ρ_L = liquid density, g./cc.
ρ_M = liquid molal density, g.-moles/cc.
ρ_V = vapor density, g./cc.
σ = surface tension, dynes/cm.

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An Experimental Study of Steady State Multiplicity in a Loop Reactor

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Steady state multiplicity in an adiabatic loop reactor was studied in experiments employing the reaction between sodium thiosulfate and hydrogen peroxide in aqueous solution. The steady state characteristics of the loop reactor were predicted by a method which utilized batch reactor data of temperature vs. time directly. The method was based on the assumption of plug flow with negligible axial dispersion and on a single-step chemical kinetic model. Experimental results verify the existence of multiple steady states on ranges of feed flow rates and recycle ratios and demonstrate the capability of the simple model for predicting the qualitative and quantitative features of the reactor steady state.

Some observations were made of the effect of large disturbances on the stability of the reactor while operating in a multiple state region. Results for such cases illustrate reactor instability in the sense that a transition to a new steady state takes place provided the disturbance is sufficiently large.

The distinctive features of steady state multiplicity and instability in continuous flow exothermic processes were first introduced to the field of chemical reactor design in a publication by Van Heerden in 1953 (*1*). Bilous and Amundson (*2*), and Aris and Amundson (*3*) examined these features for a perfectly mixed reactor on a firm mathematical basis, and subsequent theoretical studies have been numerous. At the present time a wealth of theory is available regarding steady state characteristics, stability, and control of various lumped and distributed parameter models of exothermic reaction systems. However, with the exception of a recent study by Padberg and Wicke (*4*) of a catalytic reaction in a fixed-bed reactor, experimental data or reports in the literature of actual experiences relative to steady state multiplicity and stability in chemical reactors are lacking.

This paper presents the results of an experimental study which involved a laboratory tubular reactor with recycle, referred to hereafter as a *loop* reactor, and employed the reaction between sodium thiosulfate and hydrogen peroxide in aqueous solution. The study was undertaken to obtain experimental observations and data regarding steady state multiplicity and stability and to test the capability of a simple model for describing these characteristics. Presented herein are the results of the first phase of the work which focuses on stable steady states in the multiple state regime of an adiabatic system.

The loop reactor was chosen for experimentation for two principal reasons: 1. theoretical background is available for guidance (*5* to *8*), and 2. this type of reactor provides the advantage, as will be shown later, that steady state characteristics for an adiabatic plug flow model may be predicted directly from batch reactor data of temperature vs. time without requiring a kinetic expression. Furthermore, recycle processes are of importance industrially.

Since reaction kinetic expressions are seldom sufficiently accurate to permit a complete exploration of parameters and conditions, it is a significant advantage in studies of the loop reactor that performance characteristics may be predicted directly from batch reactor data of temperature vs. time. Such data are relatively easy to obtain in a liquid system. It is possibly the lack of sufficient kinetic data or the difficulty in obtaining sufficient data that has heretofore discouraged researchers from undertaking experimental studies of nonisothermal reactors and has channeled most efforts toward theoretical work and computer simulations employing hypothetical reactions.

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BATCH EXPERIMENTS

Equipment and procedures for the batch reactor experiments are described in this section, and resulting temperature-time data are presented for later use. The theoretical basis as well as the assumptions and computational procedures involved in using these data directly to predict steady state characteristics of the loop reactor will be discussed in the next section with reference to results given here.

Since the variable of interest was the transient temperature of the reaction mixture, particular care was taken in the design of the batch reactor to avoid large heat capacities of the equipment. The reaction vessel itself was a thin 2 qt. plastic bag, available commercially as a freezer-refrigerator bag. The bag was suspended by its top and enclosed in a plexiglass cylinder to provide a relatively dead air space for insulation. The reactor contents were stirred by means of an electrically driven polyethylene impeller, and an assembly of three thin aluminum baffles were immersed in the liquid to improve mixing. The combined capacity of the plastic bag, impeller, and baffles amounted to about 0.5% of the heat capacity of the reaction mixture and was considered negligible.

The top of the apparatus was covered with a plexiglass lid to prevent excessive vaporization during a run. Millivolt signals from a copper-constantan thermocouple enclosed in a stainless steel protection tube and immersed in the reaction system were recorded for temperature-time measurements.

The starting procedure for a batch run involved manually pouring the hydrogen peroxide solution into the plastic bag already containing the thiosulfate solution. Both solutions were initially at the desired starting temperature. The total initial volume of the reaction mixture was 2,000 ml. The initial time was taken to be that instant at which the first noticeable change in temperature was recorded. This initial point was of concern only in testing the reproducibility of the temperature curve. It will become clear in a later section that only temperature differences and time differences are involved in predicting the performance of the continuous reactor and that no reference need be made to the exact starting time of the batch run.

The data to be used throughout this paper were obtained for initial mixture concentrations of 0.8 molar sodium thiosulfate and 1.2 molar hydrogen peroxide in aqueous solution and an initial temperature of 0°C. The solutions were prepared in deionized water, and concentrations were determined by volumetric analysis with potassium iodate as a primary standard for the $Na_2S_2O_3$ solution and with potassium permanganate as the titrant for the peroxide solution. Solution concentrations were always within ±0.015 moles/liter of the specified values. Further details concerning preparation and run procedures are available elsewhere (9).

The resulting temperature-time curve for these conditions is shown in Figure 1. The curve shown in that figure actually represents an average of three separate runs, no one of which produced data which deviated from that of either of the others by more than 1°C. at any instant of time. This extent of reproduciblity indicates that initial effects of pouring and mixing were negligible.

As the temperature curve of Figure 1 shows, the reaction proceeded to completion in about 55 sec. showing a maximum rate of increase of 10°C./sec. For comparison, the thermocouple-recorder assembly was capable of responding at a rate of about 100°C./sec. so that the data were unaffected by measurement lags.

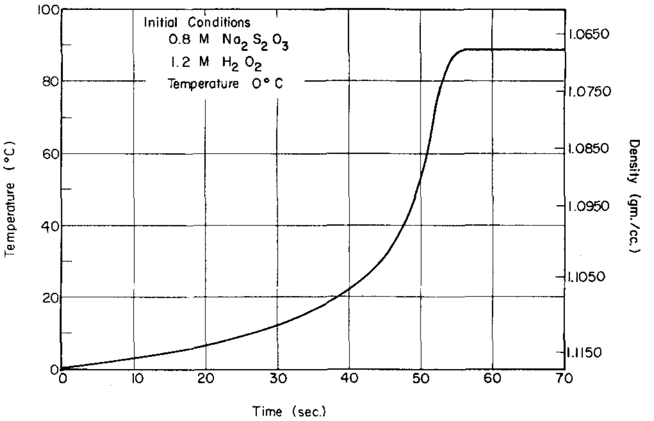


Fig. 1. Batch reactor data.

As evidence that heat losses during the period of reaction were negligible, the temperature was found to drop from its maximum value of 88.5°C. at a rate of only 1°C./min. in the final reaction mixture.

