CHAPTER 3

METHODOLOGY AND RESPONSE DATA ANALYSIS

In studying the coefficient of longitudinal dispersion D , cm^2/s , during fluid flow through packed beds , the following items will be discussed in details in this chapter : the dynamic methods in general , the pulse testing method in particular , and the response data analysis .

3.1 Dynamic Methods

To detect purposely the concentration dynamics of a packed bed system for determining its spreading characteristics and eventually its model , the general approach is to excite the system with a detectable substance and to observe its response . Several methods of introducing disturbances into the system have been experimentally suggested , for instance , sinusoidal forcing functions , step functions and pulse functions. The first method has some disadvantages such as being time consuming when allowing the system to reach steady state , or being unstable during operation because of oscillation , and difficulties in constructing and operating the apparatus required to induce sinusoidal disturbances with adequate variations in frequencies .

Although creating impulses may seem difficult but it is actually straightforward . Therefore , further studies for mixing of fluids in flow systems will make wide use of impulse injections .This method actually employs a single arbitraty pulse to excite the system with all frequencies at once . By applying a suitable calculation technique , the frequency response information as well as mixing characteristics can be extracted from the resulting response which is in turn used to construct a model . Hence the pulse testing method is practical .

3.1.1 Foundation of the method (22,25)

Suppose a stream flowing with a steady volumetric flow rate Q into a system of volume V . Then a certain amount of miscible tracer M' is introduced in a time interval as short as possible . Let c_e equal the effluent stream concentration . Thus the materiel balance gives rise to

$$M' = \int_0^\infty [c_e(t)Q]dt = \int_0^\infty [c_i(t)Q]dt$$

or

$$M'/Q = \int_0^\infty [c_e(t)dt] = \int_0^\infty [c_i(t)]dt \qquad 3.1$$

The above equation yields the total area of concentration - time response curve from which M can be found in practice when Q is known . Since the response curve shows that only a fraction of the tracer exits for a particular residence time , thus let us define it as follows :

$$Y(t) = \frac{c_e(t)}{(M'/Q)} = \frac{c_e}{\int_0^\infty [c_e(t)]dt} \qquad 3.2$$

Similarly , if the tracer is measured at the inlet , the fraction of tracer inlet can also be defined as

$$X(t) = \frac{c_i(t)}{(M'/Q)} = \frac{c_i}{\int_0^\infty [c_i(t)]dt} \qquad 3.3$$

For further mathematical treatment it is more convenient to transform this concentration distribution into a probability distribution followed by normalization . Dividing equation 3.1 with M/Q , we obtain

$$\int_0^\infty \frac{c_i(t)}{(M'/Q)}dt = \int_0^\infty \frac{c_e(t)}{(M'/Q)}dt = 1 \qquad 3.4$$

equations 3.2 and 3.3 eventually become

$$\int_0^\infty [Y(t)]dt = \int_0^\infty \frac{c_e}{\int_0^\infty c_e(t)dt} dt = 1 \qquad 3.5$$

$$\int_0^\infty [X(t)]dt = \int_0^\infty \frac{c_i}{c_i(t)dt} dt = 1 \qquad 3.6$$

This probability distribution is used to analyze response data . Furthermore considerable information can be extracted from this characteristic feature which represent the system flow pattern .

3.1.2 <u>Pulse testing method for axial dispersion measurement</u>

As one of the dynamic methods the pulse tracer has traditionally been very popular . Therefore for axial dispersion coefficient measurements in this work , a delta function of methane tracer is injected into a propane gas stream flowing through a packed bed filled with 3 Å molecular sieve carbon adsorbents . This performance provides both gases passing through the bed with none appreciably entering the adsorbent pores . Although in practice , a perfect impulse injection function is hardly a physical possibility but the short injection time of the smallest magnitude of tracer will improve this situation . Thus the response data can be recovered . And the model is optimized with the experimental data using solely the exit response which corresponds to the exit age distribution .

3.2 Response data analysis

Various mathematical treatments have been used to analyse the response data and correlate them in the form of equation 3.4 to the model parameters of the system . However , the moment analysis and frequency response analysis will be used in this study and will be presented in this section .

