An Experimental and Theoretical Study of the Transient Response of an Isothermal Tubular Reactor with Recycle

K. A. McKINSTRY, F. J. STERMOLE, and R. L. DUNN

Department of Chemical and Petroleum Refining Engineering
Colorado School of Mines, Golden, Colorado 80401

Experimental and theoretical transient response data are presented for a tubular reactor with recycle, illustrating the distributed nature of this feedback system. The transient concentration response of an isothermal tubular reactor with recycle was studied experimentally and theoretically for inlet concentration and flow upsets. The reaction studied experimentally was the second order homogeneous liquid phase saponification of methyl acetate with sodium hydroxide.

Theoretical models using residence time distribution (RTD) techniques have been developed. The fact that the theoretical model (RTD) predicts the dynamic response data for the recycle reactor with and without reaction in the recycle line for both single flow and concentration upsets verifies that this model is satisfactory for simulation of recycle tubular reactor dynamics.

Tubular chemical reactors have received much attention in the past decade, and many investigators have contributed to the literature existing on tubular reactors. Tubular reactors with recycle, on the other hand, have been considered only to a limited degree. Most work has involved analysis of steady state systems, and much of the work that has been done in theoretical for both steady state and unsteady state systems. To the authors' knowledge, no experimentally verified theory has been reported in the literature for unsteady state tubular reactor system with recycle.

The present work is an experimental and theoretical study of an unsteady state isothermal plug-flow tubular recycle reactor with and without reaction and a transportation lag in the recycle line. The objectives of this study were to investigate the transient response of the recycle reactor system to step changes for a short recycle line, assuming that no reaction occurs in the recycle line and for a recycle line when reaction occurs.

The main purpose of this investigation was to verify experimentally and to develop a theoretical model to predict the transient concentration response of a recycle reactor for upsets in flow rates and inlet concentration. The system that was studied was a tubular recycle reactor operated under isothermal conditions for a homogeneous second-order liquid phase reaction. This system can be represented by a set of nonlinear partial differential equations which have to be solved simultaneously.

One of the reasons why distributed parameter problems of this nature have been studied very little may be the complexity of the theoretical modeling because of the nonlinear nature of the describing functions. This frequently leads to the development of the lumped parameter model, which is a technique used to simplify models of distributed parameter systems. However, this paper presents a residence time distribution solution technique which the authors feel is superior to other simulation models for tubular recycle reactors. This model gives good agreement with experimental data. The equations developed for the tubular reactor with modifications will be applied to the isothermal recycle reactor.

The reaction used in the experimental study was the saponification of methyl acetate by sodium hydroxide, given by

$$CH_3COOCH_3 + NaOH \rightarrow CH_3OH + CH_3COON_a$$

This reaction was used because it is an irreversible second order reaction with a relatively high reaction rate constant at 40°C. The kinetics were obtained from a previous study (*1*).

MATHEMATICAL MODEL

In the system studied, a fraction of the effluent stream from a tubular reactor is returned through a recycle line to mix with the fresh feed at the inlet. It is assumed that the mixing between the recycle stream and the fresh feed is instantaneous and perfect. Other assumptions used throughout the analysis are that plug-flow exists in the reactor and recycle line, that there is no axial dispersion of mass, and that radial concentration gradients do not exist.

If one examines the design equation for a plug flow tubular reactor (PFTR) Equation (1) and for a batch reactor Equation (2) he can easily see that the length in a PFTR corresponds to time in a batch reactor.

$$\text{Batch, } t = C_{A0} \int \frac{dX_A}{-r_A} \tag{1}$$

Correspondence concerning this paper should be addressed to F. J. Stermole.

$$\text{Plug-flow reactor, } \tau = C_{A0} \int \frac{dX_A}{-r_A} \tag{2}$$

This analogy between the batch and the tubular reactor can be used for predicting the response of a plug-flow tubular reactor.

From Equations (1) and (2), the solutions for the second-order reaction, $A + B \xrightarrow{k} C + D$, for single concentration and flow upsets are developed in the following section for a plug-flow loop reactor shown schematically in Figure 1.

Single Concentration Upset in Inlet Reactant

Symbolically a single concentration upset in sodium hydroxide can be given as

$$C_{AI} \neq C_{AF},\; C_{BI} = C_{BF},\; F_{A0} = A_{A1},\; F_{B0} = F_{B1},\; Q_{RE} = Q_{REF}$$

Initially the recycle reactor is at a given steady state before a concentration upset is made at $t = 0$. Figure 1 shows where the symbolic flow rates and concentrations occur in the system.

For $t < 0$, the outlet steady state values are C_{A0_1} and C_{B0_1} and the effluent steady state values for the recycle lines are C_{AR_1} and C_{BR_1}. The corresponding reactor inlet conditions without reaction in recycle line are

$$C_{Ai_0} = \frac{(1-R)F_{A0}}{F_{A0}+F_{B0}} C_{AI} + RC_{A0_1} \tag{3}$$

$$C_{Bi_0} = \frac{(1-R)F_{B0}}{F_{A0}+F_{B0}} C_{BI} + RC_{B0_1} \tag{4}$$

With reaction in recycle line, Equations (3) and (4) are transformed to

$$C_{Ai_0} = \frac{(1-R)F_{A0}}{F_{A0}+F_{B0}} C_{AI} + RC_{AR_1} \tag{5}$$

$$C_{Bi_0} = \frac{(1-R)F_{B0}}{F_{A0}+F_{B0}} C_{AI} + RC_{BR_1} \tag{6}$$

At time $t = 0$, a concentration upset is made in C_{AI}. The new inlet concentration to the reactor without reaction in recycle line based upon the total throughput for the time zone $0 \leq t < \tau_1$ is

$$C_{Ai_1} = \frac{(1-R)F_{A1}}{F_{A1}+F_{B1}} C_{AF} + RC_{A0_1} \tag{7}$$

$$C_{Bi_1} = \frac{(1-R)F_{B1}}{F_{A1}+F_{B1}} C_{BF} + RC_{B0_1} \tag{8}$$

Since the residence time of the reactor does not change when a concentration upset is made, the concentrations at the outlet of the reactor remain at the old steady state value until one residence time lapses.

