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TRANSIENT RESPONSE OF AN IMPERFECTLY MIXED CONTINUOUS FLOW STIRRED TANK REACTOR TO AN UPSET OF INFLOW RATE

by

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T-1247

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ABSTRACT

Nonideal behavior of an imperfectly stirred continuous flow reactor under isothermal condition was investigated by observing the transient response of the output concentration to an upset of inlet flow rates. The saponification reaction of ethyl acetate with sodium hydroxide was adopted for the experiment.

It was shown that mixing rate has higher effect on conversion at the lower residence time than at the higher residence time. A perfectly mixed reactor and a plug flow reactor in parallel with dead space was adopted as the model of the real reactor system. This work describes the behavior of the real reactor by the fraction of inlet stream going to each stream and the volume of plug flow reactor, stirred tank, and dead space.

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INTRODUCTION

All reactors deviate to some extent from the ideal cases of perfect mixing and plug flow. In a perfectly stirred tank, the composition of the reacting fluid would have a uniform value throughout the reactor and equal to the output composition. Perfect stirring can be achieved at very high stirring rate. However, the power cost for the stirring is usually an important economic factor and the assumption of perfect mixing cannot be satisfied in many cases.

In order to study the behavior of the actual reactors, two modes of mixing, namely micromixing and macromixing, should be considered. In micromixing individual molecules are free to move about and intermix, while with macromixing molecules are visualized as grouped together in aggregates or packets.

Reactor performance can be predicted effectively by mixed models which consist of interconnected flow regions with various modes of flow such as plug flow regions, perfectly stirred regions, dead space and crossflow. Models are frequently determined with the help of age-distribution functions obtained from the tracer runs on real reactors and these models are then used to predict the behavior of the

real reacting systems.

Age-distribution functions obtained from the tracer studies give information on macromixing but not on micromixing. Therefore, tracer curves can predict the performance of the reactors only for the linear processes (first order reaction) where interactions between fluid elements do not affect reaction rates.

For the nonlinear processes, information on micromixing as well as macromixing is necessary for the description of the reactor behavior. Complete segregation and maximum mixedness are two limits for micromixing. The former considers each fluid element to be totally isolated from the other elements, while the latter considers the elements to mix at the earliest possible moment. Determining the degree of segregation will give a semi-quantitative idea of the micromixing behavior in a vessel, but it cannot be related quantitatively to the performance of a reactor.

In this study, tracer runs were not made in view of the difficulty in relating them to the actual reactor behavior for nonlinear processes. Instead, the dynamic response of the output concentration to the upset of inlet flow rate was observed. This work aims to predict the general model form by observing the trend of the response at different mixing rates.

LITERATURE

In 1935, MacMullin and Weber (1) presented the pioneering work on the effect of mixing on the chemical reactor performance. They studied the residence time distribution of a system of tanks in series with short circuiting. Methods of modeling of the flow system were first presented by Danckwerts (2) who defined certain distribution functions which give information on the mixing characteristics in vessels. The methods of experimental measurement of age distribution functions and their interpretation to detect dead regions, bypassing and non-uniform regions are summarized by Himmelblau and Bischoff (3).

Three types of models have been used to characterize nonideal flow patterns within vessels (4); namely: dispersion models, tanks in series models and mixed models.

Many of the main features of macromixing effects can be represented by a single coefficient dispersion models. Levenspiel and Bischoff (5) presented dispersion models for second order reaction and Fan and Bailie (6) presented those for the reaction orders of ¼, ½, 2, 3 as well as complete set of concentration profiles through the reactor section.

Degree of segregation as a measure of micromixing was defined by Danckwerts (7). The two limits of micromixing, namely complete segregation and maximum mixing, were defined by Danckwerts (7) and Zweitering (8), respectively. Cholette and others (9,10,11) contributed significant experimental results for mixed models.

EXPERIMENTAL

Figure 1 shows the schematic diagram for the experimental system. The reagents, 0.1 molar sodium hydroxide and 0.1 molar ethyl acetate, were fed through a constant temperature bath (80°F) and to the top of the reactor through a ¼-inch copper tube by air pressure. Reagents were stored in 5-gal bottles. Air pressure to the storage bottles was controlled by a pressure regulator. Flow rates were measured by Hicksville rotameters ranging in capacity from 20 to 200 cc per min.

The reactor consisted of a 925 ml stainless-steel cylindrical vessel which was 4 inches in diameter and 4½ inches in height mounted with 4 baffles (12/32-in. wide and 4-in. high) with cooling coil. The impeller was a three-blade stirrer of one inch diameter and was mounted one inch from the bottom of the vessel. Reactants were fed to the reactor at the flow rates of 60 ml/min each, initially. After steady state was reached, flow rate of the ethyl acetate was raised to 160 ml/min. Outlet concentration was measured with a Leeds & Northrup pH meter and the transient response of sodium hydroxide outlet concentration was obtained on a Mosley 7100B strip chart recorder.