Shown in Figure 1 along the right-hand ordinate is a scale of density of the reaction mixture. This information was obtained from a separate series of batch runs in which a total of 1,035 ml. of the same mixture as above was placed in a 1 liter flask fitted at its neck with a 100 ml. graduated column. Along with the temperature recordings, visual readings of volume change with time were taken and subsequently converted to density of the mixture vs. temperature. There was less concern in these runs for apparatus heat capacity than in those described above since the objectives of this study do not require precise density data. Nevertheless, from Figure 1, a good estimate of the change in density during the course of the reaction is available. The information was used to account for a variable velocity in tube flow and to correct rotameter readings for density variations in the continuous reactor experiments. Furthermore, the experiments showed that the total volume change upon mixing of the fresh reactant solutions at 0°C. was negligible.

PREDICTION OF LOOP REACTOR PERFORMANCE FROM BATCH DATA

Theoretical Basis and Assumptions

The state of the reacting mixture during the course of an adiabatic batch experiment as described in the previous section is one of constant enthalpy, H_F, with component mass fractions given by solutions of differential equations of the following form:

$$\frac{d\mathbf{x}}{dt} = -\frac{1}{\rho}\mathbf{A}\,\mathbf{R}\,(\mathbf{x}, H_F) \qquad (1)$$

with an inital condition:

$$t = 0: \quad \mathbf{x} = \mathbf{x}_F \qquad (2)$$

As reaction proceeds in a batch experiment, the state of the mixture might be thought of as a point traveling along some trajectory which joins initial and final states in phase space, the space of mass fractions and enthalpy. Along that trajectory, hereafter called the *state-curve*, the enthalpy is constant at H_F and mass fractions follow the solutions of Equations (1) and (2).

It is well-known that the above equations also describe the course of reaction in an adiabatic plug flow tubular reactor with negligible axial dispersion if t is defined as the age of a fluid plug measured from the time of its entrance into the tube and if the inlet state is given by H_F and $\mathbf{x}_F$.

Consider the particular case of a plug flow adiabatic loop reactor, shown schematically in Figure 2, and suppose that the fresh feed state is given by H_F and $\mathbf{x}_F$. If the reactor itself and the recycle line are adiabatic, the

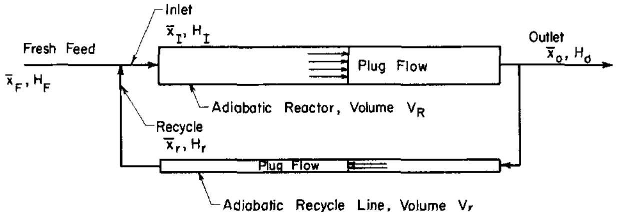


Fig. 2. Schematic diagram of loop reactor.

enthalpy remains constant throughout the system at H_F just as in the case of the batch reactor. (Kinetic and potential energies as well as work effects are unimportant in energy considerations here.) For convenience then in the following arguments, the dimensionality of the state vector may be reduced by one. Thus the state is defined by $\mathbf{x}$, and it is clear that $\mathbf{x}$ lies on the plane $H = H_F$ of the phase space.

If the inlet state, $\mathbf{x}_I$, that state formed by mixing the fresh feed with a partially reacted recycle stream, is a point on the state curve for the batch reactor, then since the batch reactor and the plug flow loop reactor obey the same differential equations, it follows that the state at any point along the reactor length, including the outlet state $\mathbf{x}_o$ and the recycle state $\mathbf{x}_r$, must also be on that state curve. Let us suppose that $\mathbf{x}_r$ is indeed a point on the state curve of the batch reactor and ask what restrictions, if any, must be imposed in order that $\mathbf{x}_I$ also be a point on that curve. It will follow that if the points $\mathbf{x}_I$ and $\mathbf{x}_r$ are always on the state curve which begins at $\mathbf{x}_F$, the data in Figure 1 are sufficient for prediction of the steady state characteristics of the loop reactor.

Material balances around the junction point of fresh feed and recycle streams give the following relationship:

$$\mathbf{x}_I - \mathbf{x}_F = r(\mathbf{x}_r - \mathbf{x}_F) \tag{3}$$

Equation (3) shows immediately that the points $\mathbf{x}_F$, $\mathbf{x}_I$, $\mathbf{x}_r$ will all lie on the same trajectory in phase space for an arbitrary value of the recycle ratio r if and only if that trajectory is a straight line. According to Equation (1) the state curve for a batch experiment is indeed a straight line if $R_i = R$ for all i; that is, if a single independent reaction occurs or if the course of a complex reaction system can be correlated in terms of a single overall rate expression on the basis of a single-step kinetic model. Clearly in this case, Equation (1) may be written as follows:

$$\frac{d\mathbf{x}}{dt} = -\frac{\mathbf{A}}{\rho} R(\mathbf{x}, H_F) \tag{1a}$$

Furthermore, the straight line then resulting from the batch experiment must be the same as that described by Equation (3) since both begin at $\mathbf{x}_F$ and both have segments that are governed by Equation (1). (The segment for the batch reactor begins at $\mathbf{x}_F$ and extends to complete reaction, while for the loop reactor it begins at $\mathbf{x}_I$ and extends to $\mathbf{x}_r$.) If a single overall rate expression applies, an added result is that all component mass fractions may be expressed in terms of a single reference component mass fraction by means of Equation (1a). The reference mass fraction in turn may be expressed in terms of temperature through the condition of constant enthalpy. Thus the function R in Equation (1a) may be expressed in terms of temperature only, and the complete state of the system is obtainable simply from the measurement of temperature. That is to say one may construct, in principle, the state curve mentioned above using only the data of Figure 1. It is this fact that forms the basis for the direct use, as described below, of Figure 1 in computations for the steady state of the loop reactor. If stoichiometric constants were known, the concentration distribution at any point on the curve of Figure 1 would be available. Present objectives, however, do not require a knowledge of the composition of the reacting mixture.

The paragraph to follow centers on the analytical and computational procedures involved in obtaining steady state solutions for a loop reactor from Figure 1. Thus the assumptions of plug flow with negligible axial dispersion and of a single-step kinetic model will be invoked. The latter assumption would not be expected to be severely restrictive since success has been reported (*10* to *12*) in correlating adiabatic batch reactor data for this same system in terms of an overall rate expression.

Subsequent comparison of experimental and predicted results will provide some assessment of the validity of the model.

Equations and Computational Methods

A temperature rise $T - T_I$ over a period of time Δt on the batch reactor curve of Figure 1 is described mathematically as

$$T - T_I = \int_{t(T_I)}^{t(T_I)+\Delta t} \frac{(-\Delta H) R}{\rho\, C_p}\, d\theta \tag{4}$$

The important point to be made is that the curve of Figure 1 gives the solution to Equation (4) for given values of T_I and Δt. That is, if T_I and Δt are specified, T is read from Figure 1 as that value on the ordinate which corresponds to a time on the abscissa greater by Δt than $t(T_I)$, the time corresponding to T_I. In order to indicate conveniently that the solution of Equation (4) for T is available from Figure 1 for specified values of T_I and Δt, the following relationship will be used in place of Equation (4):

$$T = I\ (T_I, \Delta t) \tag{5}$$

It is important to note that the function $I(T_I, \Delta t)$ depends on the initial state of the batch system since $t(T_I)$ is governed by it. However, the solution T is invariant with respect to a shift of the time axis; hence, as mentioned earlier, the exact initial time of the batch run is unimportant.

