

III. TANKS-IN-SERIES ANALYSIS

The initial analysis of the experimental data, by J. H. Frey and G. N. Brown, used a tanks-in-series model [1]. This section summarizes the theory and results of that analysis.

A. Background

1. Mixing in Continuous Systems (Gas Phase Mixing)

Macromixing is a term used to describe the distribution of residence times of fluid elements through a reactor. The degree of macromixing is quantified by the residence time distribution (RTD) or exit age distribution $E(t)$ defined so that the fraction of fluid in the exit stream with age less than t_1 is

$$\int_0^{t_1} E(t) dt \quad (3)$$

The mean residence time is given by

$$\bar{\tau} = \int_0^{\infty} t E(t) dt \quad (4)$$

$$= V/Q \quad (5)$$

The exit age distribution is obtained experimentally by injecting a pulse of tracer and measuring the response at the reactor outlet.

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) dt} \quad (5)$$

where $C(t)$ is the concentration at the reactor outlet. $E(t)$ is simply the normalized reactor outlet concentration.

The use of classical residence time distribution theory for predicting reaction conversion in reactors is valid for linear reaction systems, such as first order reactions. The conversion of a first order reaction depends only on the time allowed for reaction. In this case, two extremes of macromixing can occur. One extreme of macromixing is represented by the CSTR, which has an exponential distribution of residence times. The other extreme of macromixing is represented by the plug flow reactor (PFR). In a PFR, since every element travels through the reactor with exactly the same residence time, $E(t)$ would be a spike if a perfect impulse were injected.

Residence time distribution theory can be used with non-linear reaction systems if a premixed feed stream is available. However, macromixing characterization is not sufficient to determine reaction conversion in the non-linear reaction case. Micromixing, defined as the mixing of molecules of one age with molecules of another age, is also important for non-linear reaction kinetics. For a PFR, molecules of different ages cannot mix, so micromixing effects cannot occur. For a CSTR, Nauman and Buffman [18] state that micromixing can affect the conversion of a second order reaction by only 7%. For the LPMEOH PDU, micromixing effects were neglected and the characterization of macromixing in terms of the PFR and CSTR extremes was studied.

Once the macromixing information is experimentally obtained, the age distribution function can be used to predict reactor performance in two ways. The first way is to calculate the outlet concentration (\bar{C}_A) based on

$$\bar{C}_A = \int_0^{\infty} C_A(t) E(t) dt \quad (7)$$

$$\text{where } \frac{dC_A}{dt} = r_A$$

$$\text{with } C_A|_{t=0} = \text{feed concentration}$$

($C_A(t)$ is the concentration of A in a batch reactor.)

The alternative method is to fit the measured $E(t)$ function to a tanks-in-series model. The number of tanks and the tank residence times are used as adjustable parameters in fitting the model to the data. If the reactor behaves as a CSTR, then the model will predict one tank. If the reactor behaves as a PFR, then there will be an infinite number of tanks-in-series. The tanks-in-series model can be used to predict reactor performance by these equations.

$$\frac{dC_{An}}{dt} = \frac{C_{A(n-1)} - C_{An}}{\tau_n} - r_a \quad n = 1, \dots, N \quad (8)$$

$$\text{with } \tau_n = V_n/Q \quad (9)$$

$$\text{and } \bar{C}_A = C_{AN}$$

The number of tanks (N) and the tank residence time is evaluated by fitting the normalized data (E_N) from an impulse/response experiment to the following equations.

$$\frac{dE_1}{dt} = \frac{E_0 - E_1}{tF} \quad (10)$$

$$\frac{dE_n}{dt} = \frac{E_{(n-1)} - E_n}{\tau} \quad n = 2, \dots, N \quad (1)$$

where F = fraction of a tank
 E_0 = a Gaussian impulse

$$E_0 = \exp \left[-\frac{1}{2} \frac{(t - \bar{t})^2}{\sigma^2 (2\pi)^{1/2}} \right] \quad (2)$$

The adjustable parameters (τ , number of tanks) are adjusted by a Newton-Raphson algorithm or a two variable search algorithm until the error between the response data and E_N is a minimum.

2. Mixing in Batch Systems (Slurry Mixing)

Since the slurry phase does not leave or enter the reactor, a residence time distribution analysis is not possible. A numerical solution to a cell model with a Gaussian impulse was chosen as the mixing model to provide an analysis of the slurry consistent with the gas phase analysis. The cell model chosen for the liquid phase is similar to the gas phase model except backmixing occurs from the upper cells to lower cells and there is no outlet stream. The equations are:

$$\frac{dC_1}{dt} = \frac{C_0 + C_2 - C_1}{\tau_1} \quad (3)$$

$$\frac{dC_i}{dt} = \frac{C_{i-1} - 2C_i + C_{i+1}}{\tau_i} \quad i = 2, \dots, N-1 \quad (4)$$

$$\frac{dC_N}{dt} = \frac{C_{N-1} - C_N}{\tau_N} \quad (5)$$

(Where C_0 is given by equation 12)

The adjustable parameters in this model are N and $t_1, 2, \dots, t_N$ and are determined using a Newton-Raphson algorithm.