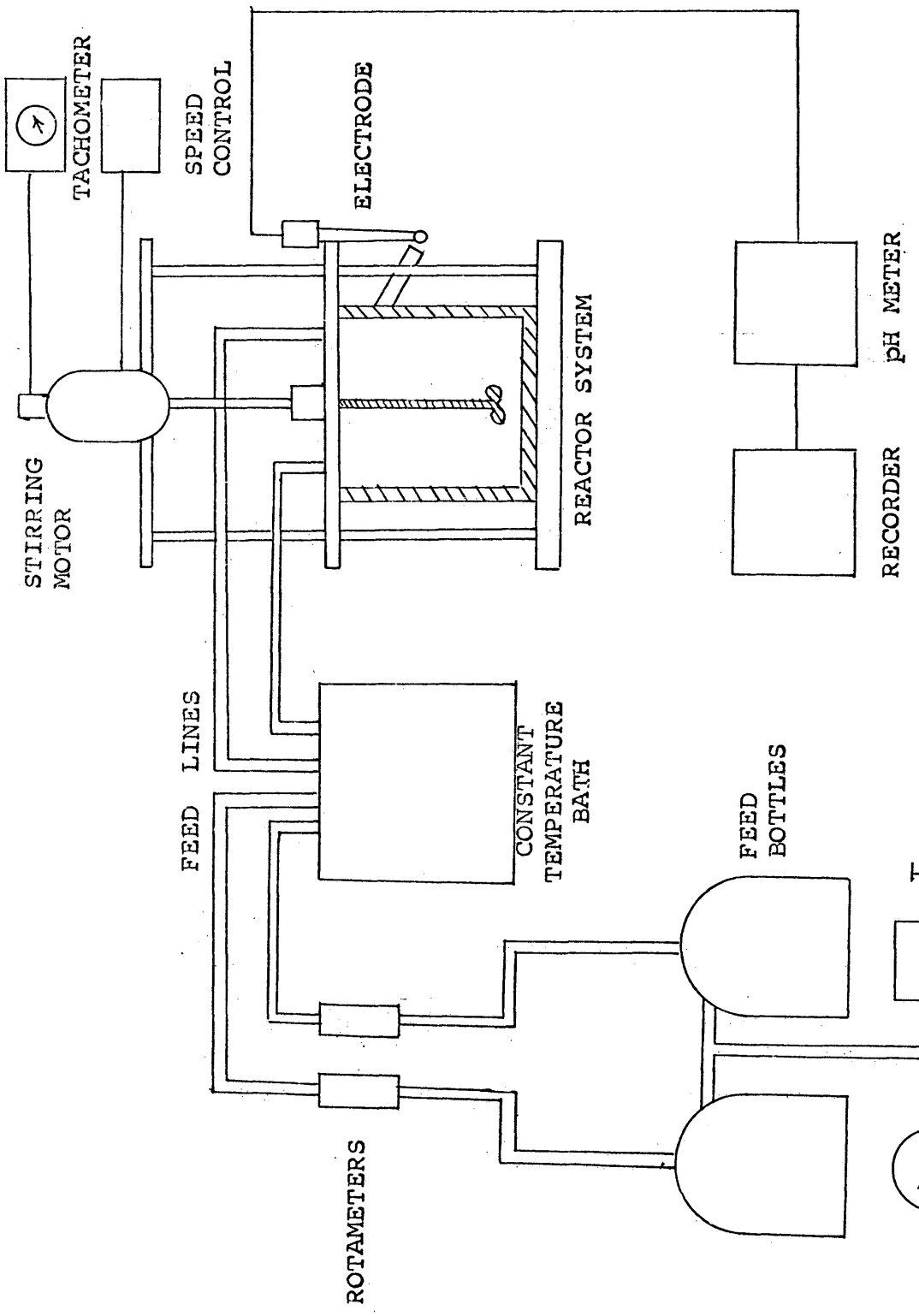


Figure 1: Schematic Flow Diagram

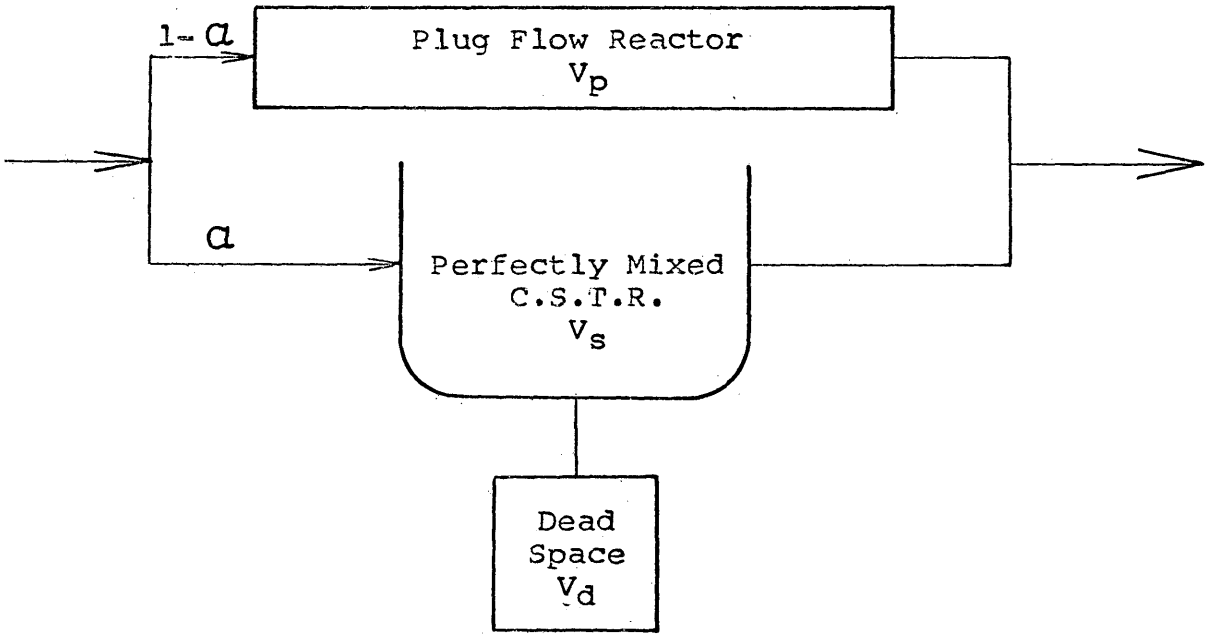
At the concentrations employed in this study, heat generation was negligible and the system was isothermal.

In each of the experimental runs, the transient curve was traced by giving a step decrease in EtAc flow rate to the initial value after the new steady state was reached. Results were essentially identical. Data presented in the appendix are those confirmed by repeated runs with retracing upsets.

Errors were approximately ±0.05% in each of the inlet concentrations and as much as ±5% in both inlet flow rates. Errors in measuring concentration during transient response were in the order of ±0.5%, neglecting measurement lags.

MODEL

Various types of mixed models were tried to fit the experimental data of the transient response of the actual reactor to an upset of inflow rate. The model as shown in Figure 2 best described the actual response.



$$V_p + V_s + V_d = 0.925 \text{ liter}$$

Figure 2. Mixed Model Adopted in this Study.

In the following sections, transient response for a perfectly mixed Continuous Flow Stirred Tank Reactor (C.F.S.T.R.) and a plug flow reactor will be discussed. The transient response for the mixed model can be calculated simply by making a material balance with those of individual C.F.S.T.R. and plug flow reactors. The actual response and those of the mixed models are then compared.

Perfectly Stirred Tank

The steady state equations for the second order reaction system are (notation is given on page 29):

$$F_{Ao}C_{Ao} - F\ C_A - kVC_AC_B = 0 \tag{1}$$

$$F_{Bo}C_{Bo} - F\ C_B - kVC_AC_B = 0 \tag{2}$$

The corresponding unsteady state equations are:

$$V\frac{dC_A}{dt} = F_{Ao}C_{Ao} - FC_A - kVC_AC_B \tag{3}$$

$$V\frac{dC_B}{dt} = F_{Bo}C_{Bo} - FC_B - kVC_AC_B \tag{4}$$

For the upset in flow rate of A, substitute

$$F = F_{ss} + F'$$

$$C_A = C_{A,ss} + C_A'$$

$$C_B = C_{B,ss} + C_B'$$

$$F_{Ao} = F_{Ao,ss} + F_A'$$

into equations (3) and (4) and then substract steady state equations (1) and (2) to get the following equations:

$$V\frac{dC_A'}{dt} = F_A'C_{Ao} - F_{ss}C_A' - F'C_{A,ss} - F'C_A' - kV(C_{A,ss}C_B' + C_A'C_{B,ss} + C_A'C_B') \quad (5)$$

$$V\frac{dC_B'}{dt} = -F_{ss}C_B' - F'C_{B,ss} - F'C_B' - kV(C_{A,ss}C_A' + C_B'C_{A,ss} + C_A'C_B') \quad (6)$$

The system of the above ordinary differential equations can be solved analytically when the perturbation terms are small. With large perturbation, solution of the system of the equations requires numerical methods. Since flow perturbation used in this study were large, solution was the latter technique.