Thus, at $t = \tau_1$, there will be a concentration change at the outlet of the reactor. Since it is assumed in this case that the recycle line has zero length, the material is instantaneously returned in the recycle line, and a concentration change will be felt every residence time τ_1 at the inlet of the reactor due to the change of the recycle concentration.

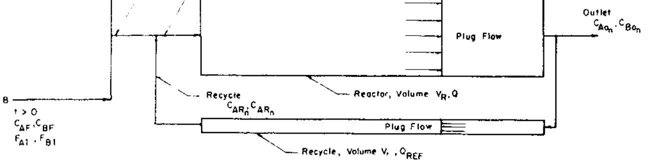

Fig. 1. Schematic diagram of tubular reactor with recycle.

In general form, the inlet and outlet concentrations for the time zone $(n-1)\,\tau_1 \leq t < n\tau_1$ will be given by the following equations

$$C_{A0_n} = \frac{M_{(n-1)}}{N_{(n-1)}\exp[M_{(n-1)}k\tau_1] - 1.0} \tag{9}$$

$$C_{Ai_n} = \frac{(1-R)F_{A1}}{F_{A1}+F_{B1}} C_{AF} + RC_{A0_n} \tag{10}$$

Thus, for single concentration upsets, Equations (3), (4), (9), and (10) predict the response of a tubular reactor with recycle, and the outlet concentration will be in the form of steps because of the residence time effect, coupled with the effect caused by recycle.

At time $t = 0$, a concentration upset is made in C_{AI} for the reactor system where reaction occurs in the recycle line. The new inlet concentrations to the main reactor based upon the total throughput for the time zone $0 \leq t < \tau_{RI} + \tau_{A1}$ are

$$C_{Ai_1} = \frac{C_{AF}(1-R)F_{A1}}{(F_{A1}+F_{B1})} + C_{AR_1}R \tag{11}$$

$$C_{Bi_1} = \frac{C_{BF}(1-R)F_{B1}}{(F_{A1}+F_{B1})} + C_{BR_1}R \tag{12}$$

Since the residence time of either reactor does not change when a concentration upset is made, the concentrations at the outlet of the main reactor remain the old steady state value until the residence time τ_{A1} of the main reactor lapses.

Since it is assumed in this case that reaction occurs in the recycle line, the fluid elements are returned through the recycle line with a transportation lag of the recycle residence time τ_{R1}. A concentration change at the inlet of the main reactor will be felt at the time of upset and will change every $\tau_{R1} + \tau_{A1}$ due to the recycle, but the concentration change will not be seen at the outlet of the main reactor for a residence time of τ_{A1}. The outlet concentration will then change every $\tau_{R1} + \tau_{A1}$ until the new steady state is reached. Thus, at $t = \tau_{A1}$, there will be a concentration change at the outlet of the reactor.

Accordingly, the outlet concentration for time zone $\tau_{A1} \leq t < \tau_{A1} + (\tau_{R1} + \tau_{A1})$ will be given by the following equations

$$C_{A0_2} = \frac{M_1}{N_1 \exp\,(M_1 k \tau_{A1}) - 1.0} \tag{13}$$

$$C_{B0_2} = M_1 + C_{A0_2} \tag{14}$$

The inlet concentration to the main reactor for the time zone $\tau_{R1} + \tau_{A1} \leq t < 2\,(\tau_{R1} + \tau_{A1})$ will be determined from the outlet concentration C_{A0_2} and C_{B0_2} and the residence time of the recycle line are given by the following equations

$$C_{AR_2} = \frac{M_1'}{N_1' \exp\,(M_1' k \tau_{R1}) - 1.0} \tag{15}$$

$$C_{BR_2} = M_1' + C_{AR_2} \tag{16}$$

$$C_{Ai_2} = \frac{C_{AF}F_{A1}(1-R)}{(F_{A1}+F_{B1})} + RC_{AR_2} \tag{17}$$

$$C_{Bi_2} = \frac{C_{BF}F_{B1}(1-R)}{(F_{A1}+F_{B1})} + RC_{BR_2} \tag{18}$$

Similarly for the time zone $\tau_{A1} + (\tau_{R1} + \tau_{A1}) \leqq t < \tau_{A1} + 2\,(\tau_{R1} + \tau_{A1})$, Equations (13) and (14) can be used by replacing subscripts 1 and 2 by 2 and 3, respectively. Likewise, for the time zone $2\,(\tau_{R1} + \tau_{A1}) \leqq t < 3\,(\tau_{R1} + \tau_{A1})$, Equations (15) to (18) can be used by replacing the same subscripts. In a more general form, one could write for a time zone $\tau_{A1} + (n-1)\,(\tau_{R1} + \tau_{A1}) \leqq t < \tau_{A1} + n\,(\tau_{R1} + \tau_{A1})$ the following for the outlet concentration of the main reactor.