3. Literature Background

An excellent review of mixing in gas-liquid reactors is provided by Shah, et al. [20]. In this review, methods for measuring residence time distributions, mixing models, data analysis, and various mixing studies are discussed. It is apparent from this review that much of the mixing work has been done with air-water systems, small columns, or low gas velocities.

Mixing references citing large scale, multiphase reactors at high temperature and pressure include articles by Nallatham and Davies [17], Tarmy, et al [21], and Field and Davidson [2]; however, the highest superficial gas velocities reported were 0.05, 0.22, and 0.18 ft/s, respectively. A mixing study on the liquid phase methanol reactor provides needed mixing data for large scale, multiphase reactors operating at high temperature, high pressure and high gas velocity with organic liquids and gases.

B. Results of Numerical Analysis

1. Gas Mixing Numerical Analysis

The most suitable place to measure the residence time distribution (RTD) is at the reactor outlet where there exists a uniform velocity profile [22]. In the LPMEOH reactor, however, gas mixing information obtained at the reactor outlet includes the mixing behavior of the gas in the slurry section and also the mixing behavior of the gas in the freeboard section. Mixing of the gas in the slurry section is of primary importance for predicting reactor behavior. To satisfy the condition of a uniform velocity profile at the measurement location and to satisfy the requirement of obtaining an RTD for the slurry section, the numerical analysis assumes the freeboard is a plug flow reactor (PFR). The response from the outlet detector is shifted in time by a time equivalent to the height of the freeboard divided by the gas velocity. The resulting RTD should be the RTD of the gas in the slurry region if the freeboard is a PFR.

The normalized data were fit to a two dimensional model. As discussed by Shah, et al. [20], evaluation of mixing parameters from the variance of an RTD curve can be inaccurate when there is uncertainty in the tail of the response curve. To minimize this error, mixing parameters were evaluated by comparing the numerical solution of a tanks-in-series model to the actual data. In this way, each point carries an equal weight in the optimization routine. For the gas phase data, the model (equation 10, 11) was a series of CSTRs of equal volume with no backmixing between CSTRs. The number of CSTRs in series and the individual residence time of each CSTR were the two parameters that were adjusted to minimize the difference between the experimental curve and the calculated curve.

The inlet impulse was defined by a time lag, a spike width, and equation 12. A lag-time parameter was used in the model fitting algorithm to account for the time which elapsed between time zero and the actual injection time. These parameters were determined for each injection by direct examination of the normalized impulse spike data. The spike lag time was determined by the following:

$$\text{Spike lag} = (\text{spike peak point} - 1) * \Delta T \text{ (sec)}$$

The spike width was determined by:

$$\text{Sigma} = \frac{(\text{Back Edge Point \#} - \text{Leading Edge Point \#}) * \Delta T (\text{sec})}{2}$$

For the analysis of the slurry level detectors, an additional time lag was included that represented the time the gas took to travel from the liquid level to the detectors above liquid level. This was done to account for the detectors not being precisely at the liquid level. In these cases, the additional time lag was estimated assuming the gas behaved like a PFR in the reactor freeboard. An example of a typical model fit from this analysis is shown in Figure III.B.1-1. For the gas phase, the analysis of the detectors directly above liquid level and the reactor outlet were of most interest and the model fits were determined using each response.

The results for the number of CSTRs in series for the gas in the slurry region are reported in Table III.B.1-1. Note that based on the outlet detectors, the number of CSTRs in the slurry increases with an increase in gas velocity and the number of CSTRs in the slurry decreases with a decrease in L/D.

The detectors directly above the slurry level were also used to analyze the gas mixing in the slurry section. The number of tanks-in-series as a function of gas velocity calculated from the slurry level detectors for cases 1-6 are illustrated in Figure III.B.1-2 and listed in Table III.B.1-1. The calculated model parameters (N, τ) are listed in Appendix C for each liquid level detector and each case. As gas velocity and L/D increases, the slurry region behaves more like a PFR. This trend agrees with that predicted by the outlet detectors. Note that in all cases except for the high velocity case, the number of CSTRs calculated from the outlet detector is slightly less than the number calculated from the liquid level detector, indicating that some degree of mixing is occurring in the gas space. Although some mixing is present, a majority of the cases show agreement in the number of CSTRs calculated from the two different detectors. Therefore, the assumption of plug flow in the gas space does not have a large impact on the number of CSTRs calculated.

Figure III.B.1-3 shows the number of CSTRs per L/D as a function of gas velocity calculated from the slurry level detectors. The two curves of Figure III.B.1-2 do not collapse perfectly into one curve when divided by L/D because there appears to be a stronger dependence on gas velocity at the lower L/D than at the higher L/D. The curve of Figure III.B.1-3 could be used for calculating reactor performance within the bounds of the outlet gas velocities (.17 < V < .5 ft/s) and L/Ds (6.7 < L/D < 10.2) studied.