Consider again the loop reactor represented schematically in Figure 2. It is recalled that under the assumption of a single-step kinetic model, the state of the system at any point is characterized completely by its temperature at that point and the fresh feed state. If the fresh feed state is identical to the initial state of the batch reactor and if T_I characterizes the inlet state formed by mixing fresh feed and recycled streams, then with the assumption of plug flow with negligible axial dispersion, the outlet temperature T_o is given by

$$T_o = I(T_I, \Delta t_R) \tag{6}$$

Similarly if flow in the recycle line is also assumed to be in plug fashion with no dispersion, the temperature T_r at the end of the recycle line is given by

$$T_r = I(T_o, \Delta t_r) \tag{7}$$

The residence times, Δt_R, for the reactor and Δt_r for the recycle line are related to volumes V_R and V_r, the mass flow rate of fresh feed, M_F, and the recycle ratio, r, by means of total material balances which may be written as

$$V_R = \frac{M_F}{1-r} \int_{t(T_I)}^{t(T_I)+\Delta t_R} \frac{d\theta}{\rho} \tag{8}$$

$$V_r = \frac{M_F r}{1-r} \int_{t(T_o)}^{t(T_o)+\Delta t_r} \frac{d\theta}{\rho} \tag{9}$$

where $t(T_o) = t(T_I) + \Delta t_R$.

Finally the temperatures T_F, T_I, and T_r are related through an energy balance around the junction point of the recycle and fresh feed streams. With the assumption that there are no appreciable heat of solution effects when the fresh feed and recycle streams are joined, this relationship is

$$T_I - T_F = r \frac{C_{pr}}{C_{pI}} (T_r - T_F) \tag{10}$$

Since heat capacity data are neither available nor easily measured in the reacting mixture, the factor C_{pr}/C_{pI} was assumed to be unity in all computations.

Equations (6) through (10) provide five equations for the unknown quantities T_I, T_o, T_r, Δt_R, and Δt_r. Various trial and error techniques for solution may be formulated. The one most frequently used in this study is outlined below; further description may be found elsewhere (9).

With values of parameters M_F, V_R, V_r, and r specified, the procedure for solution involved

1. guessing a value of $t(T_o)$ and locating the corresponding temperature T_o on the ordinate of Figure 1,
2. computing Δt_r by numerical integration of the right side of Equation (9) by the trapezoidal rule, using the density-time data of Figure 1, until the value of the integral had reached V_r,
3. obtaining T_r from Figure 1 [according to Equation (7)] using Δt_r calculated above and the guessed value of T_o,
4. computing T_I from Equation (10),
5. computing Δt_R from Equation (8) by the same method described for Δt_r in 2 above,
6. obtaining T_o from Figure 1 [according to Equation (6)] using T_I and Δt_R, comparing its value with the guessed value and repeating the previous steps until satisfactory agreement was achieved.

An interval-halving method was employed to locate the correct value of T_o with a maximum error of 0.01°C. Computation time was reduced by first converging to a solution under the assumption of constant mixture density and using the value of T_o thus computed as the initial estimate in seeking a solution for the variable density case. Obvious simplifications result in Equations (8) and (9) and thus in steps 2 and 5 when density changes are neglected.

An added result of this procedure is the predicted temperature profile along the reactor length. Once the correct value of T_o is obtained, the integration of Equation (8) by the trapezoidal rule yields a solution of incremental volume, hence reactor position, vs. incremental residence time. This incremental time is the horizontal distance measured from $t(T_I)$ in Figure 1. A correponding local temperature is given directly by the curve of that figure.

The above procedure is closely related to a computational technique employed by Luss and Amundson (7) in an analytical study of a loop reactor which utilized a hypothetical reaction rate expression. The obvious attraction of the method described here is that it does not require a kinetic expression, although, as pointed out, some assumptions regarding the kinetic model are necessary. Deviations between predicted and observed behavior may be ascribed to the flow model and to the kinetic model, but not to uncertainties in kinetic parameters. Parameter studies of V_R, V_r, M_F, and r may be carried out on the basis of a single batch curve, but a study of the effect of the feed composition and temperature requires a separate batch curve for each different feed state.

Predicted Reactor Characteristics

The computational procedures outlined in the previous section were used in exploring the steady state characteristics of the plug flow loop reactor. The volumes V_R and V_r were maintained constant in the calculations at 1,300 and 48.3 ml. respectively, to correspond to the actual volumes of an experimental system to be described in the next section. Some of the results presented here will be compared with experimental data later. The batch data of Figure 1 were employed throughout; thus the fresh feed state to the loop reactor was taken to be the initial state given earlier for the batch experiments.

The curves of Figure 3 show the effect of the two remaining parameters, the feed flow rate and the recycle ratio, on the predicted steady state outlet temperature. The feature of those curves of particular interest in this study is the multiplicity of steady state temperatures over certain ranges of the parameters. For five of the six cases shown in Figure 3, there exists three different outlet temperatures for a given recycle ratio on a certain range of recycle ratios, and hence there exists three different temperature profiles which satisfy the steady state equations.

The curves of Figure 3*a* give the outlet temperatures for a relatively high feed flow rate of 6,000 ml./min., a situation for which steady state multiplicity is predicted for recycle ratios above 0.375. This particular case presents an interesting sidelight because it predicts multiplicity even for values of r arbitrarily close to unity. As the value of r approaches unity, T_r, T_I, and T_o become identical, and the system behaves as a perfectly-mixed tank reactor with a volume of 1,348.3 ml. Hence Figure 3*a* predicts steady state multiplicity for an adiabatic mixed reactor operating at a residence time of 13.5 sec. and employing the thiosulfate-peroxide system with a feed state given by the initial state in Figure 1. A recycle ratio actually at unity is a singular case in which the residence time is infinite and the temperature everywhere in the system must be at its maximum value of 88.5°C.

As the feed rate was increased above 6,000 ml./min.

