Transient Response of a Tubular Reactor to Upsets in Flow Rate

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This study concerns the transient response of a tubular reactor in which a second-order reaction takes place under isothermal conditions. The reaction studied was the saponification of methyl acetate with sodium hydroxide. Experimental data were obtained in a tubular reactor for flow upsets.

Theoretical models using residence time distribution (RTD) techniques have been developed. The study was conducted at 36°C. The reactor was a 13-ft. long, ¼-in. diam. copper tube in the form of a spiral with a volume of 110 cc.

The agreement obtained between the experimental data and the RTD model predictions was good, verifying that this model is satisfactory for simulation of tubular reactor dynamics. Backmixing was observed in the reactor. This nonideality was accounted for empirically in the RTD model, since backmixing was observed to be mainly a function of flow rate.

Chemical reactors have received much attention in the past few years, and many workers have contributed to the literature existing on chemical reactors. However, much of the work that has been done is theoretical. Considerable work has been done on the stability of reactors, but very little experimentally verified research has been done on the dynamics of chemical reactors. The continuous flow stirred-tank reactor (CFSTR) has obtained most of the attention, and little work has been done with tubular reactors.

The main purpose of this project was to conduct transient response studies on an unpacked tubular reactor and to develop a theoretical model to predict the response. The system that was studied was a tubular reactor operated under isothermal conditions for a second-order reaction. This system can be represented by a set of nonlinear differential equations which can be solved simultaneously.

One of the reasons why distributed parameter problems of this nature have been studied very little in the past may be the complexity of the theoretical modeling. Most of the regular techniques used for developing transfer functions cannot be used because of the nonlinear nature of the describing equations. This frequently leads to the development of the lumped-parameter model, which is one of the techniques that can be used for simplifying 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 reactors. This model gives good agreement with experimental data and the method can be extended to non-isothermal systems and for tubular reactors with recycle.

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

$$CH_3COOCH_3 + NaOH \rightarrow CH_3OH + CH_3COONa.$$

This reaction was used mainly because it is an irreversible second-order reaction with a relatively high reaction rate constant between 35° and 40°C. The kinetics of this reaction were obtained from a previous study (*1*).

EXPERIMENTAL SECTION

The tubular reactor system used in this study is shown schematically in Figure 1. All flow lines used were ¼-in. polyflow tubing. The reactants as shown in Figure 1 were stored in tanks *10*, *11*, *12*, and *13*. The reactants were pumped to the reactor with the help of air 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 backpressure over 5 lb./sq. in. could be released.

The air from the regulators proceeded to the feed tanks. The feed tanks, 20-liter Pyrex-glass containers, 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 around 37°C. The preheaters were made of ¼-in. diam. copper tube.

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 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 immersion in the same thermostatic bath. Thus, essentially isothermal operation was assured. The reactor was a 13-ft. long ¼-in. diam. copper tube in the form of a spiral.

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

The average time constant of the measurement lag of the pH electrode was found to be 1.67 sec., which is very small compared with the reactor reponse time and the dispersion

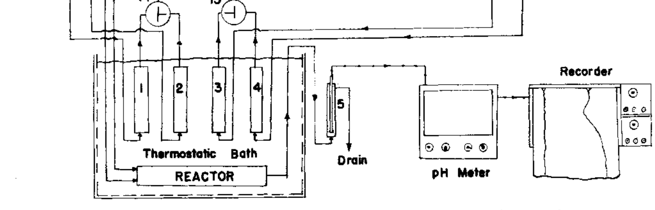

Fig. 1. Flow diagram of tubular reactor system. *1, 2, 3, 4* = preheaters. *5* = Flow cell with combination electrode. *6, 7* = Needle valves. *8, 9* = Rotameters. *10, 11, 12, 13* = Feed tanks. *14, 15* = Three-way valves. *16, 17* = Manometers. *18, 19* = Pressure regulators. *20* = Safety relief valve.

lag. 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 the flow rate. Results were reproducible within 4%. One of the important factors which determines the lag of the electrode is the way it is prepared before measurement. Before starting a run the pH electrode used was soaked in a 2 N solution of sodium hydroxide for at least 6 hr.

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 concentration of either sodium hydroxide or methyl acetate, or both. Flow upsets, either single or multiple, were made with pressure regulators *18* and *19*. Fine control was obtained with needle valves *14* and *15*.