FIGURE III.B.1-1: LAPOURTE I.P.M.E.O.H TRACER STUDY
 TYPICAL CURVE FIT TO EXPERIMENTAL DATA

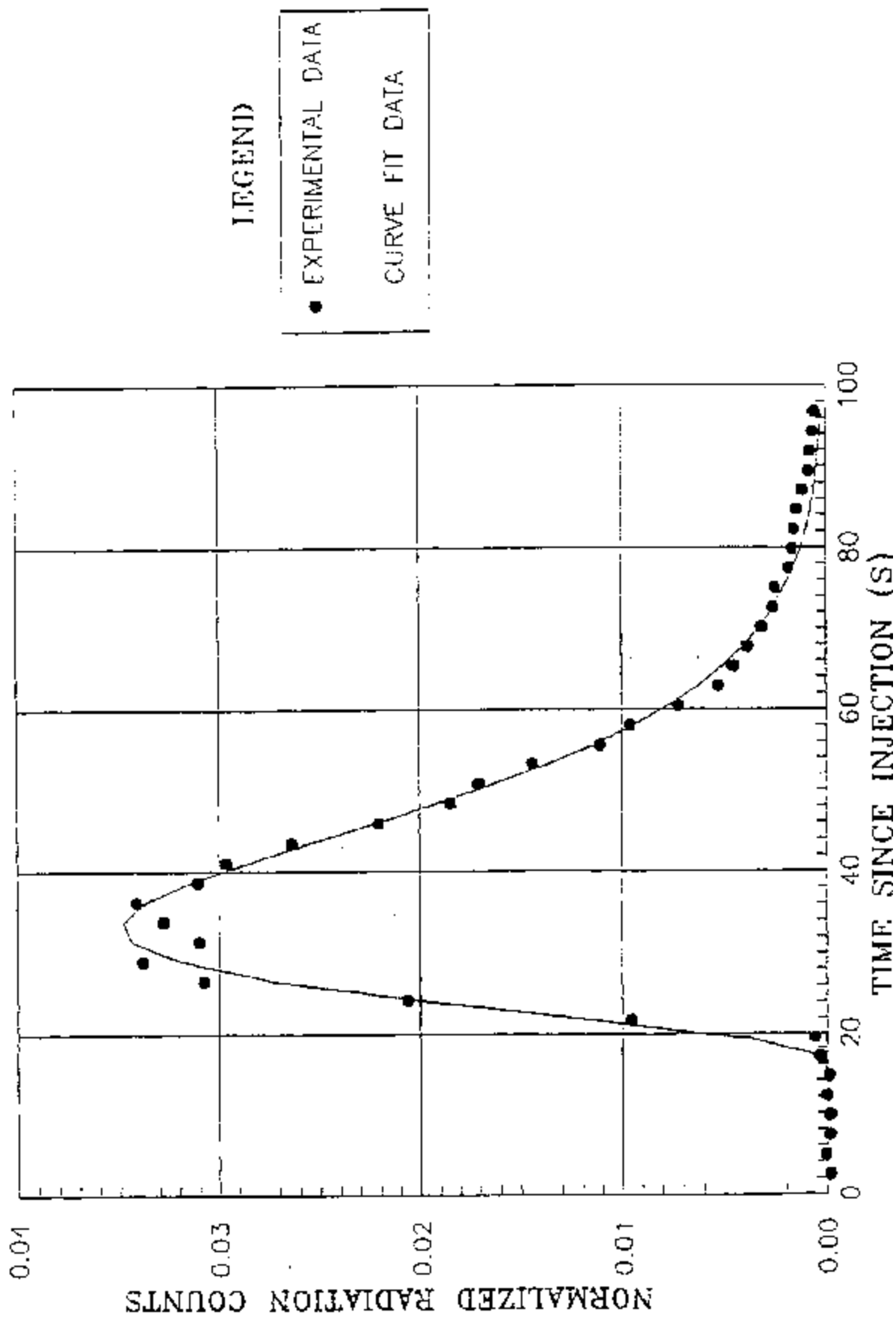


FIGURE III.B.1-2 LaPorte LPMEOH Tracer Study
 CSTRs in Series vs Superficial Gas Velocity