$$C_{A0_n} = \frac{M_{(n-1)}}{N_{(n-1)}\exp\,(M_{(n-1)}k\tau_{A1}) - 1.0} \tag{19}$$

$$C_{B0_n} = M_{(n-1)} + C_{A0_n} \tag{20}$$

The inlet concentration for the main reactor for the time zone $(n-1)\,(\tau_{R1} + \tau_{A1}) \leqq t < n\,(\tau_{R1} + \tau_{A1})$ can be obtained from the following

$$C_{AR_n} = \frac{M'_{(n-1)}}{N'_{(n-1)}\exp\,(M'_{(n-1)}k\tau_{R1}) - 1.0} \tag{21}$$

$$C_{BR_n} = M'_{(n-1)} + C_{AR_n} \tag{22}$$

$$C_{Ai_n} = C_{AF}(F_{A1} + F_{B1})/Q_f + Q_{REF}C_{AR_n}/Q_f \tag{23}$$

$$C_{Bi_n} = C_{BF}(F_{A1} + F_{B1})/Q_f + Q_{REF}C_{BR_n}/Q_f \tag{24}$$

$$C_{A0_m} = \frac{(C_{Bi_0} - C_{Ai_0})}{C_{Bi_0}/C_{Ai_0}\exp\left[\,(C_{Bi_0} - C_{Ai_0})k\left(\frac{n-m}{N}\right)\tau_{A0} + \frac{m}{N}\tau_{A1})\,\right] - 1.0} \tag{25}$$

Thus, for single concentration upsets, Equations (11) and (12) give the inlet concentration for the time zone $0 \leqq t < \tau_{R1} + \tau_{A1}$, and Equations (22) to (25) give the inlet concentration after $t > \tau_{R1} + \tau_{A1}$. Equations (20) and (21) predict the transient response of sodium hydroxide and methyl acetate at the outlet of the main reactor for time $t > \tau_{A1}$. The outlet concentration will be in the form of steps occurring every $\tau_{R1} + \tau_{A1}$ after τ_{A1} because of the residence time effect of the recycle line, coupled with the effect caused by the return of main reactor effluent. Simultaneous upsets in concentration can be handled with these same equations.

Single Flow Upset of an Inlet Reactant Stream

Symbolically a single flow upset in sodium hydroxide can be given as

$$C_{AI} = C_{AF},\ C_{BI} = C_{BF},\ F_{A0} \neq F_{A1},$$
$$F_{B0} = F_{B1},\ Q_{RE} = Q_{REF}.$$

Even though only one flow rate was changed, a close look at the actual concentrations will show more than one change, namely, $C_{A0} \neq C_{A1}$, $C_{B0} \neq C_{B1}$, and $\tau_{A0} \neq \tau_{A1}$. The residence time of the recycle line was not changed. Since the fluid residence time in the main reactor before upset is not the same as the residence time after upset, the concentration response is not in the form of steps. The response can be obtained from the equations developed in the following paragraphs for both cases with and without reaction in recycle line.

At time $t = 0$, the effect due to a change in residence time is seen at the outlet of the reactor as soon as the upset is made. However, the effect due to the concentration change is not felt until the new residence time lapses. From Equations (3) and (4) or (5) and (6), the inlet conditions before upset are obtained; the outlet concentration of sodium hydroxide for four fluid elements in the main reactor for the time zone equivalent to the new residence time $0 \leqq t \leqq \tau_{A1}$ are obtained by

$$C_{B0_m} = C_{Bi_0} - C_{Ai_0} + C_{A0_m} \tag{26}$$

where $N = 4$

m = block level, 0 to N

The concentration history of these four fluid elements are followed for the entire dynamic response as well as the fluid in the recycle line. The concentration of these four fluid elements gives the outlet concentration of sodium hydroxide. A fraction of each fluid element is returned to the inlet by the recycle line depending upon the recycle flow rate. Once time exceeds the new residence time τ_{A1}, the entire transient concentration response is caused by the upsetting of the concentration at the inlet of the main reactor by both the fluid elements initially in the recycle line and the outlet effluent that is returned by the recycle. The fluid elements initially in the recycle line produce just a concentration upset, and the outlet concentrations can be obtained from the equations developed for the concentration upset, but care must be taken to match the correct time zone.

The outlet concentrations for the time zone $\tau_{A1} \leqq t < \tau_{A1} + \tau_{R1}$ are obtained from Equations (13) and (14) with the corresponding inlet conditions obtained from Equations (7) and (8). For the next time zone $\tau_{A1} + \tau_{R1} \leqq t < \tau_{A1} + \tau_{R1} + \tau_{A1}$, the outlet concentration is affected by the fluid elements returned from the effluent by the recycle for $0 \leqq t < \tau_{A1}$. As mentioned previously, the concentration of each fluid element is followed during the response and Equations (21) and (22) are used to obtain the effluent concentration of sodium hydroxide and methyl acetate of the recycle line. The inlet concentrations to the main reactor, obtained by Equations (23) and (24), are used to find the transient response at the outlet by use of Equations (17) and (18).

For the time zone $\tau_{A1} + (\tau_{R1} + \tau_{A1}) < t < \tau_{A1} + 2\,(\tau_{R1} + \tau_{A1})$ after $t > \tau_{A1}$, Equations (21) and (22), (23) and (24), and (17) and (18) are used to determine the outlet concentrations both for the fluid elements in the recycle line and in the main reactor.