Analytic Solution

Eliminating the common term $kV(C_{A,ss}C_{B,ss}' + C_B'C_{A,ss} + C_A'C_B')$ from the equations (5) and (6): there results:

$$\frac{dC_A'}{dt} + aC_A' - b = \frac{dC_B'}{dt} + aC_B' + c \quad (7)$$

where

$$a = \frac{F_{ss} + F'}{V}$$

$$b = \frac{F_{Ao}'C_{Ao} - F'C_{A,ss}}{V}$$

$$c = \frac{F'C_{B,ss}}{V}$$

Taking the Laplace transform of equation (7) with the initial conditions, $C_A'(0) = C_B'(0) = 0$, we get,

$$s\overline{C_A'} + a\overline{C_A'} - \frac{b}{s} = s\overline{C_B'} + a\overline{C_B'} + \frac{c}{s}$$

$$\overline{C_A'} = \overline{C_B'} + \frac{b + c}{s(s + a)} \tag{8}$$

When the perturbation term is small the second order perturbation terms in equations (5) and (6) will be negligible. Thus, we neglect the second order perturbation terms in equation (6) and take its Laplace transform to get,

$$s\overline{C_B'} + d\overline{C_B'} = - e\overline{C_A'} - \frac{c}{s} \tag{9}$$

where $$d = \frac{F_{ss} + F' + kVC_{A,ss}}{V}$$

$$e = kC_{B,ss}$$

Substituting equation (8) into (9) and solving for $\overline{C_B'}$:

$$\overline{C_B'} = \frac{-c(s + a_3)}{s(s + a_1)(s + a_2)} \tag{10}$$

where $$a_1 = \tfrac{1}{2}\left[(a + d + e) + \sqrt{(a + d + e)^2 + 4a(d + e)}\right]$$

$$a_2 = \tfrac{1}{2}\left[(a + d + e) - \sqrt{(a + d + e)^2 + 4a(d + e)}\right]$$

$$a_3 = \frac{be}{c} + e + a$$

Inverting equation (10), we get,

$$C_B' = \frac{-ca_3}{a_1 a_2}\left[1 - \frac{1}{a_3(a_1 - a_2)}\left(a_2(a_1 - a_3)e^{-a_1 t} + a_1(a_3 - a_2)e^{-a_2 t}\right)\right] \tag{11}$$

The output concentration of sodium hydroxide is

$$C_B = C_{B,ss} + C'_B \tag{12}$$

The results of the analytic solution showed large deviation from the experimental data. This was as expected since the perturbation of inflow rate was significantly large.

Numerical Method

There are two powerful numerical methods in solving a system of ordinary differential equations, namely Runge-Kutta method and predictor-corrector method.

Runge-Kutta methods are self starting and require several evaluations of the function at each step and are thus time consuming. Predictor-corrector methods are iterative and use information from prior points. They give good estimates of truncation error at each step.

In this work the following predictor-corrector methods (12) was used with the help of a CDC 8090 computer.

Computing $C'_{B,1}$, $C'_{A,1}$ by the improved Euler Method

$$\frac{dC'_A}{dt} = \frac{1}{V_s}(F'_A C_{Ao} - F_{ss}C'_A - F'C_{A,ss} - F'C'_A)$$
$$-k(C_{A,ss}C'_B + C'_A C_{B,ss} + C'_A C'_B) = F(C'_A, C'_B)$$

$$\frac{dC'_B}{dt} = \frac{1}{V_s}(-F_{ss}C'_B - F'C_{B,ss} - F'C'_B)$$
$$-k(C_{B,ss}C'_A + C'_B C_{A,ss} + C'_A C'_B) = G(C'_A, C'_B)$$

$$C'_{A,1} = C'_{Ao} + \frac{h}{2}\left[F(C'_{Ao},C'_{Bo}) + F\left(C'_{Ao} + hF(C'_{Ao},C'_{Bo}),\ C'_{Bo} + hG(C'_{Ao},C'_{Bo})\right)\right]$$

$$C'_{B,1} = C'_{Bo} + \frac{h}{2}\left[G(C'_{Ao},C'_{Bo}) + G\left(C'_{Bo} + hF(C'_{Ao},C'_{Bo}),\ C'_{Bo} + hG(C'_{Ao},C'_{Bo})\right)\right]$$

Predictors for m = 1, 2, . . .

$$C'^{(0)}_{A,m+1} = C'_{A,m-1} + 2hF(C'_{A,m},\ C'_{B,m})$$

$$C'^{(0)}_{B,m+1} = C'_{B,m-1} + 2hG(C'_{A,m},\ C'_{B,m})$$

Correctors for m = 1, 2, . . .

$$C'^{(i)}_{A,m+1} = C'_{A,m} + \frac{h}{2}\left[F(C'_{A,m},\ C'_{B,m}) + F(C'^{(i-1)}_{A,m+1},\ C'^{(i-1)}_{B,m+1})\right]$$

$$C'^{(i)}_{B,m+1} = C'_{B,m} + \frac{h}{2}\left[G(C'_{A,m},\ C'_{B,m}) + G(C'^{(i-1)}_{A,m+1},\ C'^{(i-1)}_{B,m+1})\right]$$

Estimation of the Truncation Errors

$$E_T(C'_{A,m+1}) = \frac{1}{5}\left(C'^{(0)}_{A,m} - C'^{(i)}_{A,m}\right)$$

$$E_T(C'_{B,m+1} = \frac{1}{5}\left(C'^{(0)}_{B,m} - C'^{(i)}_{B,m}\right)$$

Final Values for $C'_{A,m}$ and $C'_{B,m}$ are:

$$C'_{A,m} = C'^{(i)}_{A,m} + E_T(C'_{A,m+1})$$

$$C'_{B,m} = C'^{(i)}_{B,m} + E_T(C'_{B,m+1})$$

Plug Flow Reactor

A plug flow reactor gives a step response in NaOH concentration (pH) to a step increase in ethyl acetate inflow rate as shown in Figure 3 by the solid line.

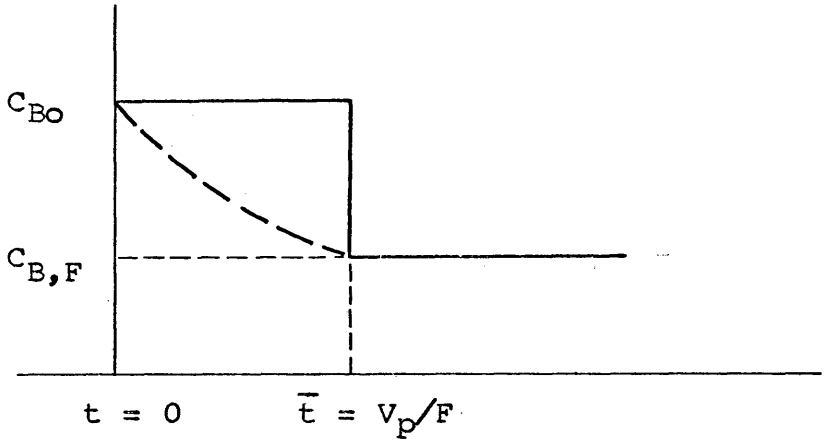


Figure 3: Transient Response of an Ideal Plug Flow Reactor to an Inflow Rate Upset.

$C_{B,F}$ can be derived as follows:

$$\bar{t} = \left(\frac{V_p}{F_{Bo}}\right) = \int_o^{X_A} \frac{dX_A}{kC_AC_B}$$

$$= \frac{1}{kC_{Bo}(M - 1)} \ln \frac{M - X_B}{M(1 - X_B)}$$

Solving for X_B

$$\frac{M - X_B}{M(1 - X_B)} = \exp\left[\bar{t}kC_{Bo}(M - 1)\right] = Y$$

$$X_B = \frac{M(1 - Y)}{1 - MY}$$

$$C_{B,F} = C_{Bo}(1 - X_B)$$

The experimental data show that there existed change in the model from a perfectly mixed C.F.S.T.R. at the higher residence times (before the inflow upset) to a mixed model at the lower residence times (after the upset). The abrupt change in output concentration for the mixed model is physically impossible. Therefore, it was assumed that the output concentration of the plug flow reactor will reach $C_{B,F}$ exponentially by the following equation:

$$C_B = (C_{B,F} - C_{Bo})(1 - e^{-t/\bar{t}})$$

as shown by dashed curve in Figure 3.