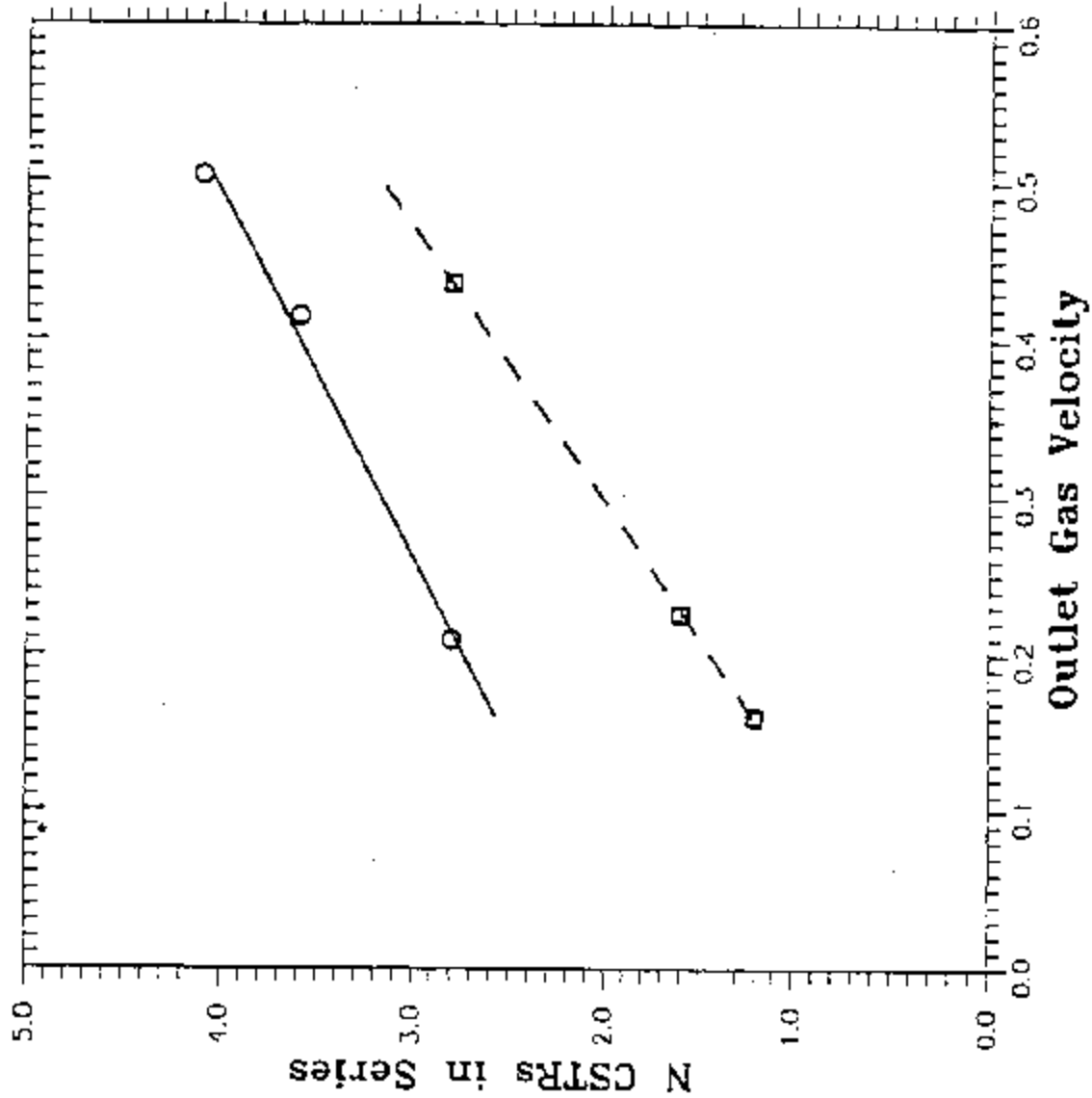
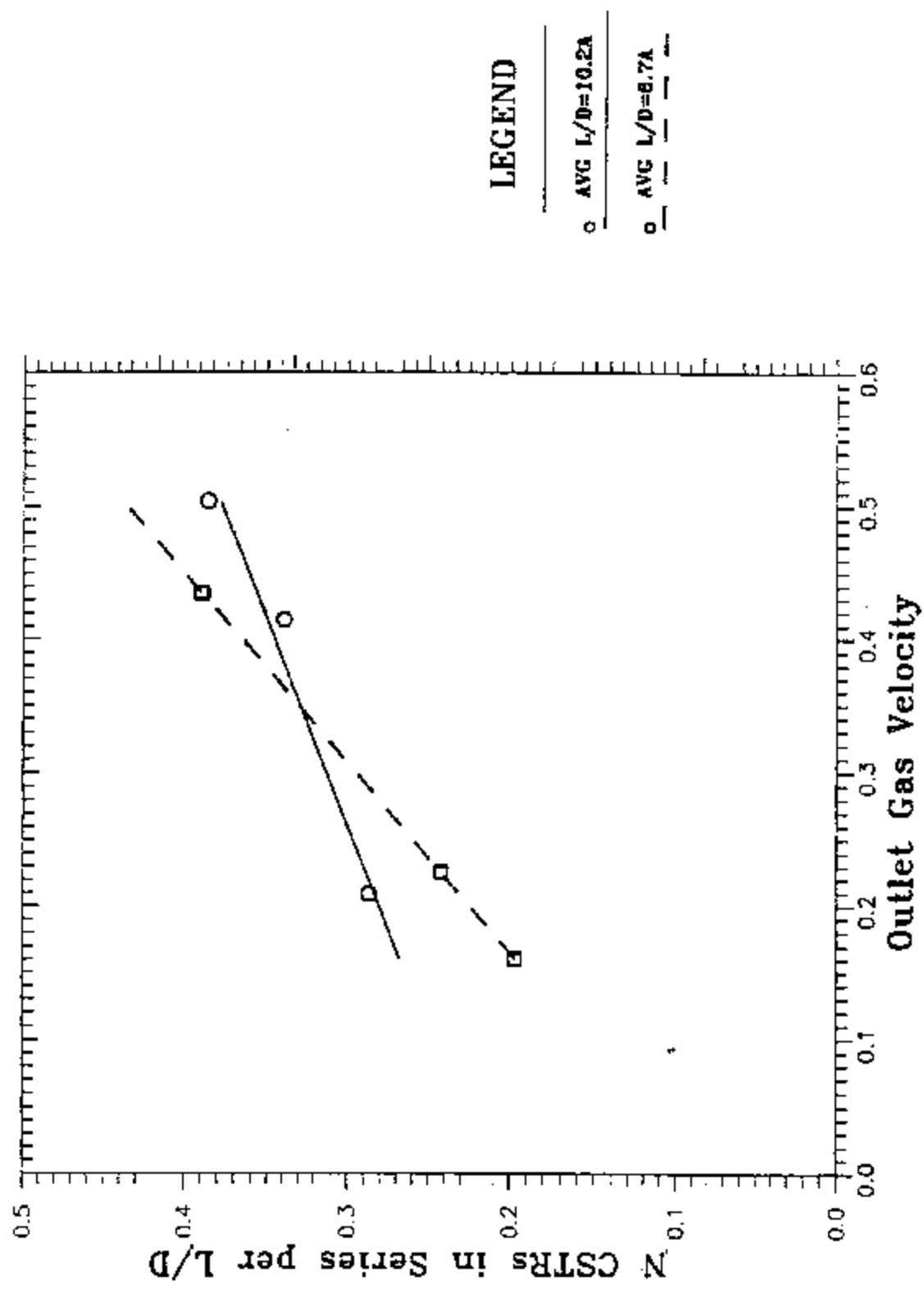