3.2.1 Frequency Response Analysis

This method fits a model in the frequency domain . From the experimental response data the transfer function is obtained by applying the Fourier transformation to both Y(t) and X(t) . By taking their ratio we obtain .

$$H_o(j\omega) = \frac{\int_0^\infty [e^{-j\omega t}Y(t)]dt}{\int_0^\infty [e^{-j\omega t}X(t)]dt} \qquad 3.7$$

Since Y(t) and X(t) are continuous functions of a bounded variable which return to their initial values after a certain time and remain so as time progress , the integrals exist and may be evaluated for each value of . In order to simplify equation 3.7 into a standard complex variable form , one can proceed as follow

$$H_o(j\omega) \quad = \quad \frac{\int_0^\infty Y(t)\cos(\omega t)dt - j\int_0^\infty Y(t)\sin(\omega t)dt}{X(t)\cos(\omega t)dt - j \ X(t)\sin(\omega t)dt} \qquad 3.8$$

Let

$$A = \int_0^\infty Y(t)\cos(\omega t)dt$$

$$B = \int_0^\infty Y(t)\sin(\omega t)dt$$

$$C = \int_0^\infty X(t)\cos(\omega t)dt$$

$$D = \int_0^\infty X(t)\sin(\omega t)dt$$

hence equation 3.8 becomes

$$H_o(j\omega) = \frac{A - jB}{C - jD} = \frac{AC + BD}{C^2 + D^2} + j\frac{AD - BC}{C^2 + D^2}$$

or

$$H_o(j\omega) = R_o(\omega) + I_o(\omega) \qquad 3.9$$

where

$$R_o(\omega) = \frac{AC + BD}{C^2 + D^2}$$

$$I_o(\omega) = \frac{AD - BC}{C^2 + D^2}$$

Similarly , the transfer function derived from an appropriate model can also be expressed in term of the frequency domain as

$$H_p(j\omega) = R_p(\omega) + jI_p(\omega) \qquad 3.10$$

If the selected model is good enough to represent the flow pattern , there must exist a corresponding set of parameter values contained in $H_p(j\omega)$ such that

$$H_p(j\omega_i) = H_o(j\omega_i) \qquad \text{for} \quad i = 1,2,--,J$$

The criterion of fit is to choose a set of parameters such that the error function ,Φ, is minimal

$$\Phi = \sum_{i=1}^{J}[(R_p(\omega_i) - R_o(\omega_i))^2 + (I_p(\omega_i) - I_o(\omega_i))^2] \qquad 3.11$$

The advantage of this method is explained by Parseval's theorem

$$\int_0^{\infty}|Y_p(t) - Y_o(t)|^2 dt = 1/\pi \int_0^{\infty}|Y_p(j\omega) - Y_o(j\omega)|^2 d \qquad 3.12$$

which implies that a minimization of response deviations in the frequency domain also leads to a minimization of response deviations in the time domain .The right hand side of equation 3.14 can be rewritten as

$$1/\pi \int_0^{\infty}|Y_p(j\omega)-Y_o(j\omega)|^2 d = 1/\pi \int_0^{\infty}|X(j\omega)|^2|H_p(j\omega)-H_o(j\omega)|^2 d \qquad 3.13$$

This implies that the minimization of the deviations between the predicted and observed transfer function in the frequency domain with respect to a given input gives rises to the minimization of the deviations of response in the time domain . On the other hand disadvantages arise from the fact that the expression for $H_p(j\omega)$ must be obtained by substituting $j\omega$ for s in $H_p(s)$ and separating it into real and imaginary parts . This is a formidable task for a complicated expression representing the model transfer function . Moreover , the real and imaginary parts for each take more computational time to compute as compared to that of the moment's method of analysis .

3.2.2 The Moment's Method of Analysis

The general procedure of this method deals with a definition of the K^{th} moment of the exit age distribution $c_e(t)$ or the probability density function , Y(t) .

$$M_{tyk} = \int_0^\infty t^k Y(t)dt \qquad k = 1,2,--, \qquad 3.14$$

or

$$M_{tyk} = \int_0^\infty t^k \left(\frac{c_e(t)}{\int_0^\infty c_e(t)dt} \right) dt = \frac{\int_0^\infty t^k c_e(t)dt}{\int_0^\infty c_e(t)dt} \qquad 3.15$$