The reactants used in this study were sodium hydroxide and methyl acetate. The concentrations used were approximately 0.25 and 0.125 N. The solutions of desired normality were prepared in an Alsop mixer by using reagent grade chemicals. The exact 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 concentration was being fed to the reactor. The concentration at the outlet of the reactor was monitored with a pH meter which was standardized with a buffer.

When the concentration reached steady state, a sample was drawn at 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 backtitration.

The upsets were then made by manipulating the respective valves. The temperature at the outlet of the reactor was also monitored to make sure isothermal conditions prevailed 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 pH readings versus concentration obtained on a semilog plot. Data for both single and simultaneous upsets in concentration and flow rate were obtained (*2*), although the discussion in this paper is restricted to flow rate upsets.

THEORY

A plug-flow reactor can be visualized as a flow of small batch reactors passing through the reactor in succession, as discussed by Levenspiel (*3*). If one takes a close look at the design equations for a plug-flow tubular reactor (PFTR) and a batch reactor, he can easily see that length in a PFTR corresponds to time in a batch reactor. The longer the PFTR the more the conversion, and the longer the time in a batch reactor the more the conversion.

The appropriate reactor equations for constant volume conditions are

$$\text{Batch reactor:} \quad t = C_{A0} \frac{dX_A}{-r_A} \tag{1}$$

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

This analogy that exists between the batch and the tubular reactor can be used conveniently for predicting the response of a PFTR. The steady state concentration of component A at the outlet of a tubular reactor of residence time T_0, is the same as the concentration of A in a batch reactor at $t = T_0$, with the following conditions: the conditions in the batch reactor at $t = 0$ must be the same as those in the PFTR at $X = 0$.

Basically, the concentration in a batch reactor depends upon the initial conditions and the amount of time the components have had to react. Of course, other variables which affect the concentration history could be listed, such as the reaction rate constant, temperature, rate of cooling. In the case of a PFTR, the amount of time which each fluid element has to react is the residence time.

It is apparent that the concentration history of a PFTR can be obtained easily by knowing the initial concentration of the fluid elements which enter the reactor and the residence time each of these elements have, before leaving the reactor. This is the fundamental basis for the RTD model presented in this paper.

The tubular reactor can be imagined as *N*-CFSTR in series. For example purposes the reactor has been represented with nine separate sections, but it is important to note that the accuracy of this method is not dependent upon the number of blocks chosen. This is an advantage of this model over finite-difference models. Block 1 is the feeding point, or the imaginary block where the feeds just mix and enter the reactor. Blocks 2 to 8 constitute the reactor, and Block 9 is the measuring chamber where the outlet of the reactor is monitored.

The residence time of each block of fluid as it moves through the reactor will depend upon the rate of feed. It should be noted that it has been assumed that the reactor always flows full, and the residence time of any fluid block depends upon the velocity with which the fluid block behind it is moving.

Referring to Equations 1) and (2), the general constant volume batch and steady state tubular reactor equations, the solution for the second-order reaction, $A + B \xrightarrow{k} C + D$, for single flow upsets is as follows.

Single Flow Upset of an Inlet Reactant Stream

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

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

Even though only one flow rate was changed, a close look at the actual concentrations and residence times will show more than one change, namely, $C_{A0} \neq C_{A1}$, $C_{B0} \neq C_{B1}$, $T_0 \neq T_1$. This is, in effect, a triple upset as far as the reactor is concerned. Since the fluid residence time before upset is not the same as the residence time after upset, different fluid elements have different velocities and therefore the concentration response is not in the form of a step. The response in part can be obtained from the following equations:

$$t = 0,\ C_A = C_{AS0};\quad t \geqq T_1,\ C_A = C_{AS1}$$

However, the region of interest is $0 < t < T_1$.

At time $t = 0$, the amount of time each fluid element has spent inside the reactor can be given by the following equations:

Block 2, $T = (1/7)\ T_0$
Block 3, $T = (2/7)\ T_0$
Block 4, $T = (3/7)\ T_0$
Block 5, $T = (4/7)\ T_0$
Block 6, $T = (5/7)\ T_0$
Block 7, $T = (6/7)\ T_0$

where T = the amount of time spent in the reactor.

When the upset is made at $t = 0$, the effect due to the change is felt in three directions: concentration changes in A and B at the inlet of the reactor and change in residence time. The effect due to change in residence time is felt as soon as the upset is made. However, the effect due to the concentration change is not felt until a period of time equivalent to the new residence time (T_1) lapses.