To summarize, Equations (3), (4), (19), and (20) are used to determine the transient concentration response for $0 \leqq t < \tau_{A1}$, and Equations (5) through (8) are used to obtain the response from the fluid initially in the recycle line at the time of upset for $\tau_{A1} \leqq t < \tau_{A1} + \tau_{R1}$. Equations (21) and (22), (23) and (24), and (17) and (18) are used for $\tau_{A1} + \tau_{R1} \leqq t < \tau_{A1} + \tau_{R1} + \tau_{A1}$. For the time $t > \tau_{A1} + \tau_{R1} + \tau_{A1}$, Equations (21) through (24), (17), and (18) are repeated until the inlet conditions to the main reactor C_{Ai_n} and C_{Bi_n} do not change. Again as in the single concentration upset, step concentration changes occur at the inlet every $\tau_{R1} + \tau_{A1}$ because of the effect due to the recycle; thus, step changes result at the outlet of the main reactor. However, in the system where reaction does not occur in the recycle line the time response is $t = \tau_1$. In the single concentration upset, step concentration changes result at the inlet of the tubular reactor every $t = n\tau_1$ because of the effect due to the recycle where no reaction occurs.

Simultaneous upsets in inlet flow or concentration, and combinations of these upsets, are predicted by using the same equations. Recycle flow upsets can be handled by using the same techniques, but the design of the physical

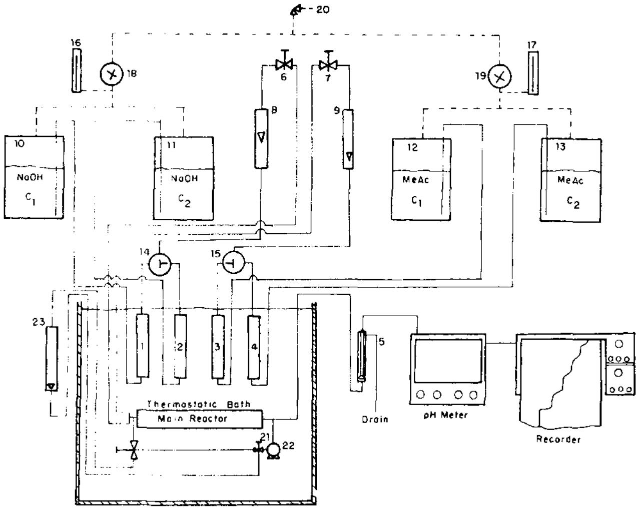

Fig. 2. Flow diagram of experimental reactor system.

reactor system does not allow these equations to predict the response. Results for the recycle flow upset were obtained (2).

EXPERIMENTAL SECTION

A flow diagram of the experimental reactor system is given in Figure 2. All flow lines used were ¼-in. polyflow tubing. The reactants as shown in Figure 2 were stored in tanks 10, 11, 12, and 13. The reactants were pumped to the reactor with air pressure controlled by the pressure regulators 18 and 19. The pressures at the outlet of the regulators were measured by manometers 16 and 17. A safety relief valve was introduced in the air line before the regulators, so any excess back pressure over 10 lb./sq. in. could be released.

The air from the regulators proceeded to the feed tanks. The 20-liter feed tanks had to be periodically filled. Tanks 10 and 11 contained sodium hydroxide; tanks 12 and 13 were used for methyl acetate.

Reactants displaced from the feed tanks by air pressure were preheated by preheaters 1, 2, 3, and 4. The preheaters were immersed in a thermostatic bath which was maintained at 40°C. The preheaters were ¼-in. diam. copper tubing.

The preheated reactants then passed through the three-way Teflon valves 14 and 15. The amount of reactants flowing was metered with rotameters 8 and 9. Control of inlet flow rates was obtained with the needle valves 6 and 7.

The metered streams of reactants then entered the reactor, which was kept at the same temperature as the preheaters by immersing in the same thermostatic bath. Thus, essentially isothermal operation was assured. The main reactor was a 50-ft. long, ¼-in. nominal diam. (0.482 — cm. I.D.) copper tube in the form of a spiral.

The recycle flow was maintained by a centrifugal pump 22 and was controlled by a vernier needle valve 21. The case with reaction in recycle line used a 20-ft. long 0.482-cm. diam. copper tube for the line. A bypass was used to spot check the recycle flow rate at steady state.

The effluent from the reactor passed through a flow cell, where the concentration was monitored with a Jena/Sargent combination electrode (range 0 to 14 *p*H). The *p*H was recorded on a Moseley strip-chart recorder.

The average time constant of the measurement lag of the *p*H electrode was found to be 2.4 sec. (2) and was verified (3), which affected the outlet response. Electrode response studies were conducted at different conditions to determine the effect of concentration and flow rate on measurement lag. In the concentration range studied, the time constant of the measurement lag is relatively steady and does not depend upon the concentration or flow rate. The electrode lag was significant and influenced experimental results. The electrode lag was assumed to be a first order delay and the time consultant τ_e was included in the outlet response of sodium hydroxide concentration. When a step change in the outlet concentration occurred the response was obtained by

$$C_A = C_{A0_{n-1}} + (C_{A0_n} - C_{A0_{n-1}})(1.0 - \exp^{t/\tau_e}) \quad (27)$$

Thus, an exponential decay resulted and affected the experimental results. One of the important factors which determines the lag of the electrode is the way it is prepared before measurement. Before a run was started the *p*H electrode used was soaked in a 2N solution of sodium hydroxide for at least 6 hr., because it was found that this procedure gave optimum reproducibility of the electrode response.

The concentration of solutions in tanks 10 and 12 was approximately double the concentration in tanks 11 and 13. The three-way valves 14 and 15 were used to make step changes in the inlet concentration of either sodium hydroxide or methyl acetate, or both. Inlet flow upsets, either single or multiple, were made with needle valves 14 and 15. Recycle flow upsets were made with needle valve 21.