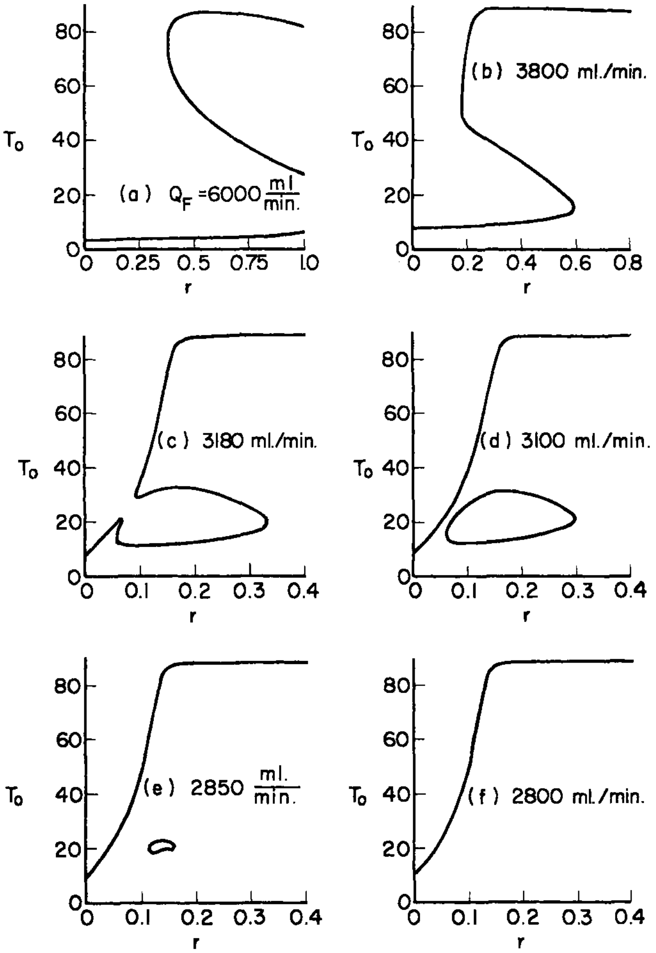
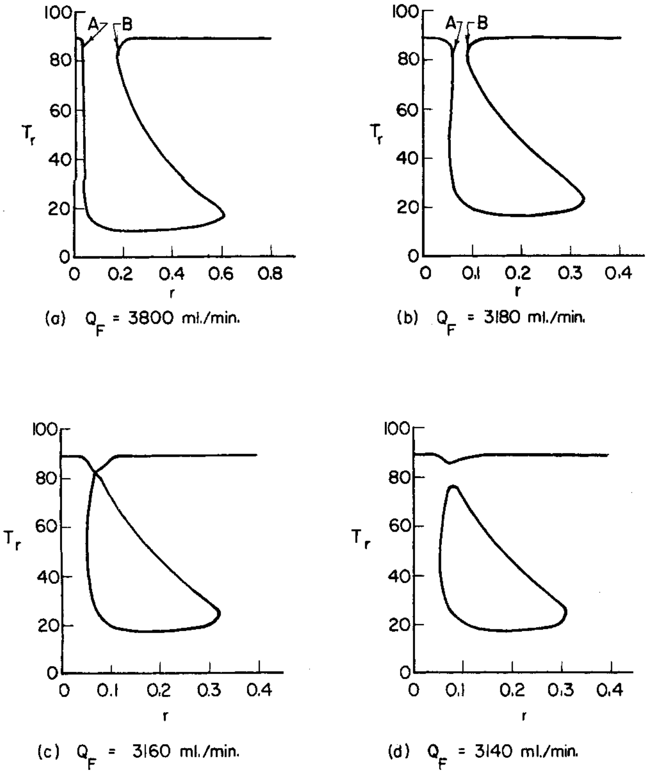


Fig. 3. Predicted steady state outlet temperatures.



(a) Q_F = 3800 ml./min.
(b) Q_F = 3180 ml./min.
(c) Q_F = 3160 ml./min.
(d) Q_F = 3140 ml./min.

Fig. 4. Predicted recycle temperatures.

in the calculations, the region of multiplicity was found to begin at higher and higher recycle ratios until at Q_F = 11,900 ml./min. the peninsular region of Figure 3*a* moved completely out of the picture leaving a unique low outlet temperature for all values of *r* up to unity.

Lowering the value of Q_F led to S-shaped curves of the type shown in Figure 3*b* for a feed flow rate of 3,800 ml./min. Here steady state multiplicity is predicted for recycle ratios between 0.177 and 0.592. As a result, a reactor operating at a feed rate of 3,800 ml./min. would traverse a hysteresis loop as the recycle ratio is first increased from zero to a value beyond 0.592 and subsequently decreased below 0.177 with the system allowed to reach a steady state following each change. Furthermore, with operation at a recycle ratio on the range of multiplicity the steady state actually existing in the reactor would depend on prior events; that is, either on start-up procedures or on temporary upsets or disturbances in parameters or conditions in the history of operation of the reactor. For example, the outlet temperature of a reactor operating at the high temperature state of 88.5°C. for a recycle ratio of 0.35 could become steady at the low temperature state of 10.5°C. following a sufficiently large upset. If so, the high temperature state would be considered unstable to that disturbance. Previous theoretical studies of the plug flow model of this type of reactor (5 to 7) have shown that the intermediate state is always unstable to infinitesimal disturbances when three states exist, and thus it could not be observed in a real reactor without some form of control. The theoretical studies have also shown that all other states are stable to very small disturbances, including any unique state. These conclusions concerning stability have been based on the assumption that the fluid density is constant. Though this assumption is not strictly valid in any real reaction mixture, the small changes in density of a liquid system would not be expected to have any gross effect on transient phenomena.

The curves of Figure 3 show an interesting change in geometry as the feed flow rate is decreased further. The evolution of a closed curve in the steady state picture is illustrated in Figures 3*c* and 3*d*. With still further decreases in Q_F, the closed curve shrinks in size (Figure 3*e*), and below a feed flow rate of 2,840 ml./min. only a unique steady state is predicted for all recycle ratios. Figure 3*f* provides an example of a unique curve predicted for a feed flow rate of 2,800 ml./min.

Certain interesting behavior is predicted as a result of the geometry of the curves shown in Figures 3*c* and 3*d*. For example, if an experiment were carried out for the case depicted in Figure 3*c* by increasing the recycle ratio from zero to a value above 0.33 and then decreasing it back to zero, two separate hysteresis loops would arise in the outlet temperature curve. In the particular case shown in Figure 3*c* one of these loops, ranging on recycle ratios between 0.055 and 0.065 would be very narrow and hence difficult to study experimentally.

For the case shown in Figure 3*d*, a reactor operated such that its outlet temperature is along the open curve cannot be shifted to the low temperature state along the bottom portion of the closed curve (extinguishing the reaction) by a change in the recycle ratio only. However, a large disturbance in some other parameter, such as Q_F, could cause a shift to the low temperature state if the recycle ratio were between 0.057 and 0.29. If a reactor were initially operating at a stable low temperature state on the closed curve, its state may be shifted to one along the open curve (igniting the reaction) either by increasing or decreasing the recycle ratio. On the other hand, the situation shown in Figure 3*b* can be ignited by increasing *r*, and that in Figure 3*a* can not be ignited by any change in the recycle ratio only. Thus once a reactor with a steady feed flow of 6,000 ml./min. is extinguished, it cannot be reignited by changing the recycle ratio only.

It is worthwhile noting that the closed curve was found not to form if reaction in the recycle line was neglected, or if V_r was assumed negligible in the computations. Its formation apparently is due to the extreme sensitivity of the recycle temperature to the flow rate in the recycle line under certain conditions and to the effect of a temperature rise in the recycle line on the total reactor temperature at certain flow rates. Further insight into this phenomenon may be gained through the curves of Figure 4 which show the predicted recycle temperature vs. the recycle ratio for four values of Q_F. In Figure 4*a* the recycle temperature rises very rapidly near a recycle ratio of 0.04. As Q_F is decreased, the gap between points (A) and (B) in Figures 4*a* and 4*b* narrows and is just closed completely (Figure 4*c*) when the closed curve has formed. The ignition then of the reaction as the recycle ratio is decreased in the case shown in Figures 3*d* and 3*e* is the result of adding to the fresh feed a recycle stream whose temperature is high because of the long

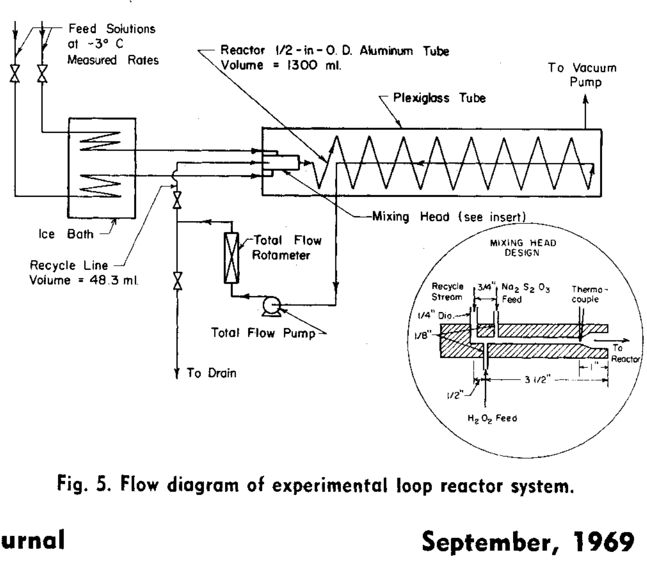


Fig. 5. Flow diagram of experimental loop reactor system.