Initially the change in residence time is felt. This effect occurs as a change in the amount of time each fluid element spends inside the reactor. During this process the residence time gradually changes from T_0 to T_1, and this change is accomplished in T_1 min.

This concept becomes clear if one takes a closer look at a typical fluid element. Block 7 as discussed before has spent (6/7) T_0 min. inside the reactor at $t = 0$; and if no change in flow rate was made, this fluid element would have stayed in the reactor for T_0 min. before hitting the measuring probe. But, since the flow rate has changed, the new residence time for this fluid element with be $\left(\frac{6\,T_0}{7} + \frac{T_1}{7}\right)$ min. and the concentration of this element as it leaves the reactor will be given by

$$C_A = \frac{M_0}{N_0 \exp\left\{M_0 k\left(\frac{6T_0}{7} + \frac{T_1}{7}\right)\right\} - 1.0} \qquad \text{if } C_{A0} \neq C_{B0} \qquad (3)$$

or

$$C_A = \frac{1}{\frac{1}{C_{A0}} + k\left(\frac{6T_0}{7} + \frac{T_1}{7}\right)} \quad \text{if } C_{A0} = C_{B0} \qquad (4)$$

This fluid element will be seen by the measuring probe at $t = T_1/7$. This argument can be extended to all the fluid elements. Hence for the time zone $0 < t < T_1$ the concentration of sodium hydroxide at the outlet of the reactor is given by Equations (5) and (6).

$$t = \frac{n}{N} T_1$$

If $C_{A0} \neq C_{B0}$

$$C_A = \frac{M_0}{N_0 \exp\left\{M_0 k\left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1\right)\right\} - 1} \qquad (5)$$

If $C_{A0} = C_{B0}$

$$C_A = \frac{1}{\frac{1}{C_{A0}} + k\left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1\right)} \qquad (6)$$

where N is the number of times reactor is divided (also can be looked upon as the number of points desired for the response curve), and n is the block level, going from 1 to N in increments of one. Thus the overall response for a single flow upset can be given by Equations (7) and (8).

$$t = 0;\ C_A = C_{AS0}$$

$$t \geq T_1;\ C_A = C_{AS1}$$

$0 < t < T_1$;

$$C_A = \frac{M_0}{N_0 \exp\left\{M_0 k\left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1\right)\right\} - 1} \qquad \text{if } C_{A0} \neq C_{B0} \qquad (7)$$

or

$$C_A = \frac{1}{\frac{1}{C_{A0}} + k\left(\frac{N-n}{N} T_0 + \frac{n}{N} T_1\right)} \quad \text{if } C_{A0} = C_{B0} \qquad (8)$$

Concentration upsets, simultaneous upsets in concentration or flow rate, and combinations of those upsets are handled in the similar manner (2).

Even though plug flow was assumed, dispersion was observed in certain cases. Dispersion was seen at low flow rates and whenever there was a sharp change in concentration inside the reactor. However, if the change in concentration was gradual, no matter what the flow rate, the dispersion observed was negligible; for example, response for simultaneous flow upsets with $F_{A0}/F_{A1} = F_{B0}/F_{B1}$.

The dispersion observed was found empirically to be a function of the flow rate of the reactants. Accordingly, the RTD model that includes dispersion is given by the following empirical equations:

$t \leq 0.826\, T_1$, C_A = Same as calculated by the RTD model without dispersion

$t = 0.826\, T_1$, dispersion effect starts

$t > 0.826\, T_1$

$$t = 0.826\, T_1 + \Delta T$$

$$C_A = C_{A2} + (C_{AS1} - C_{A2})\left[1 - \exp\left(-\frac{\Delta t}{t_D}\right)\right]$$

where t_D = time constant of dispersion

$= 1.83 \exp\left[-17.78\,(F_{A1} + F_{B1})\right]$

$$C_{A2} = \frac{1}{\frac{1}{C_{A0}} + k(0.826\, T_1)} \quad \text{if } C_{A0} = C_{B0}$$