FIGURE III.B.1-3 LaPorte LPMEOH Tracer Study
 CSTRs in Series per L/D vs Superficial Gas Velocity



By assuming that the freeboard may be modeled as plug flow, the response of the detectors from above the liquid level may be used without interference from tracer that has backmixed from the upper gas space. If the assumption is correct, the response from the reactor outlet should be identical to the response from the liquid level but shifted by a time representing the time to travel between detectors. If the assumption is incorrect, mixing will occur in the upper gas space and the outlet detector response will be much broader than the liquid level detectors response. Figure III.B.1-4 illustrates that at high gas velocities and L/D, the assumption is good since the outlet detector response is only slightly broader than the liquid level response. At the lower gas velocities and especially when there is a small L/D (large freeboard), the outlet detector response appears to be much broader than the liquid level response and the freeboard plug flow assumption may be in jeopardy. (See Figure III.B.1-5.)

The total residence time for the slurry section using the two detectors described above was calculated by multiplying the individual tank residence time by the number of tanks. The values of the total residence time are listed in Table III.B.1-1. The total residence time from the outlet detector should be identical to the residence time from the slurry level detector since the outlet response was already shifted in time by the freeboard residence time. In all cases, the residence times calculated from the outlet detector are larger than the times calculated from the slurry level detector. At least three effects could be responsible for this:

- 1) The radioactive argon is not passing through in plug flow in the freeboard, but rather some is remaining for longer times and contributing to a higher residence time for the outlet detector. The total residence time is probably quite sensitive to a small amount of tailing because the product $tE(t)$ will contribute significantly to the integral $\tau = \int_0^{\infty} tE(t)dt$ at large times.
- 2) Shielding and the width of the reactor may cause the liquid level detector to miss the low levels of radiation that pass through in the tail, while the outlet detector may detect this tail.
- 3) As discussed by Levenspiel and Turner [22], a nonuniform velocity profile at the slurry level may contribute to a different residence time than observed where a uniform velocity profile exists.

The plug flow assumption in the freeboard is a good assumption to use as a first approximation. For the slurry residence time, the results that obey the assumption very well are the results at

Table III.B.1-1

Gas Mixing Behavior of the Slurry Volume
Based on Two Different Responses

<u>Case</u>	<u>Gas Velocity ft/s</u>	<u>Based on Slurry Level Detector</u>		<u>Based on Outlet Detector</u>	
		<u>Number of CSTRs</u>	<u>Total Residence Time (sec) for slurry section</u>	<u>Number of CSTRs</u>	<u>Total Residence Time (sec) for slurry section*</u>
1	.25	2.8 ± .4	48 ± 3.	2.2 ± .7	64.6 ± .8
2	.5	3.6 ± .5	25 ± 1.	3.3 ± .2	31.4 ± .8
3	.6	4.1 ± .9	22 ± 2.	4.2 ± .1	26.8 ± .6
4	.5	2.8 ± .3	18 ± 1.	2.2 ± .7	27.6 ± .7
5	.25	1.6 ± .5	40 ± 9	1.01 ± .01	77.7 ± .8
6	.18	1.2 ± .1	67 ± 11	7.02 ± .01	108 ± 3

* times have been reduced to account for gas volume above slurry

Table III.B.1-2

Theoretical Residence Time (V/Q)