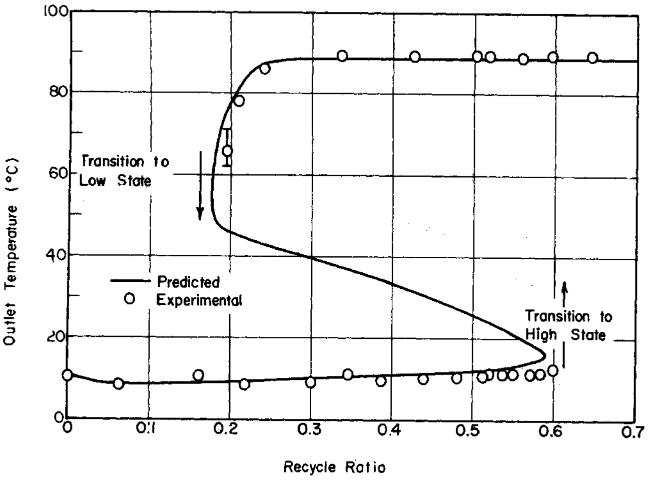


Fig. 6. Experimental and predicted outlet temperatures for Q_F = 3,800 ml./min.

residence time in the recycle line.

As a final point of interest concerning the steady state solutions, the effect of density variations was found to be negligible in all cases for which the effect was examined. For example, for points on the closed curve of Figure 3*d* the outlet temperature predicted on the assumption of constant density deviated by less than 1°C. from that resulting when variable density was taken into account. The critical points, the points of infinite slope, on that curve were virtually unaffected. Deviations on the steepest portion of the open curve of Figure 3*d* amounted to no more than 3°C. which is clearly negligible in view of the large effect on outlet temperature of a small error in recycle ratio on that portion of the curve.

Situations represented by the curves of Figures 3*b*, 3*d*, and 3*f* were studied in an experimental loop reactor system. Results and comparisons will be discussed later in this paper; the experimental apparatus and procedures are described in the following section.

DESCRIPTION OF THE EXPERIMENTAL LOOP REACTOR SYSTEM

A flow diagram of the experimental reactor system is given in Figure 5.

Feed solutions of 1.6 molar sodium thiosulfate and 2.4 molar hydrogen peroxide in deionized water were stored in polyethylene drums and cooled to about −3°C. by means of a circulating brine coolant prior to the start of a run. Total storage capacity for each solution was about 30 gal. which permitted run durations of 60 to 90 min. for the flow rates studied.

During a run the feed solutions were each pumped through a rotameter, through a needle valve for manual flow adjustment and through 24 ft. of coiled aluminum tubing immersed in an ice bath for preheating to 0°C. In no case did the feed temperatures deviate from 0°C. by more than ± 0.25°C. The feed flows were maintained at equal volumetric rates so that the fresh feed mixture concentration was the same as that of the initial mixture in the batch experiments described earlier. The rotameters were calibrated with water, and the resulting calibration curves were corrected for solution densities. The corrected calibration was checked at a few points by direct calibration with the feed solutions and found to be accurate with a maximum deviation of one percent.

The two fresh feed streams were joined with the recycle stream in a mixing head which was designed to promote rapid and intimate mixing. Some of the details of the design are shown in the insert of Figure 5; others are available elsewhere (9). The main features of the mixing head, which was machined from a 2 in. diam. solid aluminum cylinder 6 in. in length, were a ¼ in. diam. central bore into which the recycle stream was injected and two ⅛ in. diam. passages which joined the central bore tangentially. The fresh feed streams were fed through the ⅛ in. passages which were separated by 120 deg. angularly and spaced ¼ in. apart along the bore. The maximum residence time in the mixing head for all experiments was about 0.05 sec., while the minimum residence time in the reactor itself was about 10 sec.

A copper-constantan thermocouple enclosed in a stainless steel protection tube was located 1 in. upstream from the end of the mixing head. The recording from this thermocouple was taken to be the inlet temperature T_I.

Visual observations of the degree of mixing with the above design were carried out with a similar mixing head constructed of plexiglass. In these tests, water was injected through the main bore, a basic solution containing phenolphthalein in one tangential passage and a slight excess of acid for neutralization in the other. In all tests the pink color of the phenolphthalein indicator disappeared before the end of the mixing head.

The total reaction mixture flowed from the mixing head into a 0.444 in. I.D. aluminum tube (wall thickness 0.028 in.). The aluminum tube was about 37 ft. long and was wound over 24 ft. of its length in a helical coil configuration having a 3 in. radius of curvature. The curvature of the tube should induce secondary flows, thus flattening the axial velocity profile, enhancing radial mixing and making the assumption of plug flow more nearly a reality than would be the case in an equal length of straight tubing.

The major portion of the tube was enclosed in a large plexiglass cylinder which was evacuated during a run to about 15 mm. of mercury so that heat losses and equipment heat capacities were minimized. (The equipment heat capacity, of course, has no effect on steady state performance, but a large capacity is undesirable because of its effect on the time required to reach a steady state.) All lines external to the plexiglass cylinder were insulated.

The reaction mixture flowed through a total flow centrifugal pump and a rotameter for total flow measurement before being split into a recycle stream and an outlet stream. The recycle line consisted of about 12 in. of 0.444 in. I.D. aluminum tubing and contained a needle valve for manual recycle flow adjustment. The total flow rotameter was calibrated with water, and readings were corrected to the reaction mixture density by means of the density data given in Figure 1. A single run was carried out with the reaction system and no recycle flow in order to check the accuracy of this correction. In this run the total feed mass flow rates taken from the feed rotameters tended to be slightly lower than the mass flow rates obtained from the total flow rotameter. However, since the differences between the two measurements never exceeded