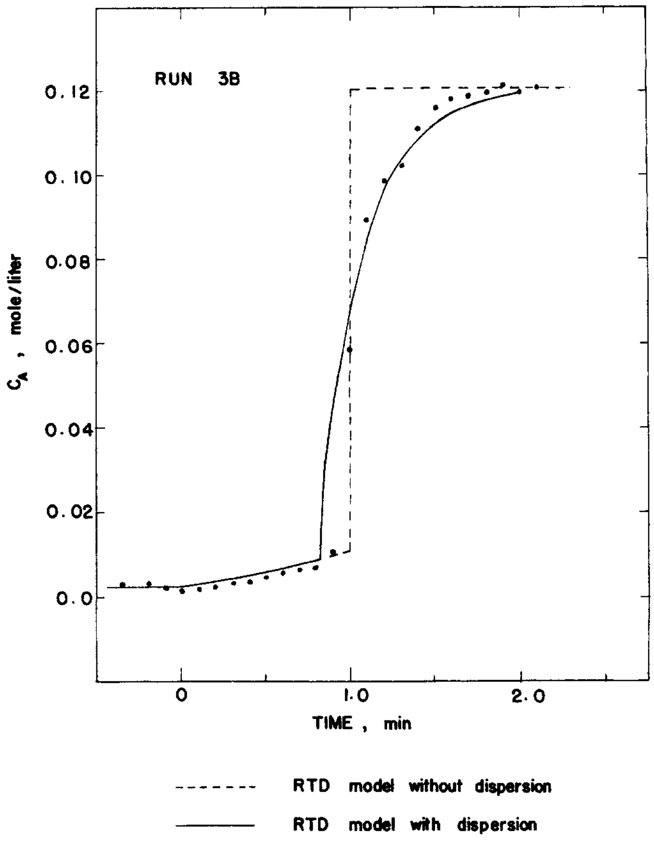

Fig. 2. Transient response of outlet sodium hydroxide concentration to flow upset (increase) in sodium hydroxide (run 3B).

$$C_{A2} = \frac{M_0}{N_0 \exp\{M_0 k(0.826\, T_1)\} - 1.0} \text{ if } C_{A0} \neq C_{B0}$$

Δt : time increment

Because this method is empirical, it has to be used with caution. This method accounts for dispersion as a function of flow rate alone and does not account independently for molecular diffusion.

RESULTS AND DISCUSSION

Table 1 lists the experimental conditions. Figures 2, 3, and 4 show the experimental data and the theoretical predictions.

Dispersion was observed in this study as shown in Figures 2, 3, and 4, and discussed in the previous section. It is felt that the dispersion lag is predictable from the laminar flow velocity profiles and that the dispersion will not be observed in the turbulent flow region. Step changes in concentration at the inlet probably do not get carried through the reactor tube in a wave, but get spread out due to fluid flowing faster near the center of the tube than at the wall. The observed effect is a form of backmixing and is directly proportional to fluid flow rate. As can be seen from the experimental curves, the effect of backmixing was more pronounced than forward mixing, which it should be, based on the proposed laminar flow relationship.

Figures 2, 3, and 4 show response curves observed for single flow upsets in a reactant stream (see Table 1). When a flow upset is made, there is more than one inlet condition change. First, there is a residence time change, and second there is a concentration change. Therefore a single flow upset actually gives simultaneous upsets in inlet concentration and residence time. This yields the response curves observed in Figures 2, 3, and 4 for flow upsets in both methyl acetate and sodium hydroxide.

Figure 2 shows the response for an increase in the flow rate of sodium hydroxide (run 3B). When sodium hydroxide flow is increased, the overall residence time decreases, and the concentration of the sodium hydroxide at the inlet of water reactor increases ($C_{A1} > C_{A0}$). Both these effects increase the effluent concentration of sodium hydroxide, as can be seen in Figure 2. This is one of the reasons why the conventional methods, like lumped-parameter models, do not predict the concentration response well. The actual solution must come out in two time zones (where $t <$ residence time and $t \geqq$ residence time) and the boundary conditions are different in each time zone. The fit between data and theory is good.