<u>Case</u>	<u>Gas Velocity ft/s</u>	<u>L/D**</u>	<u>V/Q (sec)</u>	<u>V/Q (sec)</u>
			<u>Using Gas Volume in Slurry Section</u>	<u>Using Total Gas and Slurry Volume in Slurry Section</u>
1	.25	9.6	20.6	72.1
2	.5	10.5	14.2	39.2
3	.6	10.6	12.4	32.9
4	.5	7.4	9.9	27.9
5	.25	6.5	13.5	49.5
6	.18	6.2	14.4	63.4

**total L/D of reactor = 13.3

FIGURE III.B.1-4: LAPORTE LPMEOII GAS PHASE TRACER STUDY
EXTENT OF MIXING IN REACTOR FREEBOARD

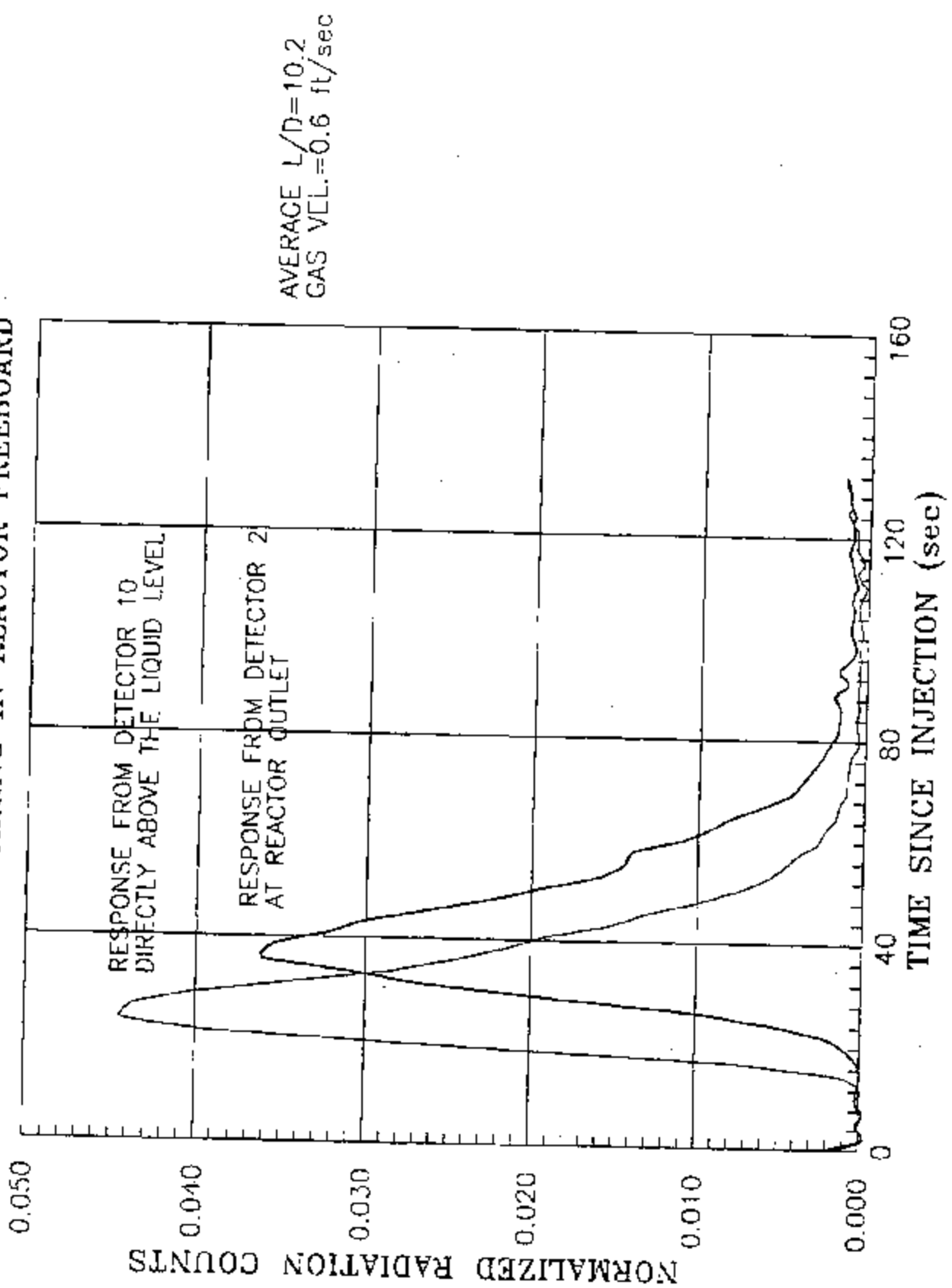
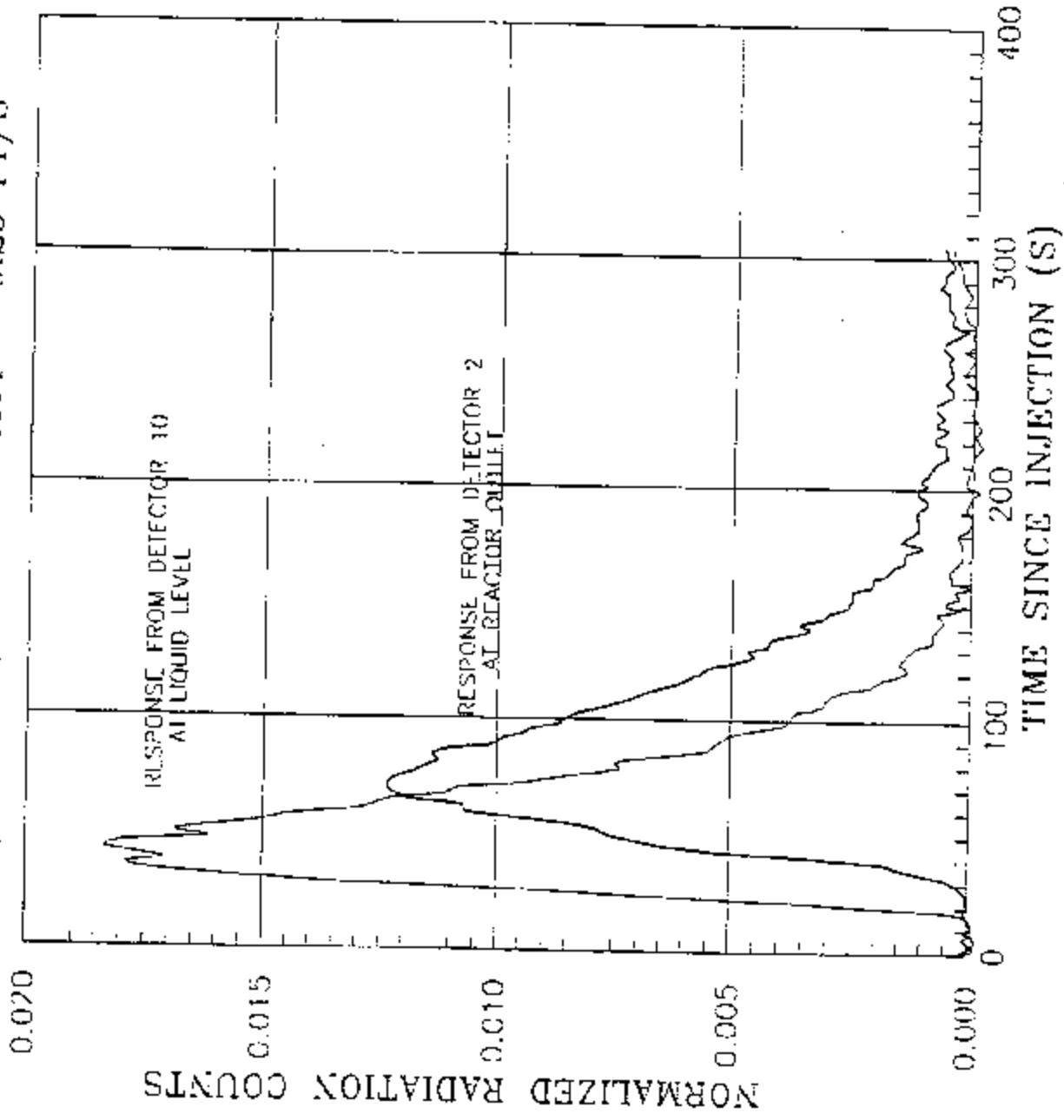