The reactants used in this study were sodium hydroxide and methyl acetate. The concentrations were approximately 0.25 and 0.125 N. The solutions of desired normality were prepared with reagent grade chemicals. The concentrations of the solutions prepared were obtained through standard titration techniques.

The system was started by closing all the valves except the air valve. Then the air in the feed lines was purged by opening valves 6 and 7. The position of the three-way valves 14 and 15 determined what concentrations were being fed to the reactor. The concentration at the outlet of the reactor was monitored with a *p*H meter, which was standardized with a buffer. The flow in the recycle line was adjusted by needle valve 21 for the initial conditions.

When the concentration reached steady state, a sample was drawn at the outlet and titrated to obtain the sodium hydroxide concentration of the reactor effluent. The sample drawn was quenched with excess hydrochloric acid in order to stop the saponification reaction. Then the concentration of sodium hydroxide which was present was obtained through back titration.

The upsets were then made by manipulating the respective valves. The temperature at the outlet of the reactor was monitored to insure that isothermal conditions would prevail during the run.

When the new steady state was reached, the concentration of sodium hydroxide in the exit stream was determined as mentioned before. The results were interpreted through a calibration curve of *p*H readings versus concentration. Data for both single and simultaneous upsets in concentration and flow rate were obtained (2).

TABLE 1. EXPERIMENTAL INLET RECYCLE REACTOR OPERATING CONDITIONS

Run*	C_{AI}	C_{BI}	F_{A0}	F_{B0}	Q_{RE}	C_{AF}	C_{BF}	F_{A1}	F_{B1}	Q_{REF}	Figure
8	0.1151	0.2974	0.300	0.300	0.150	0.1151	0.0916	0.300	0.300	0.150	3
16	0.2776	0.1682	0.300	0.250	0.150	0.2776	0.1682	0.300	0.350	0.150	4
40	0.2380	0.3119	0.100	0.100	0.400	0.2380	0.1159	0.100	0.100	0.400	5
42	0.2380	0.3119	0.100	0.100	0.400	0.1017	0.3119	0.100	0.100	0.400	6
43	0.1017	0.3119	0.100	0.100	0.400	0.1017	0.3119	0.100	0.200	0.400	7
46	0.2380	0.1159	0.100	0.200	0.400	0.1017	0.1159	0.100	0.100	0.400	8
45	0.2380	0.3119	0.200	0.200	0.400	0.2380	0.1159	0.100	0.200	0.400	9

* Runs correspond to results obtained in (3).

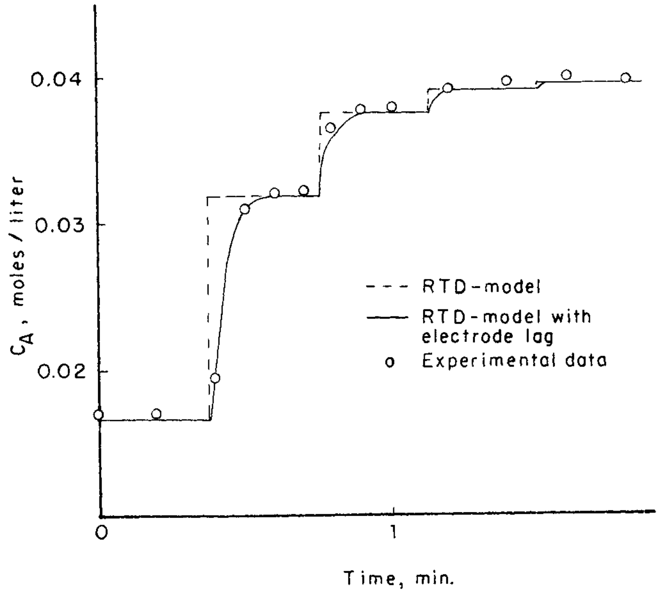

Fig. 3. Transient response of outlet sodium hydroxide concentration to single concentration upset (decrease) in methyl acetate (Run 8).

DISCUSSION OF RESULTS

Table 1 lists the experimental conditions. Figures 3 through 9 show experimental data and theoretical predictions for typical results obtained (3). Included in the theoretical predictions shown on the graphs are results when the electrode lag was neglected and results when the electrode lag was included in the theoretical model. All figures indicate that in general the experimental outlet concentration of sodium hydroxide is always slightly higher than the RTD-model predicted because of the fact that the recycle reactor was not in plug-flow and dispersion occurred in the reactor.

For Figure 3, the methyl acetate concentration is decreased at the inlet. The initial steady state is seen for the first residence time τ_1. When the methyl acetate concentration decreases, the outlet sodium hydroxide concentration increases to a new pseudo steady state for the second residence time because the reaction rate term kC_AC_B decreases. Since the outlet concentration of A and B at the second residence time is fed back instantaneously to the inlet by the recycle line to be mixed with the fresh feed, another methylacetate concentration decrease is produced at the inlet of the reactor. The upset at the inlet will be seen as another sodium hydroxide concentration increase at the outlet during the third residence time. There is a step change of inlet methyl acetate concentration after each residence time due to step changes in the recycle concentration, and the magnitude of these upsets attenuates to zero as the new final steady state conditions are approached. Thus, a series of step increases occur in outlet concentration of sodium hydroxide. When discernible upsets no longer occur at the reactor inlet, the recycle reactor reaches the final steady state.

