative percentage area is plotted against the corresponding sampling time on logarithmic probability paper, the following conversions are involved in obtaining the first and second moments on the arithmetic scale. The first moment about the origin of sampling time is

$$\mu = \exp[\ln T' + S^2/2] \qquad \text{(B-11)}$$

where $S = \ln T'' - \ln T'$

 $T' =$ Sampling time corresponding to log-normal distribution mean (at 50%).

 $T'' =$ Sampling time corresponding to one standard deviation in log-normal distribution (at 84%).

The second moment about origin of sampling time is

$$\sigma = \mu \, [\exp(s^2) - 1]^{1/2} \tag{B-12}$$

Since the dimensionless sampling time $\theta = t/T_m = t/\Delta\mu$

$$(\sigma_\theta)^2 = \frac{\sigma^2}{T_m^2} = \frac{2}{Pe} \tag{B-13}$$

For liquid mixing experiments using two RTD curves to estimate the variance, the above equation becomes

$$(\Delta\sigma_\theta)^2 = \frac{\Delta\sigma^2}{T_m^2} = \frac{2}{Pe} = 2\,\frac{D_1}{U_z L} \tag{B-14}$$

Substituting values calculated from Equations B-11 and B-12 into Equation B-14, the Peclet number and dispersion coefficient can be calculated.

Sensitivity of P_e on Parameters s, μ, and σ

The application of the method of moments to estimate the dispersion coefficient is straightforward, as illustrated by Equation B-14. The value of P_e, however, is greatly influenced by the difference of the second moments. As the values of $\Delta\sigma^2$ approach zero, error associated with the Pe calculation increases rapidly.

In general, the first moments can be estimated with less relative error than the second moments. As can be seen from the logarithmic probability plot (Figure B-1) for the liquid mixing data, the first moment is estimated at a single point (50%) and is relatively insensitive to the slope of the line. The second moment, estimated from the difference between 84% and 50% points (one standard deviation), is very sensitive to the slope of the line.

The slope of the line is determined by the distribution of the cumulative area under the RTD curve, which in turn is affected by the value of the base line for the RTD curve. Based on analysis of the cold-flow liquid mixing data, a guideline was established for selecting a proper base line concentration. In general, if the initial sulfur concentration agrees closely with the average sulfur concentration of the tail, the average of the two is chosen. When this is not the case, the average sulfur concentration of the tail is chosen as the base line.

Variability between tests may also be estimated by comparison of results of experiments performed at similar conditions. Table B-I contains two such comparisons.

NOMENCLATURE FOR APPENDIX B

A	Cross-sectional area of the column.
C	Sulfur concentration, ppm.
$C(s)$	Laplace transform of C.
D_1	Dispersion coefficient, cm^2/sec.
$F(s)$	Laplace transfer function, Equation B-8.
Pe	Peclet number.
Q	Amount of tracer injected into the system.
S	Standard deviation or square root of the variance in log scale.
T	Sampling time corresponding to C, sec.
T'	Sampling time corresponds to log-normal mean.
T''	Sampling time corresponds to one log-normal standard deviation.
T_m	Mean residence time, sec.
U_z	Average linear liquid velocity, cm/sec.
z	Axial position, cm.
z	Axial position, dimensionless (z/L).

Greek

θ	Sampling time, dimensionless.
σ	Second moment or square root of the variance.
σ_θ	σ/T_m.
μ	First moment or mean of the RTD curve.

REFERENCES FOR APPENDIX B

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TABLE B-I

VARIABILITY BETWEEN DENSE-PHASE LIQUID MIXING RESULTS

Run No.	U_g (cm/Sec)	U_l (cm/Sec)	D_l (cm²/Sec)
490-11	2.80	2.96	76.0
490-20	2.90	2.95	72.2
490-23	2.87	2.90	94.3
Mean			80.83 ± 11.81
Standard Error 14.6%, 2 df			
490-8	0	2.96	9.10
490-14	0	2.95	12.50
490-15	0	3.05	7.68
490-16	0	2.96	13.3
Mean			10.65
Standard Error 25.2%, 3 df			

Figure B-1

PROBABILITY PLOT FOR RUN 490-08