The transient response of the mixed model was calculated making the component material balance on Figure 2 for sodium hydroxide, using the results in perfectly stirred and plug flow reactor sections, and were compared with the experimental data as shown in Figures 4 through 9.

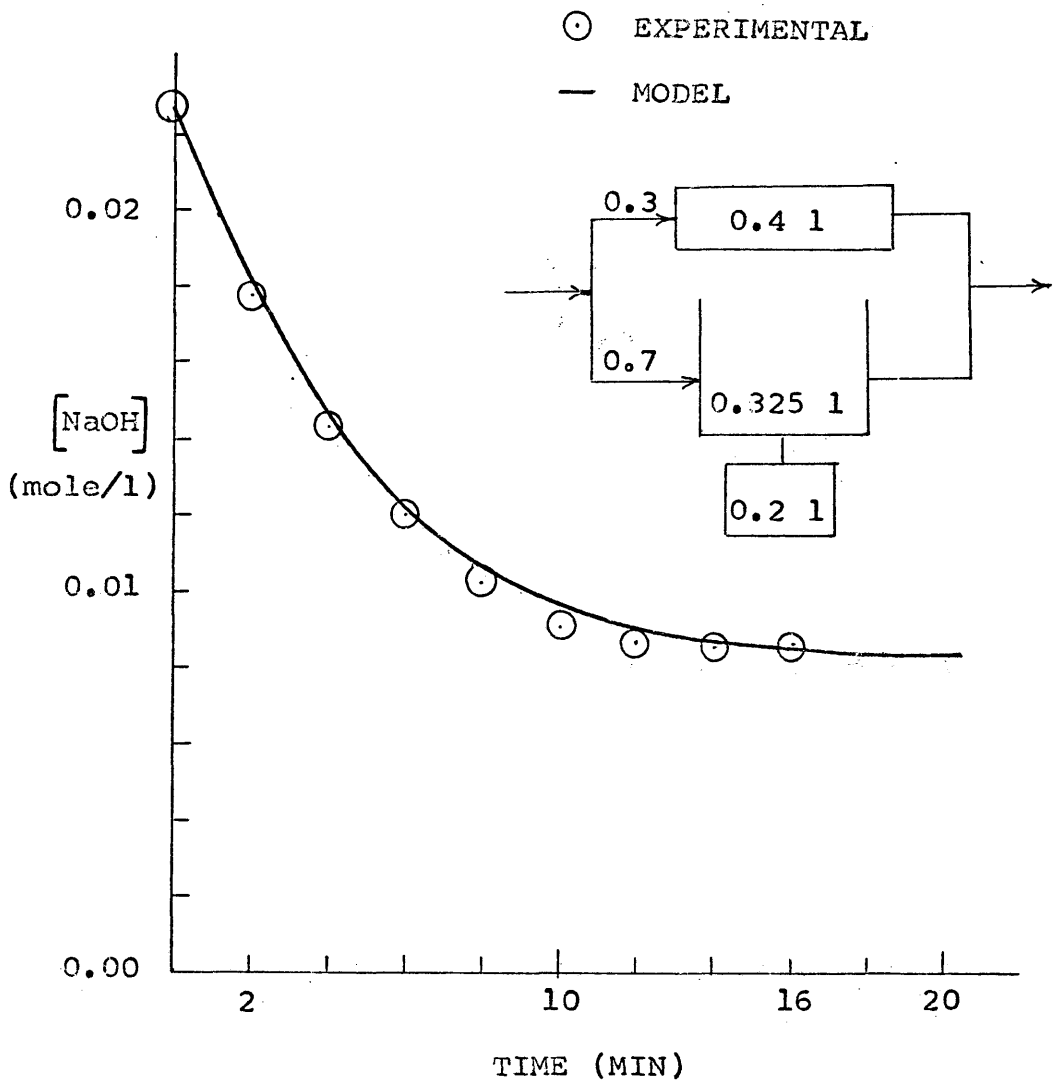


Figure 4: Transient Response of Outlet NaOH Conc. to Upset of Inflow Rate of EtAc

(Run 1: No Mixing)

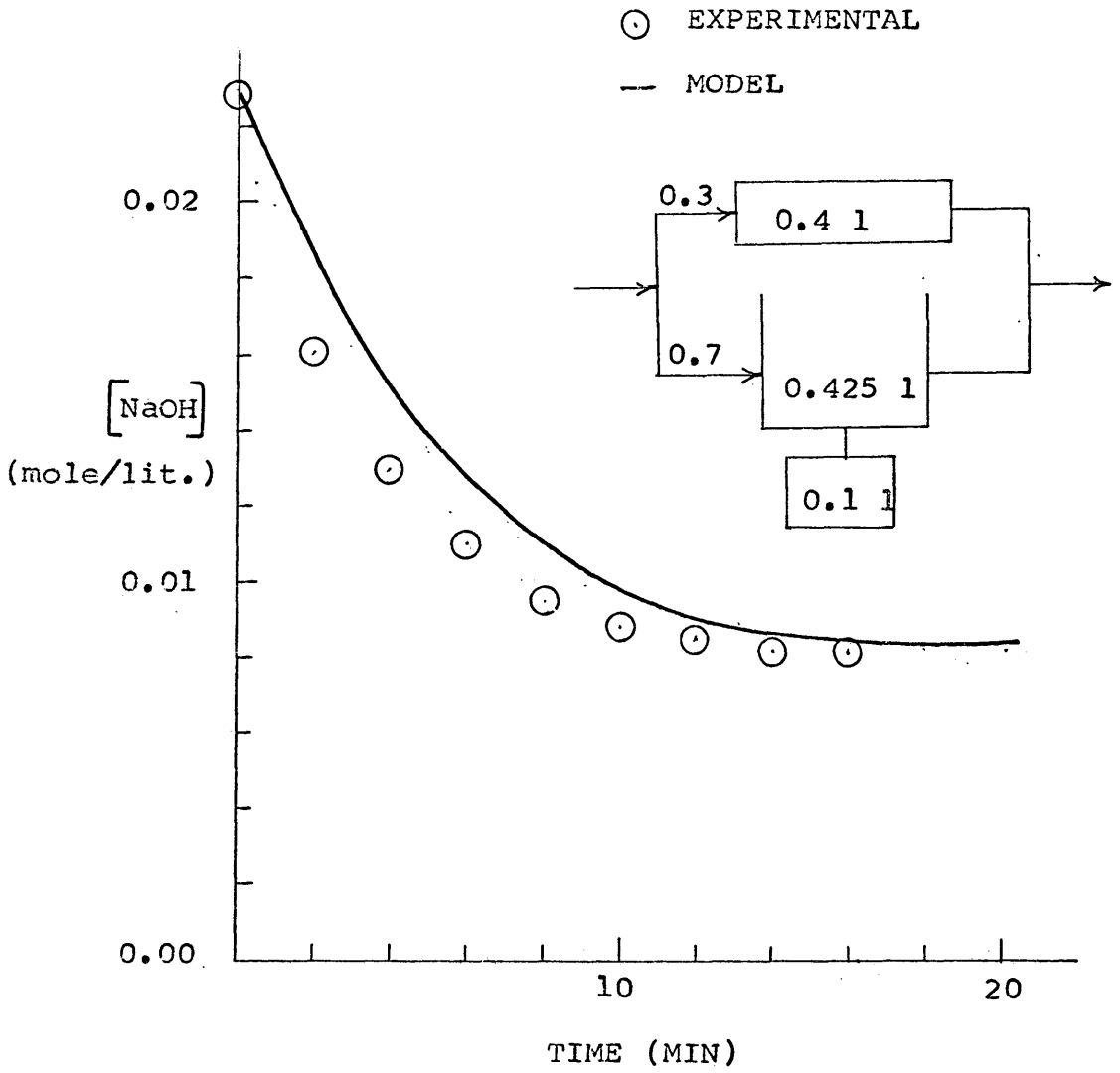


Figure 5: Transient Response of Outlet NaOH to Upset of Inflow Rate of EtAc

(Run 2: 240 rpm)