Figure 4 shows the response for a single flow upset. When an inlet flow upset is made, there is more than one fresh feed condition change. First, there is a residence time change; secondly, there is a concentration change. A single flow upset actually gives a simultaneous upset. Figure 4 shows a flow increase in methyl acetate. As the methyl acetate flow increased, the reactor residence time decreased, the inlet concentration of methyl acetate increased, and the inlet concentration of sodium hydroxide decreased because of dilution from the larger methyl acetate stream. Since the residence time decreased, there was less time for reaction, less sodium hydroxide used, and the concentration of sodium hydroxide at the outlet of the reactor increased. As soon as the new residence time lapsed, the concentration effect from the inlet concentration upsets was seen at the outlet, and a step decrease in outlet sodium hydroxide occurred. Due to recycle, the decrease of outlet sodium hydroxide concentration at the end of the first residence time produced a decrease in sodium hydroxide concentration during the second residence time; the concentration upsets continued for each residence time until the final steady state was reached.

For Figure 5, the methyl acetate concentration is decreased at the inlet. The initial steady state is seen for the first residence time τ_{A1}. As the concentration of methyl acetate was decreased, the reaction rate term decreased, and less sodium hydroxide was used; hence, the concentration of sodium hydroxide at the outlet of the reactor increased to the first pseudo steady state concentration at the second residence time, as can be seen in Figure 5. At the time of the upset, the recycle and fresh feed mixed and

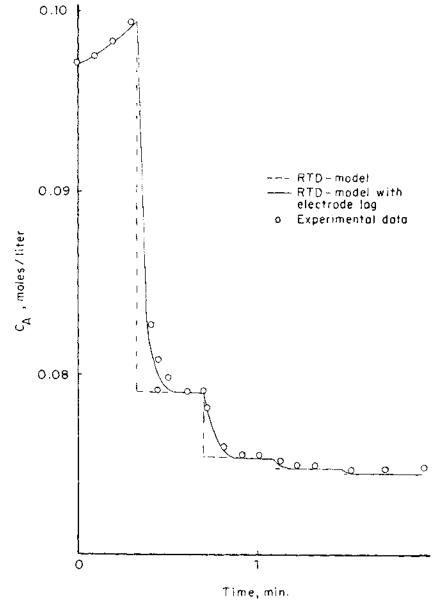

Fig. 4. Transient response of outlet sodium hydroxide concentration to single flow upset (increase) in methyl acetate (Run 16).

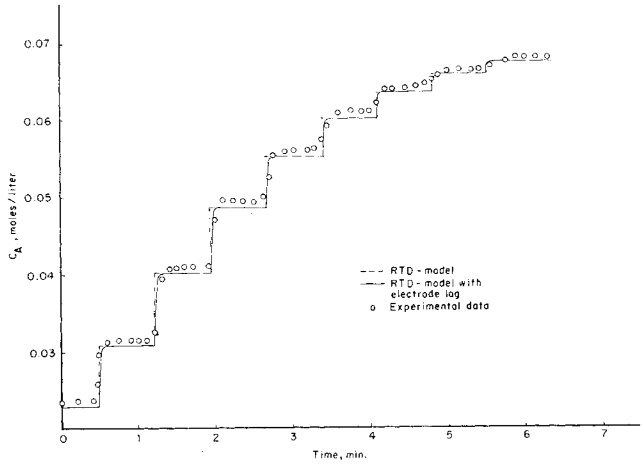

Fig. 5. Transient response of outlet sodium hydroxide concentration to single concentration upset (decrease) in methyl acetate (Run 40).

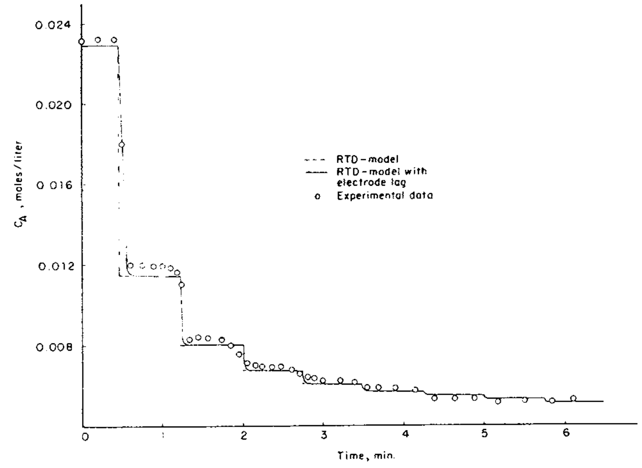

Fig. 6. Transient response of outlet sodium hydroxide concentration to single concentration upset (decrease) in sodium hydroxide (Run 42).

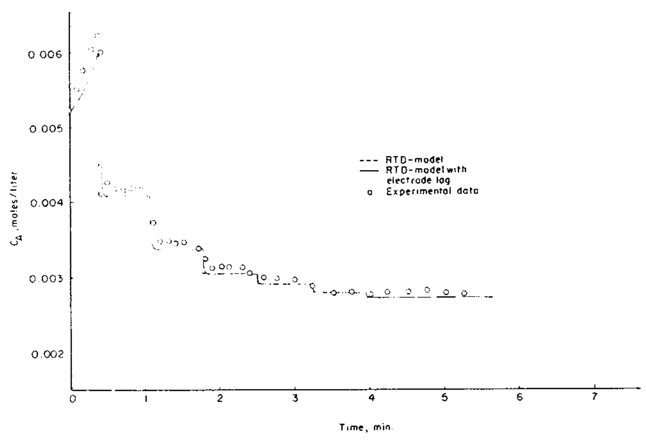

Fig. 7. Transient response of outlet sodium hydroxide concentration to single flow upset (increase) in methyl acetate (Run 43).

produced a decrease of methyl acetate at the entrance of the main reactor. The methyl acetate decrease caused the increase of sodium hydroxide at the outlet after time τ_{A1} for $\tau_{R1} + \tau_{A1}$ min. At τ_{A1} the outlet concentration was returned with a lag of τ_{R1} to be mixed with fresh feed, giving another methyl acetate concentration upset at the entrance of the main reactor. This methyl acetate concentration decrease was less severe than the previous one, and a second pseudo steady state change was observed at time $\tau_{A1} + \tau_{R1} + \tau_{A1}$. The step decreases in methyl acetate concentration continued until the decrease caused by the mixing of the fresh feed and recycle damped out. Then, the outlet sodium hydroxide reaches the new steady state.