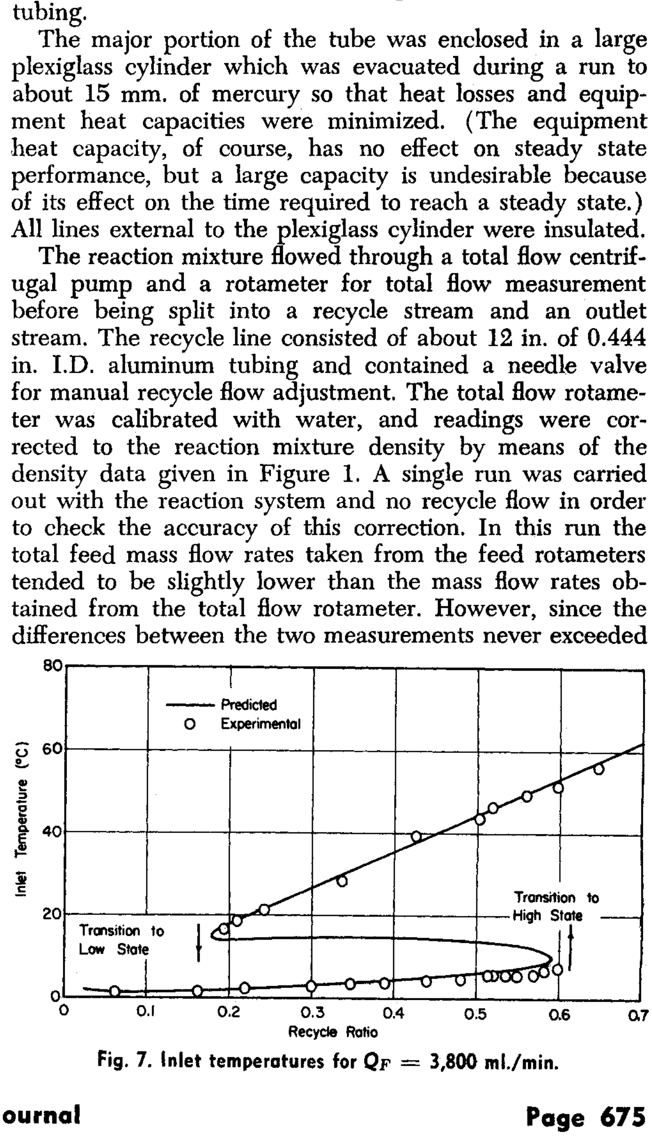


Fig. 7. Inlet temperatures for Q_F = 3,800 ml./min.

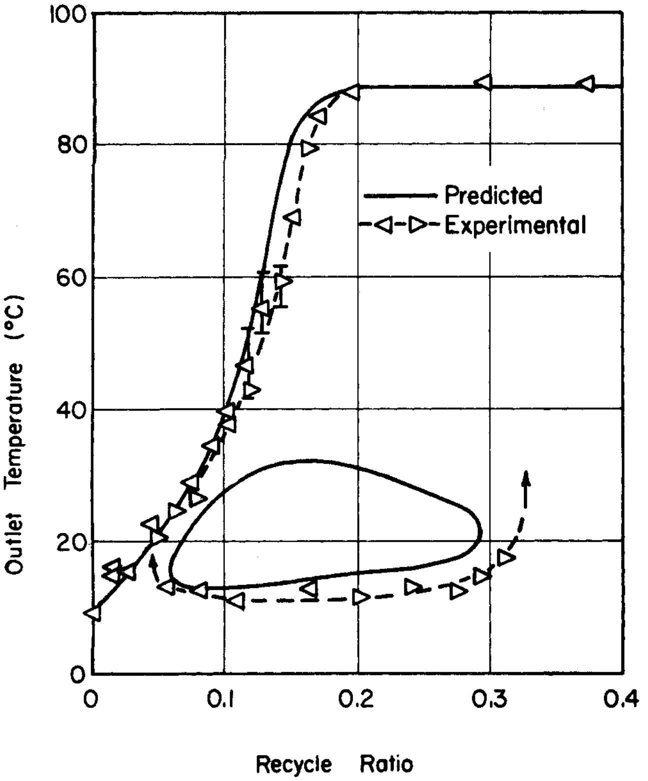


Fig. 8. Outlet temperatures for $Q_F = 3{,}100$ ml./min.

2% of the feed rate, the correction was considered to be sufficiently accurate.

Volumes in the reactor assembly were determined by measuring the volume of water required to fill the apparatus or particular sections of the apparatus. By this method V_R was found to be 1,300 ml. and V_r, 48.3 ml. The volume V_R includes the central bore of the mixing head as well as the volume of the pump head and the total flow rotameter; that is, the entire volume from the point of injection of the recycle stream into the mixing head to the splitting point of recycle and outlet streams.

In addition to the thermocouple probe for inlet temperature measurement mentioned earlier, probes were located 5 in. upstream of the recycle-outlet splitting point for outlet temperature measurement and in the recycle line 5 in. upstream of its entry into the mixing head for recording of the recycle temperature. Three surface temperature sensors were located along the length of the aluminum tube between the mixing head and the total flow pump for measurement of temperature profiles. The locations of these thermocouples in terms of fractional reactor volume were estimated from known dimensions of the aluminum tube and measured system volumes. A surface sensor was also placed on the outside of the tube at the location of the outlet temperature probe to examine the agreement between the liquid and wall temperatures. The two temperatures were found to agree with a maximum deviation of 1°C. in all runs.

The recycle ratio was determined from the difference between the total mass flow rate, as measured with the total flow rotameter, and the sum of the two feed mass flow rates.

Heat losses and accuracy of the thermocouples were tested by running hot water through the entire system and allowing steady state to be reached. In such tests no measureable temperature drop occurred through the system, and recordings from all thermocouples including probes and surface sensors were virtually identical.

The general startup procedure in experiments with the reaction system was to allow a steady state to be reached with water flowing at room temperature before switching in the peroxide and thiosulfate feed solutions.

One point concerning materials is worth mentioning. The generation of hydrogen sulfide was found to be catalyzed in the reaction system by some metals. This did not occur with aluminum or type 316 stainless steel.. Other materials with which the reacting mixture came into contact in the apparatus were polyethylene, glass, and teflon.

PRESENTATION OF RESULTS, COMPARISONS AND DISCUSSION

Steady State Temperatures

Experiments with the loop reactor system were carried out for the three feed flow rates corresponding to the situations depicted in Figures 3*b*, 3*d*, and 3*f*. Results for the first of these cases are illustrated in Figures 6 and 7. Figure 6 shows the predicted and experimental outlet temperatures versus the recycle ratio for a total feed flow rate of 3,800 ml./min. The solid curve represents results predicted from the batch data, and the circles indicate experimental data. The predicted results were discussed earlier in connection with Figure 3*b*. The principal observations relative to Figure 6 are that steady state multiplicity is indeed verified by the experimental results and that experimental loop reactor data show good agreement with the predicted curve.

The experimental data shown in Figure 6 and in all subsequent figures were obtained in several independent runs. Data points along the low temperature branch of the S-shaped curve were obtained by increasing the recycle ratio from a low starting value until a transition to a high temperature state occurred. The hysteresis loop was completed by subsequent decreasing of the recycle flow in order to achieve temperatures along the upper portion of the curve until the transition to a low state took place. Sufficient time was allowed for temperature recordings to reach steady values following each change. In most cases this time was about 5 or 6 min. One entire run was devoted to studying the transition from the low branch to the high branch of the curve and to obtaining steady states

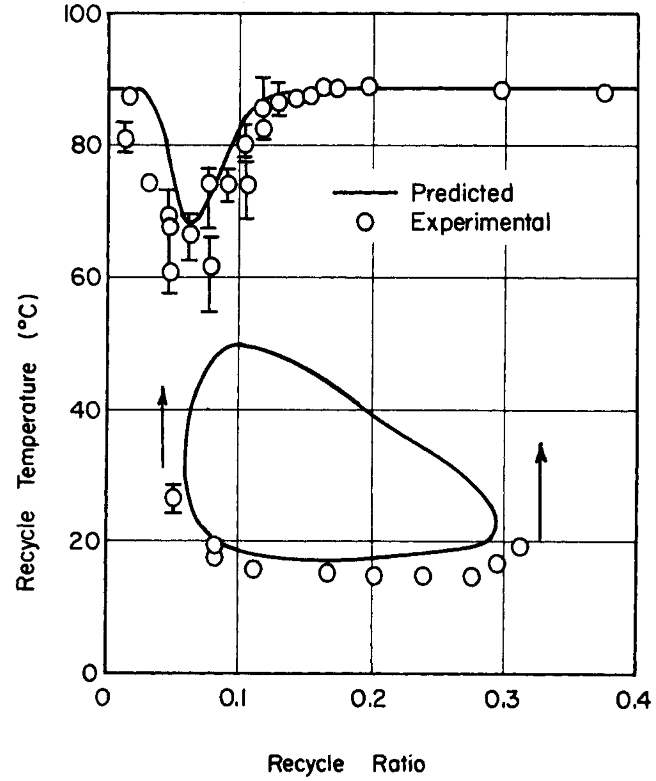


Fig. 9. Recycle temperatures for $Q_F = 3{,}100$ ml./min.