Runs 1*A* and 1*B*, presented in Figures 3 and 4, were single flow upsets in methyl acetate. As the methyl acetate flow is decreased, the overall residence time is increased and the concentration of methyl acetate at the inlet of the reactor is decreased ($C_{B1} < C_{B0}$). Since the overall resi-

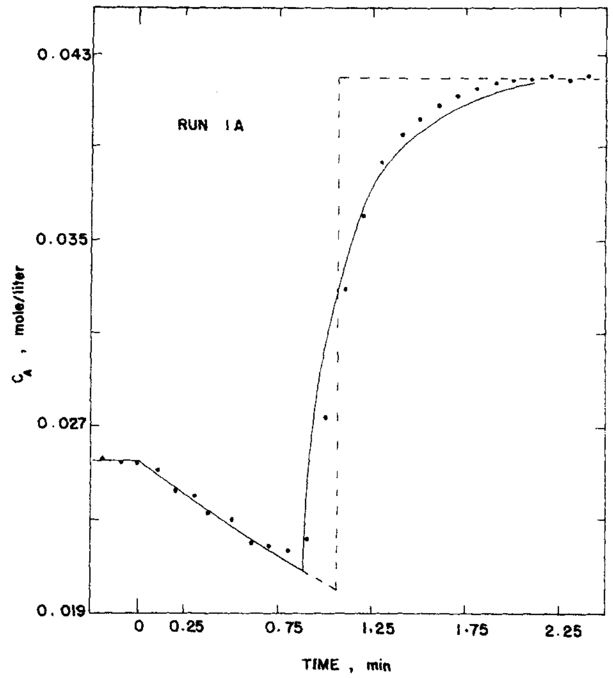

Fig. 3. Transient response of outlet sodium hydroxide concentration to flow upset (decrease) in methyl acetate (run 1A).

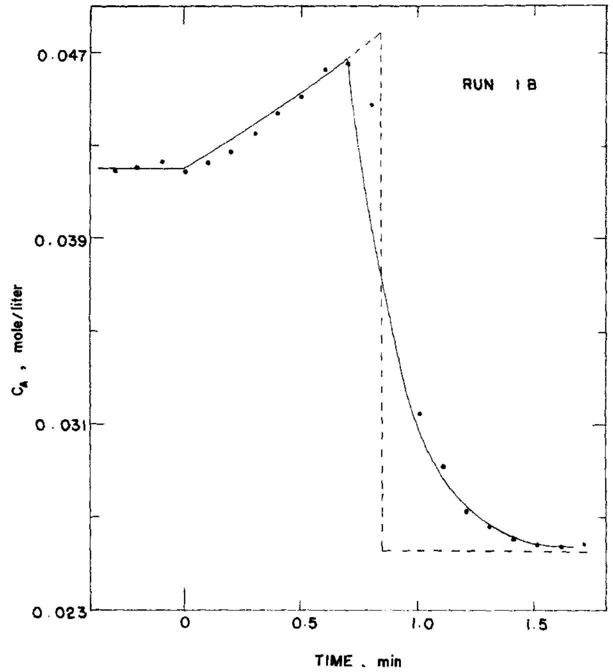

Fig. 4. Transient response of outlet sodium hydroxide concentration to flow upset (increase) in methyl acetate (run 1B).

TABLE 1. EXPERIMENTAL INLET REACTOR OPERATING CONDITIONS

Run	C_{A1}	C_{B1}	F_{A0}	F_{B0}	C_{AF}	C_{BF}	F_{A1}	F_{B1}	Figure No.
				Single Flow Upset (methyl acetate)					
1 A	0.2486	0.2221	0.052	0.079	0.2486	0.2221	0.052	0.052	3
1 B	0.2486	0.2221	0.052	0.052	0.2486	0.2221	0.052	0.079	4
				Single Flow Upset (sodium hydroxide)					
3 B	0.2486	0.2221	0.016	0.031	0.2486	0.2221	0.079	0.031	2

Run numbers refer to the original data, reference 1.

dence time is increased, there is more time for reaction; hence more sodium hydroxide is used, and the concentration of sodium hydroxide at the outlet of the reactor starts dropping, as can be seen in Figure 3. But as soon as a time equivalent to the new residence time lapses, the concentration effect comes into play and the sodium hydroxide concentration increases. The response curve takes a reverse direction when methyl acetate flow is increased, as can be seen in Figure 4. The tests were conducted at different flow rates; it was found that for even small changes in flow rate the response followed the pattern described below.

In conclusion, there are many factors which affect reactor outlet concentration response, but the important factors that determine the shape of unsteady state response curves are changes in residence time and changes in concentration of the reactants at the inlet of the reactor. The RTD model presented in this paper satisfactorily simulates the dynamics of a tubular reactor for these types of upsets.