FIGURE H1.B.1 5 : LAPORTE LPMEOH TRACER STUDY
 LIQUID LEVEL, DETECTOR RESPONSE and REACTOR OUTLET RESPONSE
 $L/D = 10.2$; GAS VELOCITY = 0.25 FT/S



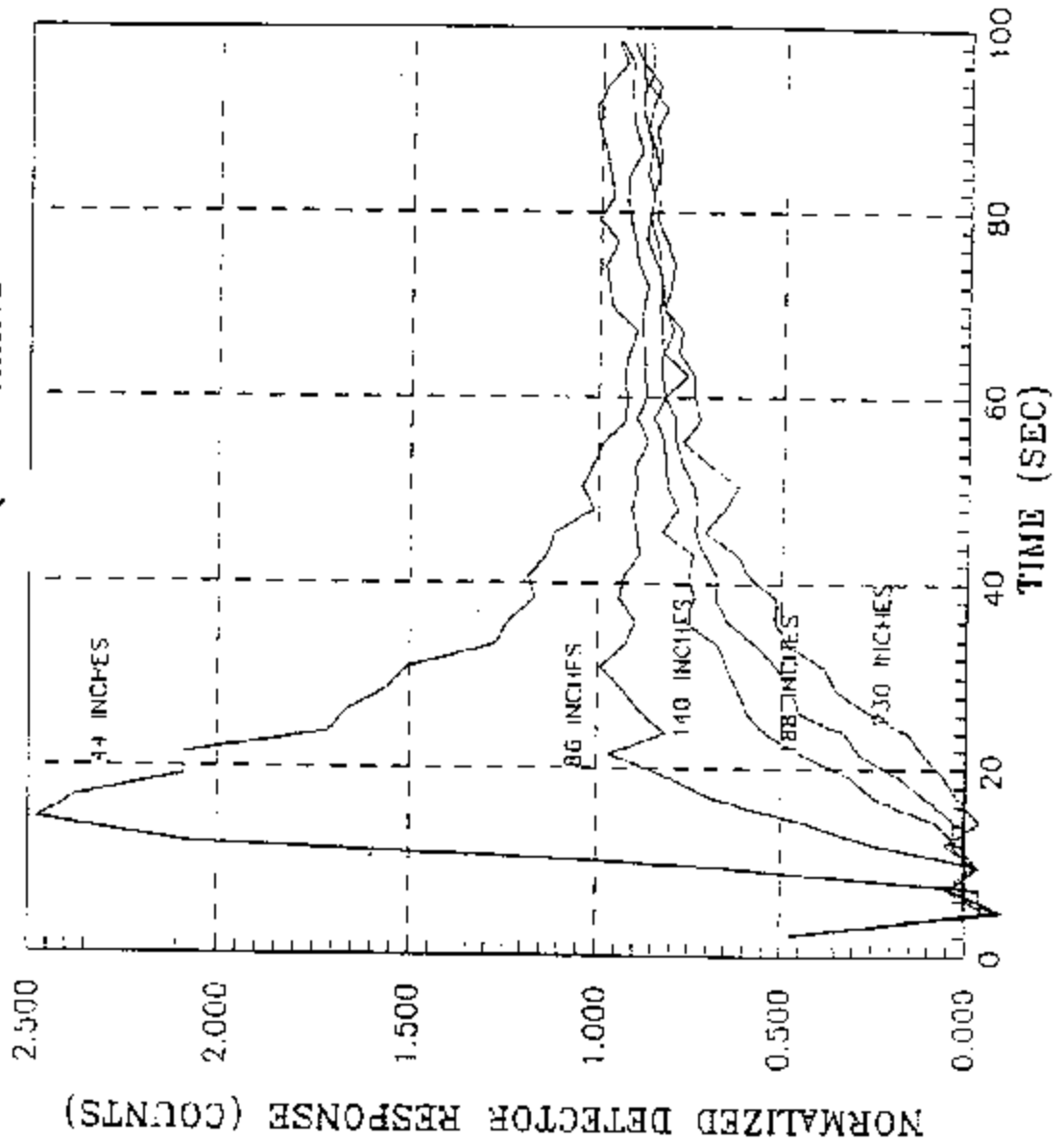
inlet gas velocities greater than or equal to 0.5 ft/s at the high L/D. The residence times for the low velocity cases at the low L/D with the plug flow assumption are in poor agreement for the two different detectors.

A theoretical residence time (V/Q) was calculated and compared to the residence time calculated in the curve fitting. Unfortunately, the volume (V) that the tracer gas "sees" is not well defined for the liquid phase methanol reactor. The theoretical residence times based on the gas holdup volume in the slurry and based on the total reactor volume in the slurry section are listed in Table III.B.1-2. In all cases the theoretical residence times calculated using these two volumes shown in Table III.B.1-2 provides bounds to the curve fit residence time from the liquid level detector shown in Table III.B.1-1. This indicates that argon gas (like CO and H₂) is soluble in the slurry and that the volume the argon "sees" is between the gas holdup volume and the total slurry volume. The Air Products' thermodynamic data base (Peng-Robinson equation of state) predicts that gases such as Ar, CO, and H₂ are 10-20 mol% soluble in the oil at the operating conditions.

2. Liquid Mixing Numerical Analysis

A 3-cell model (equations 12 - 14) was compared to the liquid mixing data at elevations of 44, 86, and 230 inches. The reverse flow rate was set to be equal to the forward flow rate. The analysis for the liquid tracer concentrated on finding mixing time constants for each mixing cell. The experimental data at all elevations are shown in Figure III.B.2-1. A Gaussian curve centered at 11.4 seconds, with a width defined by sigma of 5.9 seconds, was used to simulate the non-ideal impulse spike. The result of the model fit to the data is shown in Figure III.B.2-2 with cell time constants of 7.4, 20.6, and 13.4 seconds. The 3-cell model qualitatively accounts for the observed behavior. However, the model curves do not reproduce the mixing behavior precisely. The model reaches an equilibrium, concentration at 60 seconds, but the observed behavior shows a slow approach to the equilibrium value. Nevertheless, a majority of the Mn₂O₃ is well mixed within 60 seconds. However, since it appears that a significant amount of the gas is dissolved in the liquid, some of the effects of liquid mixing are accounted for in the gas residence time distribution.

FIGURE III.B.2-1 LAPOINTE LPMEOH LIQUID TRACER STUDY
 REACTOR LIQUID MIXING



NOTE: HEIGHTS SHOWN ABOVE ARE FROM INJECTION POINT.

FIGURE III.B.2-2 LAPORTE LPMEOH LIQUID TRACER STUDY
REACTOR LIQUID MIXING MODEL