Now let us consider a general Laplace transform of Y(t)

$$Y(s) = \int_0^\infty e^{-st} Y(t)dt \qquad 3.16$$

If we differentiate equation 3.16 successively with respect to s and take the limit as s approaches zero we obtain

$$\lim_{s\to 0} \frac{d^kY(s)}{ds^k} = (-1)^k M_{tyk} \qquad k = 1,2,--- \qquad 3.17$$

when K = 1 this expression results in the first moment of Y(t) in the time domain which equals to the mean of Y(t) . That is

$$\mu_{ty} = \frac{\int_0^\infty tc_e(t)dt}{\int_0^\infty c_e(t)dt} = \int_0^\infty tY(t)dt = M_{ty1} = -\lim_{s\to 0} \frac{dY(s)}{ds} \qquad 3.18$$

Its second moment is defined as a variance which can be written as

$$\sigma^2_{ty} = \int_0^\infty (t-\mu_{ty})^2 Y(t)dt$$

$$= \int_0^\infty (t-\mu_{ty})^2 \left(\frac{c_e(t)}{c_e(t)dt}\right) dt$$

$$= \frac{\int_0^\infty (t-\mu_{ty})^2 c_e(t) \ dt}{\int_0^\infty c_e(t)dt}$$

$$= M_{ty2} - \mu_{ty}^2$$

$$= \lim_{s \to 0} \left[\frac{d^2Y(s)}{ds^2} - \left(\frac{dY(s)}{ds} \right)^2 \right] \qquad 3.19$$

Similarly , it can be expressed as a mean and a variance of X(t) , in the following forms , respectively .

$$\mu_{tx} = \frac{\int_0^\infty tc_i(t)dt}{\int_0^\infty c_i(t)dt} = \int_0^\infty tX(t)dt = M_{tx1} = -\lim_{s \to 0} \frac{dX(s)}{ds} \qquad 3.20$$

$$\sigma^2_{tx} = \int_0^\infty (t-\mu_{tx})^2 X(t)dt$$

$$= \frac{\int_0^\infty (t-\mu_{tx})^2 \, c_i(t) \, dt}{\int_0^\infty c_i(t)dt}$$

$$= \lim_{s \to 0} \left[\frac{d^2X(s)}{ds^2} - \left(\frac{dX(s)}{ds} \right)^2 \right] \qquad 3.21$$

From the system transfer function , the relationship between the K^{th} moment and the transfer function can be expressed as follows

$$H(s) = \frac{Y(s)}{X(s)} \qquad 3.22$$

and

$$\lim_{s \to 0} Y(s) = \lim_{s \to 0} \int_0^{\infty} [e^{-st} Y(t)]dt = \int_0^{\infty} [Y(t)]dt = 1 \qquad 3.23$$

$$\lim_{s \to 0} X(s) = \lim_{s \to 0} \int_0^{\infty} [e^{-st} X(t)]dt = \int_0^{\infty} [X(t)]dt = 1 \qquad 3.24$$

hence

$$\lim_{s \to 0} H(s) = \lim \frac{Y(s)}{X(s)} \qquad 3.25$$

If we take successive differentiations of equation 3.22 , the results are

$$\frac{H'(s)}{H(s)} = \frac{Y'(s)}{Y(s)} - \frac{X'(s)}{X(s)} \qquad 3.26$$

$$\left[\frac{H''(s)}{H(s)} - \frac{(H'(s))^2}{H^2(s)}\right] = \left[\frac{Y''(s)}{Y(s)} - \frac{(Y'(s))^2}{Y^2(s)}\right] - \left[\frac{X''(s)}{X(s)} - \frac{(X'(s))^2}{X^2(s)}\right] \qquad 3.27$$

As s approaches zero and the relations derived in equation 3.16 through 3.21 are used we obtain

$$\lim_{s \to 0} \frac{dH(s)}{ds} = -(\mu_{ty} - \mu_{tx}) = -\Delta\mu_{tyx} \qquad 3.28$$

$$\lim_{s \to 0} \left[\frac{d^2H(s)}{ds^2} - \left(\frac{dH(s)}{ds}\right)^2\right] = \sigma^2_{ty} - \sigma^2_{tx} = \Delta\sigma^2_{tyx} \qquad 3.29$$

These last two expressions imply that the parameter values in the model transfer function can be fitted to the experimental data using such relationships .