For Figure 6 the inlet concentration of sodium hydroxide was decreased. The sodium hydroxide concentration decrease in fresh feed produced a decrease in outlet sodium hydroxide after time τ_{A1}. The concentrations at the outlet continued to decrease every $\tau_{R1} + \tau_{A1}$ min. until the sodium hydroxide decrease at the entrance of the main reactor caused by the mixing of recycle and fresh feed damped out; then the new steady state was reached.

Figure 7 presents the response curve observed for a single flow increase in methyl acetate similar to Figure 4 data but for a lower range. When a flow upset was made, the residence time changed, and the concentration of the inlet fresh feed changed. As the methyl acetate flow was increased, the residence time of the main reactor fluid was decreased, and the concentration of methyl acetate at the fresh feed was increased; the concentration of sodium hydroxide at the fresh feed decreased. Since the residence time was decreased, there was less time for reaction; hence, less sodium hydroxide was used, and the concentration of sodium hydroxide at the outlet of the reactor started increasing. But as soon as a time equivalent to the new residence time τ_{A1} lapsed, the concentration effect caused the sodium hydroxide concentration to decrease due to the methyl acetate increase and the decrease in the incoming sodium hydroxide concentration. From the mixing of the recycle line and new fresh feed conditions, the concentration of methyl acetate and sodium hydroxide at the inlet of the main reactor changed to new inlet concentrations. The concentration upset at the entrance of the main reactor occurred every $\tau_{R1} + \tau_{A1}$ min., and the response of the outlet sodium hydroxide would result in a step decrease every $\tau_{R1} + \tau_{A1}$ min., after τ_{A1}. When the inlet concentration upset damped out, the response at the outlet reached the new steady state.

Simultaneous upsets in concentration and flow rate are shown in Figures 8 and 9. When a flow rate and inlet concentration were changed, the net result on the system was a residence time change and a concentration change of the reactants in the fresh feed.

For Figure 8, the sodium hydroxide concentration was decreased, and the methyl acetate flow rate was also decreased. Since the flow rate was decreased, the residence time τ_{A1} increased. This increase of residence time increased the reaction time, and the concentration of sodium hydroxide at the outlet of the reactor decreased. A decrease

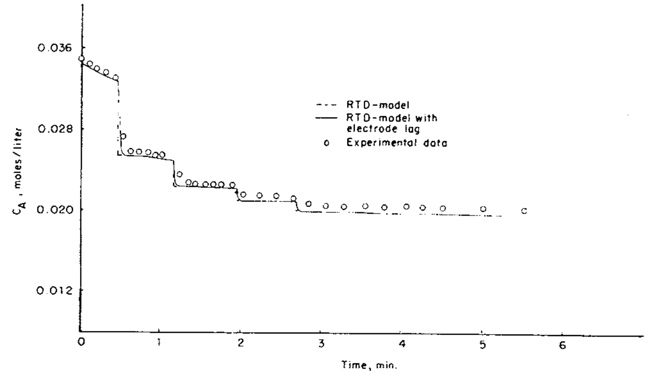

Fig. 8. Transient response of outlet sodium hydroxide concentration to simultaneous upset in sodium hydroxide concentration (decrease) and methyl acetate flow (decrease) (Run 46).

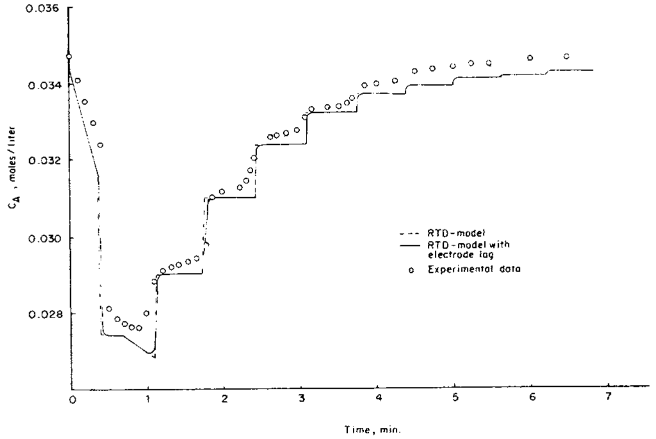

Fig. 9. Transient response of outlet sodium hydroxide concentration to simultaneous upset in methyl acetate concentration (decrease) and sodium hydroxide flow (decrease) (Run 45).

of sodium hydroxide concentration in the incoming stream had a negative effect on sodium hydroxide at the inlet of the main reactor; however, decreasing the flow rate of methyl acetate had a positive effect. The effect due to the sodium hydroxide concentration decrease was greater than the effect due to methyl acetate flow rate decrease, and the concentration of sodium hydroxide at the outlet dropped every $\tau_{R1} + \tau_{A1}$ until the upset at the inlet damped out. Then the new steady state was reached.