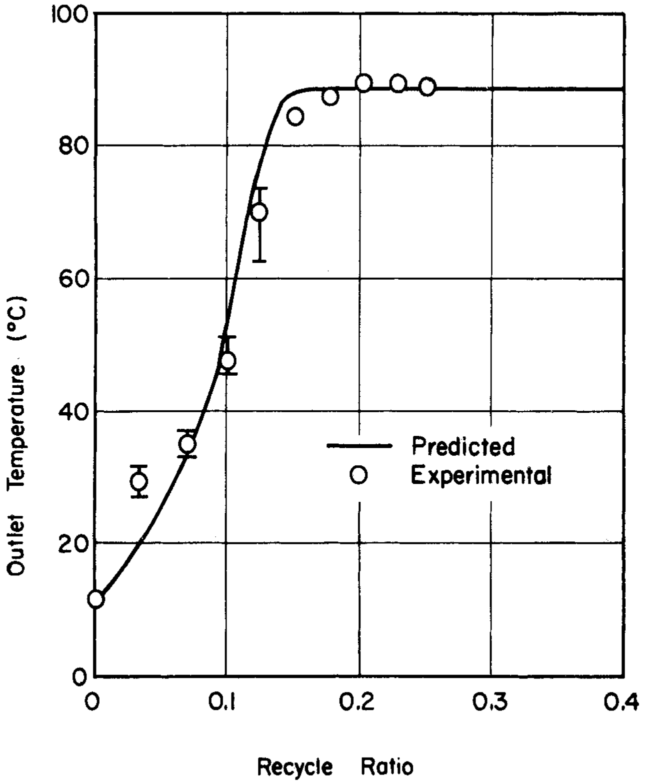


Fig. 10. Outlet temperatures for $Q_F = 2{,}800$ ml./min.

near that transition. Although there are no gross deviations between experimental and predicted results in Figure 6, it is only near this transition that any appreciable deviations were noted. States in this region as well as the transition point itself were very difficult to study due to the length of time required for a steady state to be reached. For example, the transition to a high-temperature state occurred when the recycle ratio was changed from 0.60 to 0.613, but at the latter value a period of about 20 min. had elapsed before the temperature had increased by more than a few degrees. Thereafter the temperature rose rapidly to a high value. Twenty minutes of time near the transition point corresponded to about eighty reactor residence times. It is quite possible that some of the apparently steady experimental points just to the left of the transition point in Figure 6 would have increased by a few more degrees or perhaps even all the way to the high state if operation could have been carried out for a couple of hours. One would expect equipment heat capacities to have considerable effect on transients in this region and that steady states would be somewhat affected by small heat losses. Furthermore slight errors in the model on which the predicted curve was based would probably be most apparent near the critical points of the curve. A computer similation of transients in this region would be informative but were beyond the scope of the objectives in this phase of the study.

The transition from high temperature states to low states, which occurred when the recycle ratio was decreased from 0.195 to 0.160 was much faster. However, on the very sensitive portion of the curve near the critical point, there was considerable fluctuation in the temperature recordings. The fluctuations apparently were caused by small variations in flow rates. The flow rates were held as steady as possible by manual adjustment of needle valves, but small changes were unavoidable. The data point at a recycle ratio of 0.195 represents an approximate time average of the temperature recordings. The ends of the vertical line through that point indicate the extent of the observed fluctuations at steady conditions.

Shown in Figure 7 are the predicted and observed inlet temperatures which correspond to the outlet temperature data of Figure 6. Here again agreement between experimental and predicted temperatures is good, indicating that the assumptions involved in Equation (10) and the assumption of equal heat capacities for fresh feed and recycle mixtures are valid. Further experimental proof of the validity of these assumptions may be found in (9).

Figure 8 presents the predicted and measured steady outlet temperatures for a total fresh feed flow rate of 3,100 ml./min. This case was discussed earlier in connection with Figure 3*d*. As can be seen from Figure 8, experimental data, which roughly follow the dashed curves, agree qualitatively with the predicted temperatures given by the solid curve, but quantitative agreement is not as good as in the previous case.

Data points along the open curve were obtained by starting the system with no recycle, then increasing the recycle flow in steps and allowing a steady state to be reached after each change. Steady state temperatures obtained in this manner are indicated by the triangles pointing to the right in Figure 8. Subsequent decreasing of the recycle ratio gave those points indicated by triangles pointing to the left. As shown in Figure 8, all such states lie along a single curve.

Operation of the system along the stable portion of the closed curve was achieved by allowing the system temperatures to become steady at a low-temperature state for a feed flow of 3,800 ml./min., the case shown in Figures 6 and 7, then changing the flow rate to 3,100 ml./min. and adjusting the recycle ratio to about 0.2. The low temperature states indicated by triangles pointing to the left in Figure 8 were obtained by decreasing the recycle ratio and allowing a steady state to be reached after each change until the transition to the open curve was observed. That transition occurred at a recycle ratio of 0.045. The low temperature points represented by triangles pointing to the right were obtained by increasing the recycle ratio until the transition to a high temperature state took place. That transition was observed at a recycle ratio of 0.325.

The larger deviations between the predicted and observed temperatures in this case might have been expected for a number of reasons. In the first place states along the open curve are very sensitive to flow disturbances. In fact, operation along the steepest portion of the curve was characterized by random fluctuations in temperatures. The

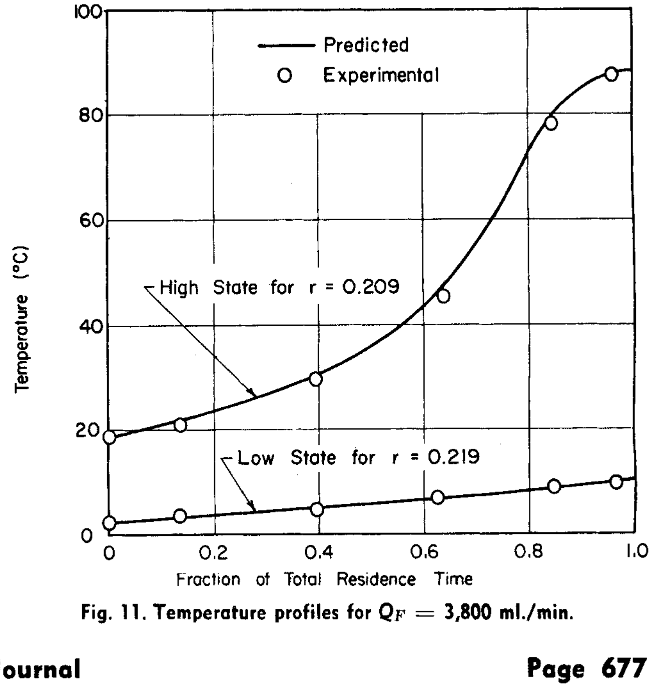


Fig. 11. Temperature profiles for $Q_F = 3{,}800$ ml./min.