The moment's method described here seems to be the simplest means of fitting models to experimental data since this method requires less computational time than other methods . However , a serious fault of this method is that too much weight is placed on the tail part of Y(t) corresponding to large values of t . Furthermore the tail portion of Y(t) may not be reliable due to the difficulty of measuring tracer concentration accurately at low concentrations . In case there is a necessity of using higher moments for fitting a model , this method tends to become less reliable . Another disadvantage is that the results of the analysis provide no information on how well a particular model fits the data , unless other methods are chosen to compare the response of the model with the experimental response in the time domain after the parameters have been computed .

3.3 Modification of data analysis for this study

Due to the convenience of the moment's method in response data handling all experimental parameters will be derived from the mathematical treatment using such method in this study . As only a number of equidistant measured data points are involved , the equations from 3.18 to 3.21 acquired in the last section need to be modified so as to yield the following expressions (24) :

$$\mu_{ty} = \frac{\Sigma t c_e(t)\ t}{\Sigma c_e(t)\ t} = \Sigma t \left(\frac{c_e(t)}{\Sigma c_e(t)} \right) = \Sigma t F_y(t) dt = -\lim_{S \to 0} \frac{dY(s)}{ds} \qquad 3.30$$

$$\sigma^2_{ty} = \frac{\Sigma (t-\mu_{ty})^2\ c_e(t)\Delta t}{\Sigma c_e(t)\Delta t} = \Sigma (t-\mu_{ty})^2 \left(\frac{c_e(t)}{\Sigma c_e(t)} \right)$$

$$= \Sigma (t-\mu_{ty})^2 F_y(t) = \lim_{s \to 0} \left[\frac{d^2Y(s)}{ds^2} - \left(\frac{dY(s)}{ds} \right)^2 \right] \qquad 3.31$$

$$\mu_{tx} = \frac{\Sigma t c_i(t)\Delta t}{\Sigma c_i(t)\Delta t} = \Sigma t \left(\frac{c_i(t)}{\Sigma c_i(t)} \right) = \Sigma t F_x(t) dt = -\lim_{S \to 0} \frac{dX(s)}{ds} \qquad 3.32$$

$$\sigma^2_{tx} = \frac{\Sigma (t-\mu_{tx})^2\ c_i(t)\ t}{\Sigma c_i(t)\ t} = \Sigma (t-\mu_{tx})^2 \left(\frac{c_i(t)}{\Sigma c_i(t)} \right)$$

$$= \Sigma (t-\mu_{tx})^2 F_x(t) = \lim_{s \to 0} \left[\frac{d^2X(s)}{ds^2} - \left(\frac{dX(s)}{ds} \right)^2 \right] \qquad 3.33$$

Owing to the use of delta inputs as forcing functions in this work , the μ_{tx} and σ^2_{tx} terms vanish . Consequently equations 3.28 and 3.29 become

$$\lim_{s \to 0} \frac{dH(s)}{ds} = -\mu_{ty} \qquad 3.34$$

$$\lim_{s \to 0} \left[\frac{d^2H(s)}{ds^2} - \left(\frac{dH(s)}{ds} \right)^2 \right] = \sigma^2_{ty} \qquad 3.35$$

By making successive differentiations of the transfer function given in the previous chapter ,(equation 2.28), and by allowing s to approach zero we obtain [6]

$$\mu_{ty} = -\lim_{s \to 0} \frac{dH(s)}{ds} = \bar{t} \qquad 3.36$$

$$\sigma^2_{ty} = \lim_{s \to 0} \left[\frac{d^2H(s)}{ds^2} - \left(\frac{dH(s)}{ds} \right)^2 \right] = \bar{t}^2 \left[\frac{2}{Pe} - \frac{2}{Pe^2} + \frac{2e^{-(Pe)}}{Pe^2} \right] \qquad 3.37$$

6/The derivation of equations 3.36 and 3.37 is presented in appendix E

In order to confirm the reliability of values obtained from the moment's method , it was suggested to fit the two computed parameters obtained to the proposed model in the frequency domain as referred to in equation 2.30 . Since the minimum error function shown in equation 3.11 requires the transformation of experimental data into the frequency domain . It , thus , increases the difficulty of this analysis . To ease the problem and to guarantee the best fit in the least squares sense , the inversion of the derived fourier's form model into the time domain is done . Ultimately both model and experiment are fitted using the criteria given below :

$$\phi = \Sigma[c_{exp}(i) - c_{theo}(i,Pe,\tau)]^2 \qquad 3.38$$