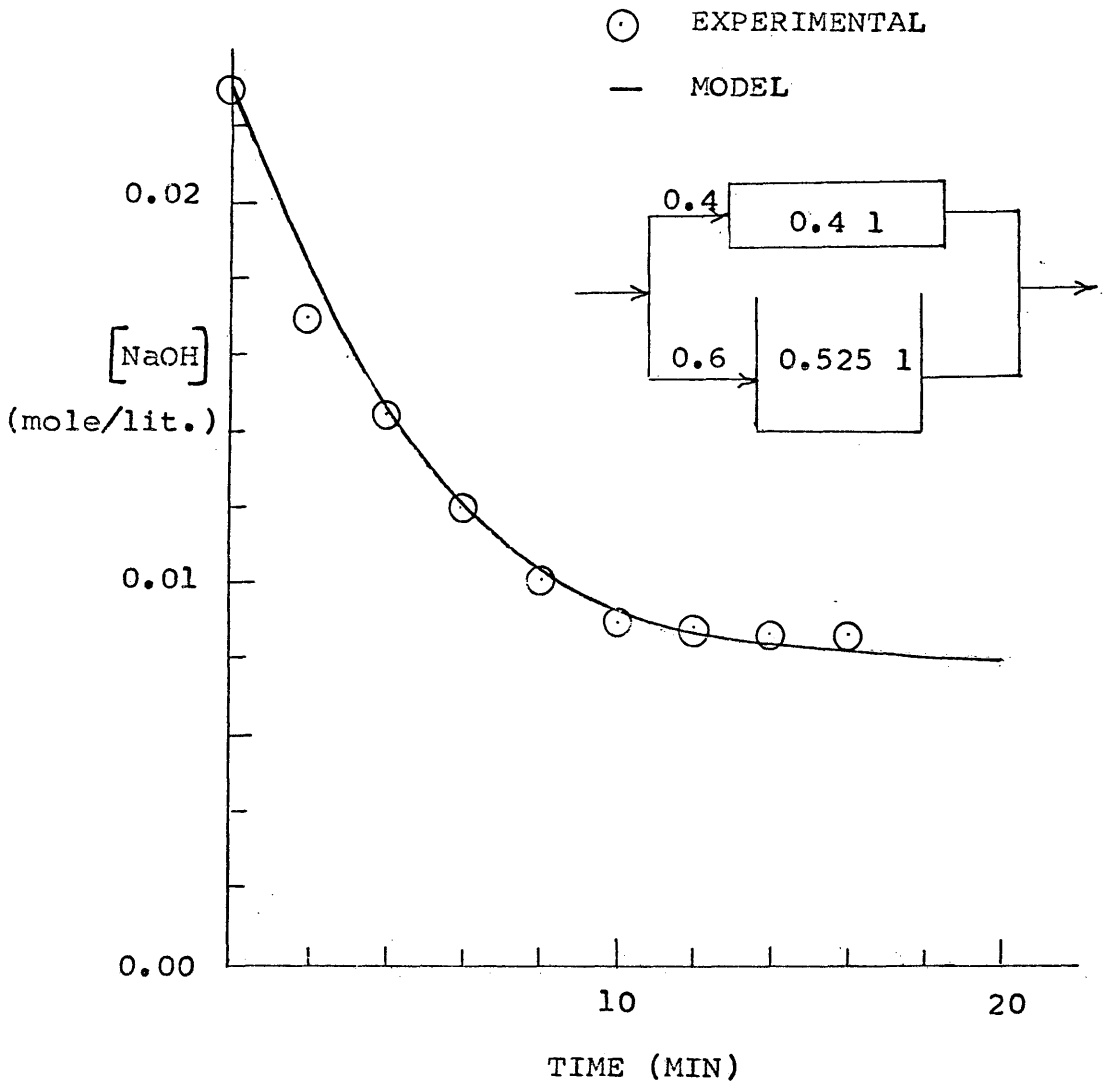


Figure 6: Transient Response of Outlet NaOH to Upset of Inflow Rate of EtAc

(Run 3: 485 rpm)

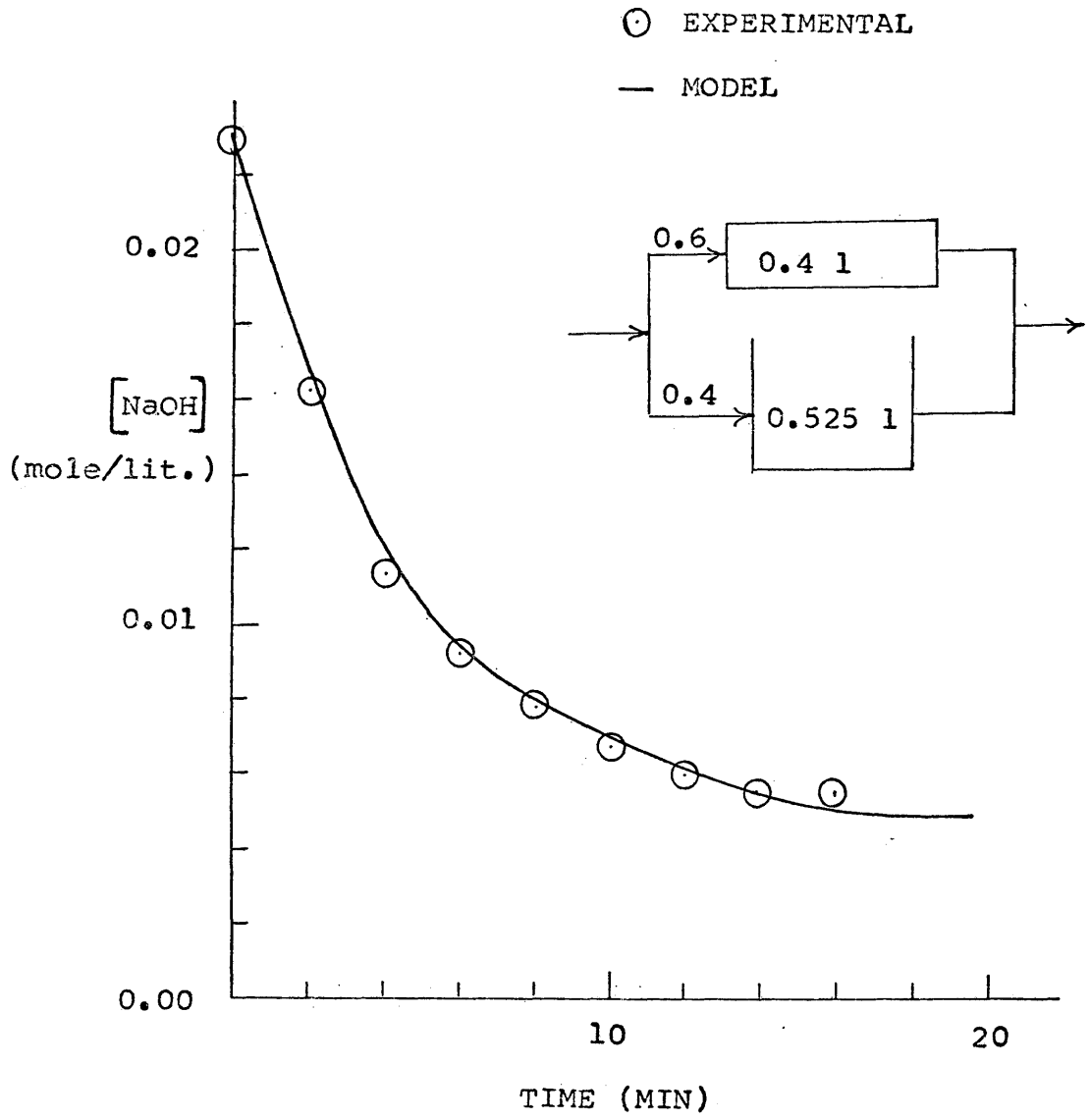


Figure 7: Transient Response of Outlet NaOH to Upset of Inflow Rate of EtAc

(Run 4: 725 rpm)