Perhaps the most interesting response observed in the entire study (2) is presented in Figure 9. The methyl acetate concentration was decreased, and the flow rate of sodium hydroxide was also decreased. Since the flow rate was decreased, the residence time was increased. This increase of residence time increased the amount of time available for reaction and decreased the concentration of sodium hydroxide at the outlet of the reactor for $t \leqq \tau_{A1}$. The decrease of methyl acetate concentration in the incoming stream had a positive effect on sodium hydroxide concentration at the inlet of the main reactor; however, decreasing the flow rate of sodium hydroxide had a negative effect. The decrease of sodium hydroxide concentration at the inlet of the main reactor from the mixing of the recycle and fresh feed concentrations at the time of the upset was greater than the decrease of methyl acetate at the same time. This effect was seen as a net decrease in sodium hydroxide concentration. Thus, after the first residence time τ_{A1}, the outlet sodium hydroxide decreased in a step. The outlet continued to decrease at $\tau_{A1} + \tau_{R1}$ because of the outlet sodium hydroxide returned by the recycle continued to decrease the inlet sodium hydroxide concentration. For the time zone $\tau_{A1} < t < \tau_{A1} + \tau_{R1} + \tau_{A1}$, the sodium hydroxide concentration at the inlet of the main reactor increased and continued to increase the remainder of the response, because of the relative changes in flow rates, and the methyl acetate concentration at the inlet continued to decrease. These two effects now complement each other and the outlet concentration of sodium hydroxide continued to increase every $\tau_{R1} + \tau_{A1}$ after $\tau_{A1} + \tau_{R1} + \tau_{A1}$ until the new steady state was reached.

Although plug-flow was assumed to develop the models for this study, it is evident that from the experimental data that dispersion existed in varying degrees for most runs. However, the RTD-models still gave good agreement with the dynamic response data for the system.

CONCLUSIONS

The principle results of this study are (1) the attainment of experimental data showing the transient concentration response of a second-order reaction in an isothermal tubular recycle reactor with and without reaction in the recycle line to step upsets in concentration and flow, and (2) the proving of the adequacy of the residence time distribution (RTD) model for predicting the transient concentration response of a tubular recycle reactor with and without reaction in the recycle line.

NOTATION

C_A = concentration of outlet sodium hydroxide of reactor, mole/liter
C_{AI} = concentration of A entering reactor (based on stream A) before upset, mole/liter
C_{A0} = concentration of A entering mixing point of fresh feed before upset, mole/liter
C_{BI} = concentration of B entering reactor (based on stream B) before upset, mole/liter
C_{B0} = concentration of B entering mixing point of fresh feed before upset, mole/liter
F_{A0} = flow rate of A before upset, liter/min.
F_{B0} = flow rate of B before upset, liter/min.
Q_{RE} = flow rate of recycle line before upset, liter/min.
C_{AF} = concentration of A entering reactor (based on stream A) after upset, mole/liter
C_{A1} = concentration of A entering mixing point of fresh feed after upset, mole/liter
C_{BF} = concentration of B entering reactor (based on stream B) after upset, mole/liter
C_{B1} = concentration of B entering mixing point of fresh feed after upset, mole/liter
F_{A1} = flow rate of A after upset, liter/min.
F_{B1} = flow rate of B after upset, liter/min.
Q_{REF} = flow rate of recycle line after upset, liter/min.
V_R = volume of main reactor, liter
V_r = volume of recycle line, liter
C_{Ai_n} = concentration of A at the inlet of the main reactor at $(n-1)(\tau_{A1} + \tau_{R1}) \leqq t < n(\tau_{A1} + \tau_{R1})$, mole/liter
C_{A0_n} = concentration of A at the outlet of the main reactor at $(n-1)(\tau_{A1} + \tau_{R1}) \leqq t < n(\tau_{A1} + \tau_{R1})$, mole/liter
C_{AR_n} = concentration of A at the outlet of the recycle line at $(n-1)(\tau_{A1} + \tau_{R1}) \leqq t < n(\tau_{A1} + \tau_{R1})$, mole/liter
C_{Bi_n} = concentration of B at the inlet of the main reactor at $(n-1)(\tau_{A1} + \tau_{R1}) \leqq t < n(\tau_{A1} + \tau_{R1})$, mole/liter
C_{B0_n} = concentration of B at outlet of the main reactor at $(n-1)(\tau_{A1} + \tau_{R1}) \leqq t < n(\tau_{A1} + \tau_{R1})$, mole/liter
C_{BR_n} = concentration of B at the outlet of the recycle line at $(n-1)(\tau_{A1} + \tau_{R1}) \leqq t < n(\tau_{A1} + \tau_{R1})$, mole/liter
Q = main reactor throughput before upset, liter/min.
Q_f = main reactor throughput after upset, liter/min.
R = recycle ratio, recycle flow/reactor throughput
$A0$ = residence time of main reactor before upset, min.
$A1$ = residence time of main reactor after upset, min.
$R0$ = residence time of recycle line before upset, min.
$R1$ = residence time of recycle line after upset, min.
e = time constant for electrode, min.
M_n = concentration difference between B and A at inlet of main reactor at any time, mole/liter
N_n = concentration ratio B/A at inlet of main reactor at any time
M_n' = concentration difference between B and A at inlet of recycle line at any time, mole/liter
N_n' = concentration ratio B/A at inlet of recycle line at any time
t = time, min.
k = reaction rate constant, liter/mole-min.
N = number of fluid elements of response data for a residence time
m = block level or fluid element from 0 to N
n = positive integer, 0, 1, 2, 3, . . .

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