NOTATION

C_A = concentration of sodium hydroxide at the outlet of the reactor, mole/liter
C_{A1} = concentration of sodium hydroxide entering reactor before upset, *mole/liter (based on stream A)*
C_{A1} = actual concentration of sodium hydroxide at the inlet of the reactor, after upset (based on mixed *streams of A* and *B*) $= \frac{F_{A1}}{F_{A1}+F_{B1}} C_{AF}$ mole/liter
C_{AF} = concentration of sodium hydroxide entering reactor after upset, mole/liter (based on stream *A*)
C_{AS0} = steady state concentration of sodium hydroxide at the outlet of the reactor before upset, mole/liter
C_{AS1} = steady state concentration of sodium hydroxide at the outlet of the reactor after upset, mole/liter
C_{A0} = actual concentration of sodium hydroxide at the inlet of the reactor before upset (based on mixed streams of *A* and *B*) $= \frac{F_{A0}}{F_{A0}+F_{B0}} C_{AI}$ mole/liter
C_{B1} = concentration of methyl acetate entering reactor before upset, mole/liter (based on stream *B*)
C_{B1} = actual concentration of methyl acetate at the inlet of the reactor, after upset, (based on mixed streams of *A* and *B*) $= \frac{F_{B1}}{F_{A1}+F_{B1}} C_{BF}$ mole/liter
C_{B0} = actual concentration of methyl acetate at the inlet of the reactor, before upset (based on mixed streams of *A* and *B*) $= \frac{F_{B0}}{F_{A0}+F_{B0}} C_{BI}$ mole/liter
C_{BF} = concentration of methyl acetate entering reactor after upset, mole/liter (based on stream *B*)
F_{A1} = flow rate of sodium hydroxide after upset, liter/min.
F_{B1} = flow rate of methyl acetate after upset, liter/min.
F_{A0} = flow rate of sodium hydroxide before upset, liter/min.
F_{B0} = flow rate of methyl acetate before upset, liter/min.
M_0 = $C_{B0} - C_{A0}$
N_0 = C_{B0}/C_{A0}
$-r_A$ = reaction rate, moles/(liter)(min.)
t = time
T_1 = residence time after upset, $V/(F_{A1} + F_{B1})$ min.
T_0 = residence time before upset, $V/(F_{A0} + F_{B0})$ min.
V = volume of reactor, liter
X_A = conversion of *A*
τ = space time

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Stretching of Viscoelastic Liquids

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Analyses of stretching of a viscoelastic liquid have been interpreted as showing that there is a maximum stretch rate to which the material can be subjected, and several physical phenomena have been explained on this basis. It is shown here theoretically and experimentally that the concept of a limiting stretch rate does not have general validity.

Analyses of the stretching of a viscoelastic liquid have been interpreted to show that extremely large tensile stresses will be experienced in elongational processes which are rapid relative to a characteristic liquid relaxation time (*6, 7*). We show here that the notion of a limiting stretch rate does not have general validity.

THEORY

We assume that the liquid behavior can be represented by a convected Maxwell model

$$\tau^{ij} + \lambda \frac{\mathfrak{d}\tau^{ij}}{\mathfrak{d}t} = 2\,\mu d^{ij} \tag{1}$$

$$T^{ij} = -\,pg^{ij} + \tau^{ij} \tag{2}$$

Here $\mathfrak{d}/\mathfrak{d}t$ is Oldroyd's derivative

$$\frac{\mathfrak{d}\tau^{ij}}{\mathfrak{d}t} = \frac{\partial \tau^{ij}}{\partial t} + v^k \tau^{ij}{}_{,k} - \tau^{kj} v^i{}_{,k} - \tau^{ik} v^j{}_{,k} \tag{3}$$

We visualize the stretching of a column of liquid whose axis is oriented in the x^1 direction, for which the kinematics are represented in Cartesian coordinates by

$$v^1 = \Gamma(t)x^1, \quad v^2 = -\frac{1}{2}\Gamma(t)x^2 \quad v^3 = -\frac{1}{2}\Gamma(t)x^3 \tag{4}$$

$\Gamma(t)$, the stretch rate, is an arbitrary function of time. Equation (1) then reduces to the uncoupled system

$$\tau^{11} + \lambda\left[\frac{\partial \tau^{11}}{\partial t} - 2\Gamma(t)\tau^{11}\right] = 2\,\mu\Gamma(t) \tag{5}$$

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