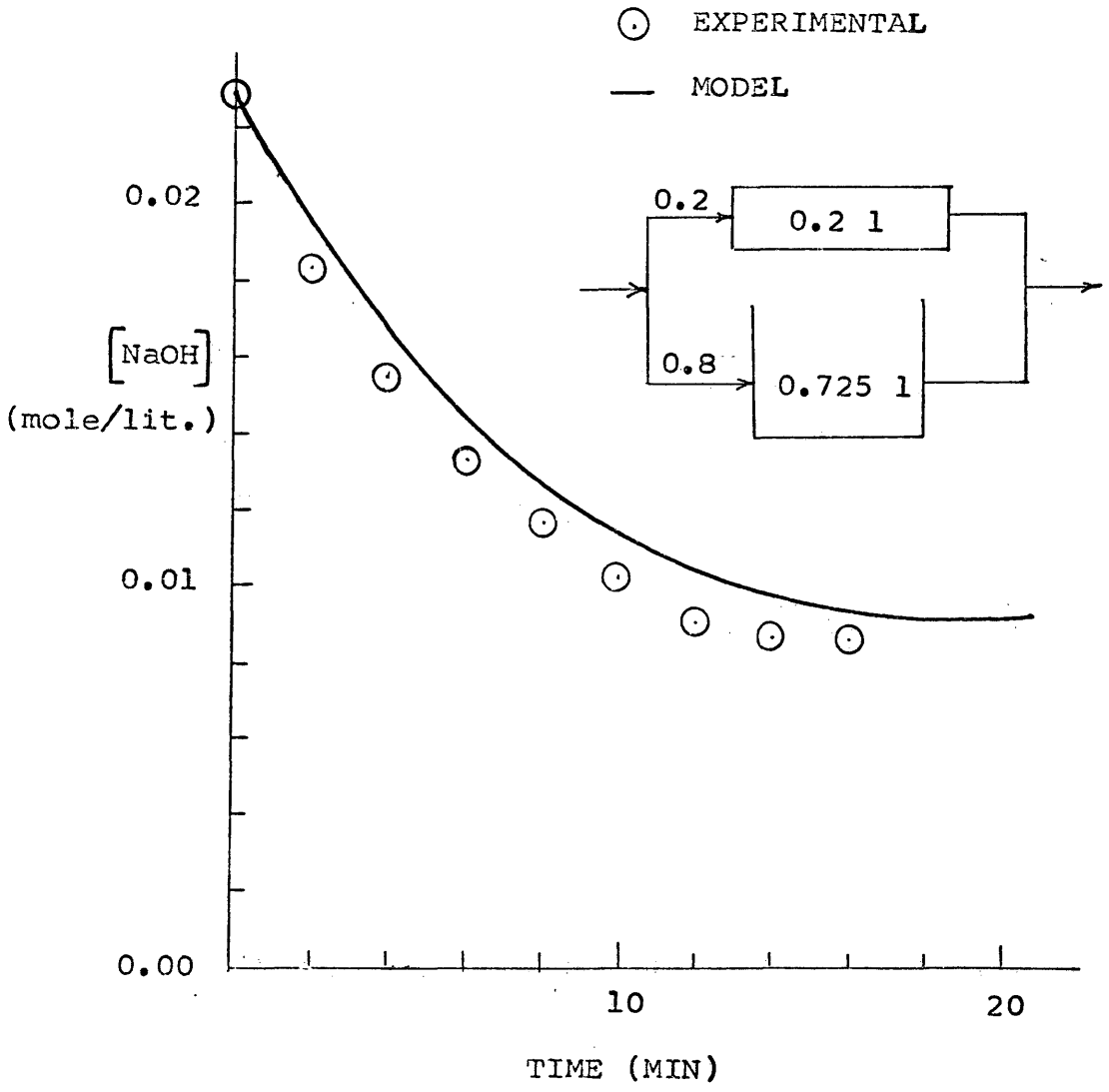


Figure 8: Transient Response of Outlet NaOH to Upset of Inflow Rate of EtAc

(Run 5: 980 rpm)

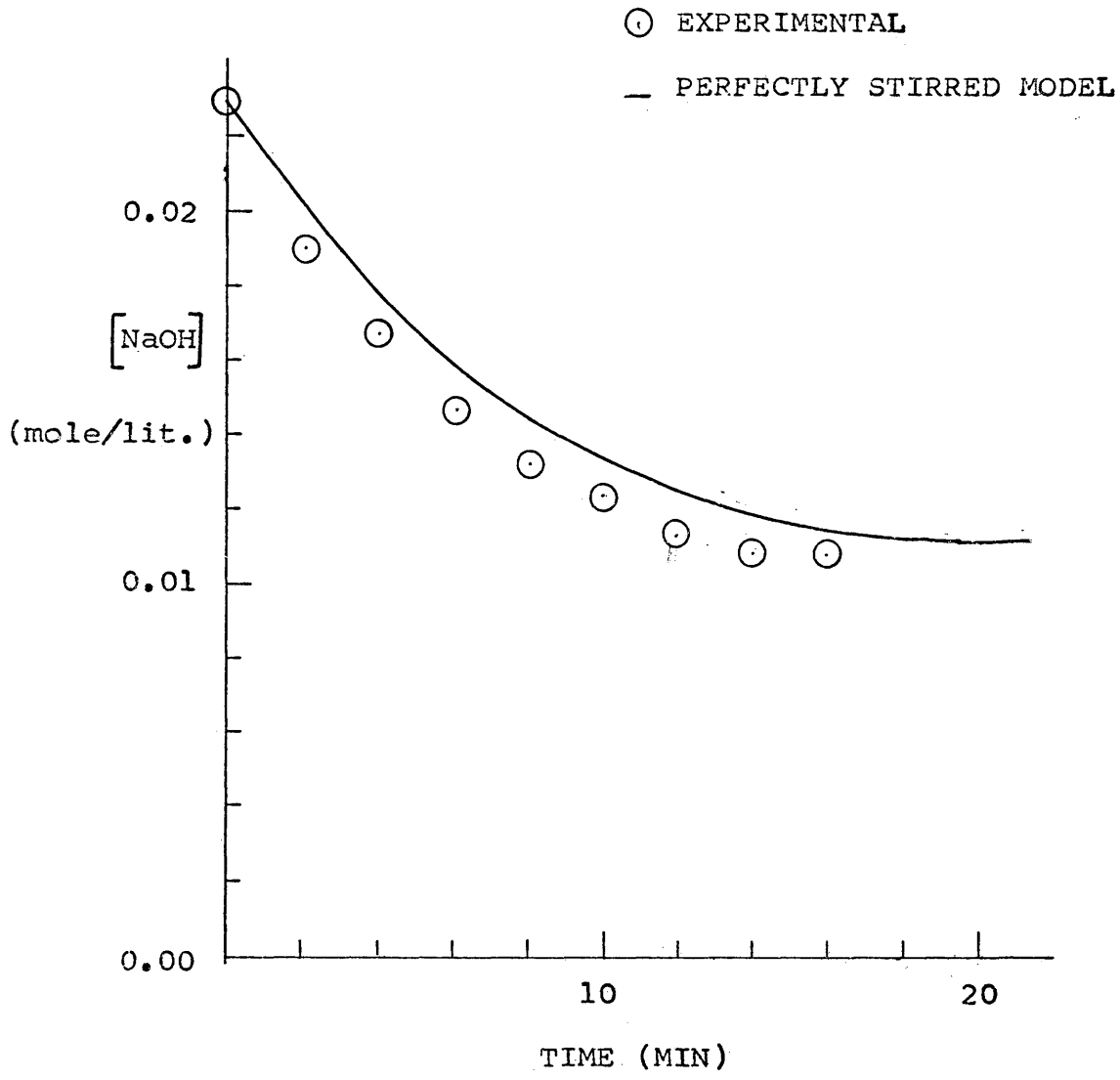


Figure 9: Transient Response of Outlet NaOH to Upset of Inflow Rate of EtAc

(Run 6,7: 1220 & 1725 rpm)

RESULTS AND DISCUSSION

The experimental data of the output sodium hydroxide concentration response to an upset of 100 ml in ethyl acetate flow rates are given in the Appendix. The response at six different mixing rates are shown in Figures 4 through 9.

Since response did not change with the increase of the mixing rates beyond 1220 rpm, it was assumed that the reactor behaves as a perfectly stirred tank beyond 1220 rpm. The rate constant was calculated by the steady state equation for a perfectly stirred tank with the initial steady state value of sodium hydroxide concentration obtained by the experiment at 1220 rpm. The resulting value of k, 6.7/(mole/l)/min, was in close agreement with the data given by the International Critical Tables (13) and by Saldick et al (14).

There was no marked differences in initial steady state sodium hydroxide concentrations at different mixing rates, while the final steady state values were a function of mixing rates as shown in Figure 10. The differences of initial and final steady state sodium hydroxide concentration as a function of mixing rate is shown in Figure 11. At the lower flow rates, residence time is high and the pattern of reac-

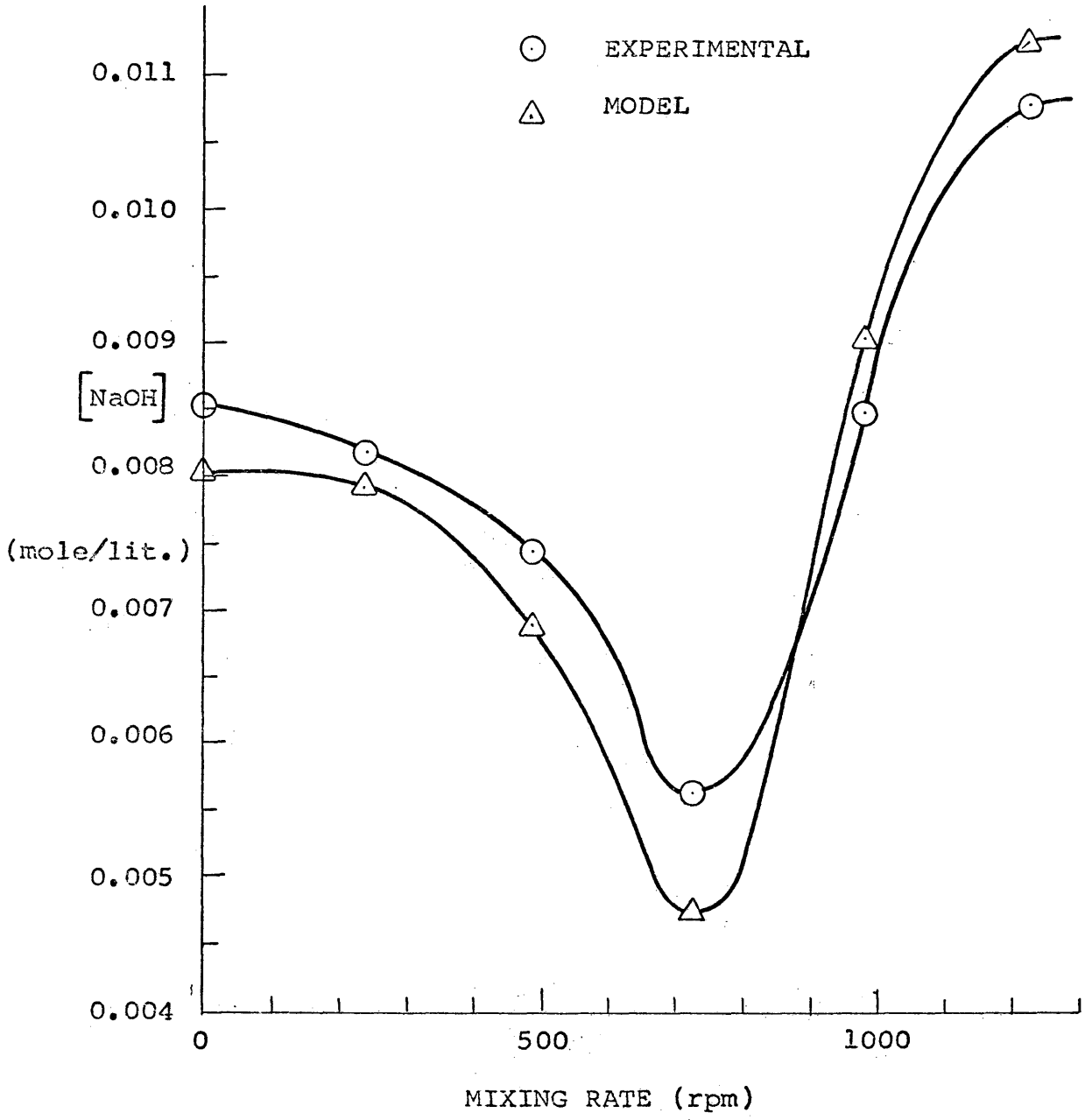


Figure 10: Final Steady State NaOH Conc. as Function of Mixing Rate

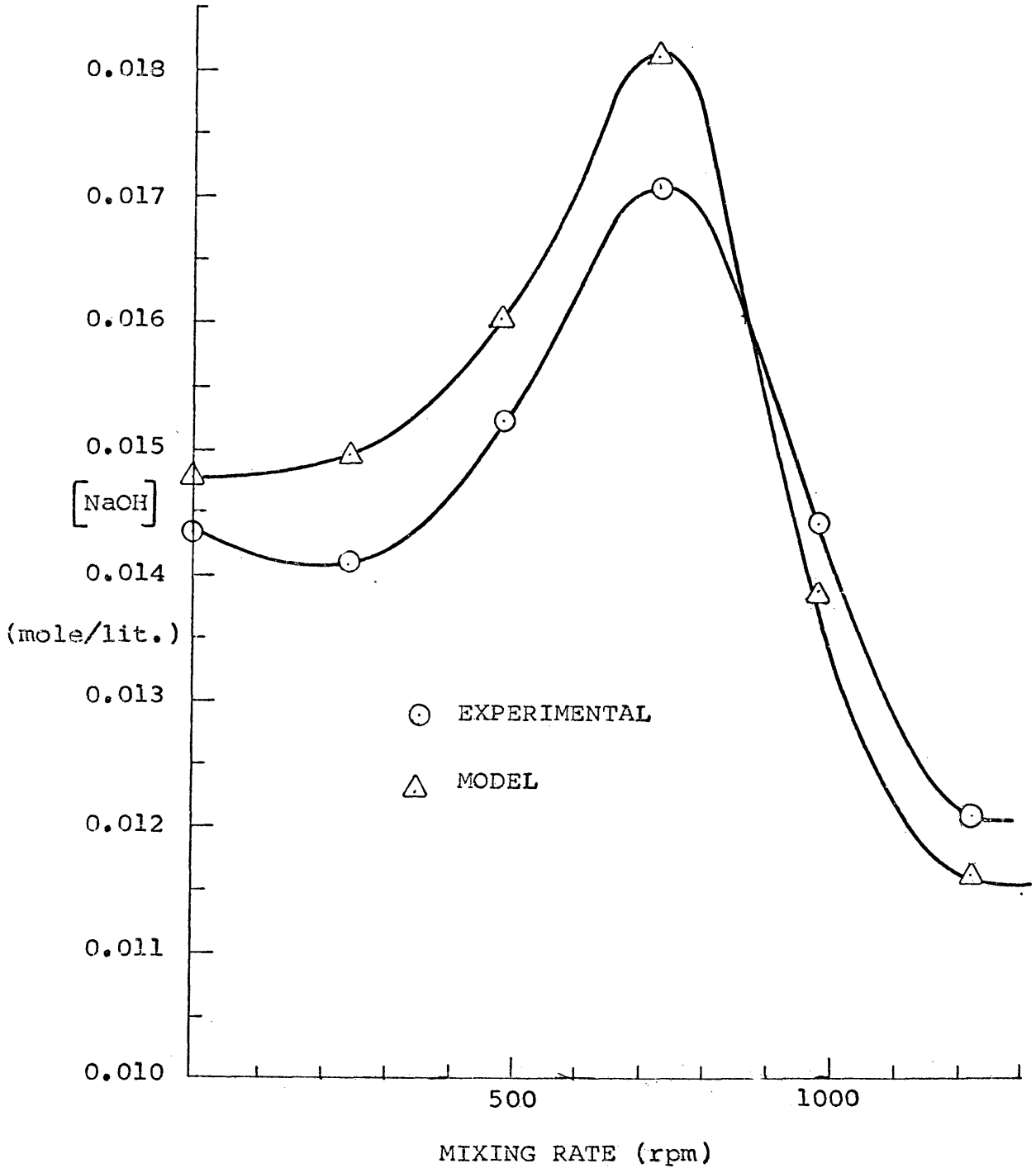


Figure 11: Difference Between Initial and Final Steady State Values of NaOH Conc. as Function of Mixing Rate

tor behavior is well established, and every molecule has enough time to intermix during its sufficiently high residence time. Thus it can be concluded that at reasonably high residence time the mixing rate has negligible effect on conversion as experimentally shown.

The final steady state sodium hydroxide concentration was the lowest at approximately 800 rpm. Up to 800 rpm, the final steady state concentration decreased with the increase of the mixing rate, while it increased with the increase of the mixing rate above 800 rpm. The fact that conversion was higher at the lower rpm than at maximum rpm (perfectly stirred case) shows that there was an effect of segregation. It can be assumed that at lower mixing rates the degree of segregation is higher. However, at no or very low mixing, there exist dead spaces. Thus, the conversion was highest at the moderate mixing range (approximately 800 rpm) where the dead space was no longer present and effect of segregation showing the plug flow effect still existed. These facts enables one to adopt the model as described in Figures 4 through 9.

The fractions of inflow going to C.F.S.T.R. and plug flow portions and fractions of V_p, V_s, V_d were chosen by trial with the above facts in mind. The choice of these factors were rather arbitrary; a choice of larger fraction to plug flow portion with a choice of smaller plug flow volume would have resulted the same response. The important

point shown from the transient curves was that the effect of segregation was the highest in the medium mixing range, with dead space becoming more important as zero mixing is approached, and at sufficiently high stirring speed, a perfectly mixed stirred tank reactor model holds.

The results presented in Figures 10 and 11 show a greater conversion of reactants in the medium mixing range than for either low stirring (large dead space) or perfect mixing. Since the reaction system is second order, this is to be expected if some degree of segregation is present. It has been well established that a completely segregated system gives a higher conversion than a perfectly mixed one for reaction orders greater than unity.

CONCLUSIONS

Observation of the transient response of the output concentration to a large flow rate upset may provide one with a qualitative description of an imperfectly mixed stirred tank reactor.

The experimental data obtained show that a perfectly mixed reactor in parallel with a plug flow reactor and dead space adequately describe the general trend of the real reactor system response to flow rate upsets at different mixing rates.

An upset of 100 ml/min in ethyl acetate flow rate was used where flow rates of both ethyl acetate and sodium hydroxide were 60 ml/min and both inlet concentrations were 0.1 N. Final steady state value of sodium hydroxide concentrations is shown to be maximum at 800 rpm, which is well below the rpm for perfect mixing.

Mixing rate appears to have higher effect on conversion at the lower residence time (higher flow rates) than at the higher residence time (lower flow rates). At no or very low mixing there exists dead space. The degree of segregation increases to a maximum then decreases with mixing rate.

Since the mixing pattern is a strong function of the reactor geometry, results of this work should be interpreted as qualitative rather than quantitative.

LIST OF NOMENCLATURES

C: Concentration (mole/liter); $C = C_o(1-X)$

F: Volumetric flow rate (liter/min); $F = F_{Ao} + F_{Bo}$

h: Time interval for predictor-corrector methods

k: Reaction rate constant (liter/mole min)

M: C_{Bo}/C_{Ao}

V: Volume of the reactor (liter)

X: Fractional conversion

Subscripts

A: Ethyl acetate

B: Sodium hydroxide

d: Dead space

o: Inlet conditions

p: Plug flow reactor

s: Perfectly stirred reactor

ss: Steady state conditions

Superscripts

' : Perturbation

(i): i-th iteration in the correctors of predictor-corrector methods

APPENDIX

EXPERIMENTAL DATA

$C_{Ao} = C_{Bo} = 0.1$ mol/lit $\qquad F_{Ao} = F_{Bo} = 0.06$ lit/min

Temperature = 80^{o} F $\qquad F_{A}' = 0.1$ lit/min

C_B (concentration of NaOH, mol/lit)

RUN NO.	1	2	3	4	5	6 & 7
rpm / Time (min)	0	240	485	725	980	1220 & 1725
0	0.0229	0.0224	0.0227	0.0227	0.0229	0.0229
2	0.0178	0.0158	0.0170	0.0162	0.0182	0.0191
4	0.0143	0.0131	0.0120	0.0114	0.0156	0.0166
6	0.0120	0.0112	0.0101	0.00921	0.0132	0.0145
8	0.0102	0.0095	0.00851	0.00785	0.0117	0.0132
10	0.00898	0.0087	0.00798	0.00681	0.0102	0.0123
12	0.00859	0.0084	0.00751	0.00600	0.0090	0.0112
14	0.00855	0.0082	0.00748	0.00563	0.0086	0.0108
16	0.00855	0.0082	0.00748	0.00563	0.0085	0.0108

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