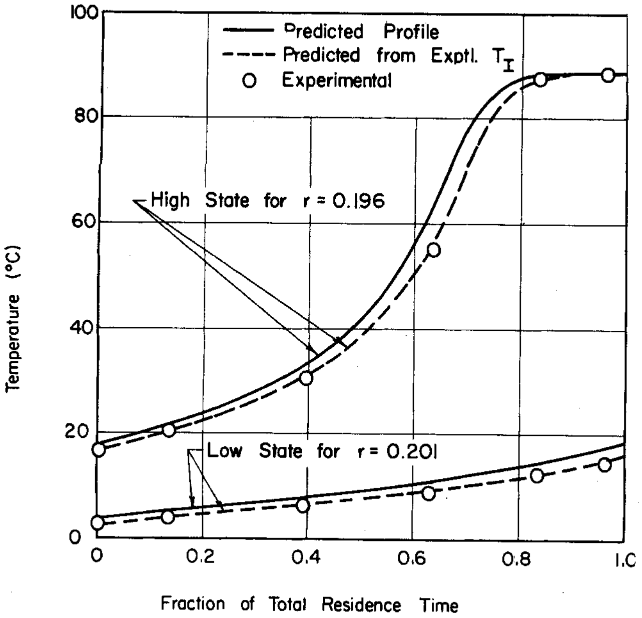


Fig. 12. Temperature profiles for Q_F = 3,100 ml./min.

vertical lines extending from such data points in Figure 8 indicate the extent of temperature fluctuations. The data points themselves represent approximate time averages of the temperature recording. On two occasions large fluctuations immediately following a change in recycle ratio near a value of 0.12 caused an extinction of the reaction, that is, a transition to a low temperature state along the closed curve. Such a transition was found to be avoidable if care was taken to change the recycle ratio slowly and in small steps.

Another factor which probably contributed to the larger deviations in this case was the lower range of recycle ratios involved. Computation of the recycle ratio from differences between total and feed flows was much more prone to errors at low recycle flows.

For the recycle ratios employed in obtaining the experimental data in Figure 8, Reynolds numbers in the reactor tube ranged from 5,800 to 14,600 and in the recycle line from 100 to 8,750. One would expect the assumption of plug flow to be of questionable validity, particularly in the recycle line for the very low Reynolds numbers. However, an examination of temperature profile data, which will be presented shortly, gave no indication of significant deviations from plug flow predictions that could not be attributed to uncertainties in flow measurements.

Figure 9 presents measured and predicted recycle temperatures for the same case. The solid curve in Figure 9 represents predicted temperatures for the actual thermocouple location, which was 5 in. upstream of the mixing head as described in the previous section. As shown, measured and predicted temperatures again show qualitative agreement. Fluctuations in the recycle temperature were even more pronounced than those described earlier for the outlet temperature. The extent of such fluctuations is indicated by the vertical lines extending from the data points in Figure 9.

Figure 10 shows the results for a fresh feed rate of 2,800 ml./min. This is an example for which a unique state is predicted for all recycle ratios. Experimental data in Figure 10 lead to the same conclusion and generally agree well with predicted temperatures. Various starting procedures designed to locate stable states on a closed curve, if indeed a closed curve such as that shown in Figure 8 did exist, all led to states along the unique curve. As in the previous case, steady temperatures here were found to fluctuate due to small flow variations. The vertical lines extending from some of the data points in Figure 10 indicate the limits of these fluctuations.

Further affirmation of the quantitative accuracy of the predictions is available through an examination of the temperature profiles. Shown in Figure 11 are the measured and predicted steady state temperature profile data which correspond to two of the experimental data points in Figure 6. One is the low temperature state for a recycle ratio of 0.219 and the other the high temperature state at a recycle ratio of 0.209. The scale on the abscissa of Figure 11 is the fraction of the total residence time, $(\Delta t_R + \Delta t_r)$. Thus, the experimental data point at zero on this scale represents the inlet temperature measurement, and the point near unity, the measured recycle temperature. The second data point from the right is the measured outlet temperature, and the three remaining points were obtained from the surface sensors along the coiled aluminum reactor tube.

For the two profiles shown in Figure 11 there is very little deviation between predicted and measured temperatures. Similar agreement was found in many other cases examined, but a number of cases were found to be of the type shown in Figure 12. In that figure the solid curves represent predicted profiles for the high and low temperature states corresponding to recycle ratios of 0.196 and 0.201 respectively for the case shown in Figure 8. While the experimental data deviate noticeably from predicted temperatures, it is interesting to note that the dashed curves, which represent predicted profiles arrived at by using the experimental inlet temperature, fit the data almost perfectly. Hence the deviations are not necessarily a result of errors in the plug flow model or the kinetic model but perhaps of the sensitivity of the profiles to small errors in measured parameters. In fact calculations showed that if the reported total feed flow rate were low by 1.5% (a reasonable value of the error in light of earlier discussion concerning the feed and total flow rotameter calibrations), the predicted profile and the data points in Figure 12 show as good an agreement as those in Figure 11.

Effect of Large Disturbances

Attention is focused here on the transient response of the loop reactor to large disturbances. All discussion pertains to the multiple steady state regime for a total feed flow of 3,800 ml./min. represented in Figures 6 and 7. In this regime, the high and low temperature states are stable to small disturbances, but it is intuitive that they are not globally stable; that is, a sufficiently large perturbation from either of the two stable states for a given recycle ratio will cause a shift to the other stable state. Such behavior has been elucidated previously in an analytical

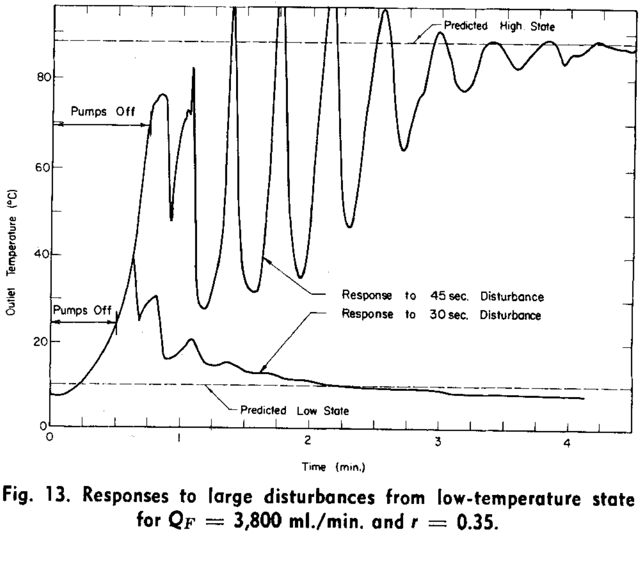


Fig. 13. Responses to large disturbances from low-temperature state for Q_F = 3,800 ml./min. and r = 0.35.

study of a loop reactor (6); experiments described below were aimed at illustrating experimentally this instability to large upsets.

With steady operation at a low temperature state and a recycle ratio of 0.35, a temporary upset was created by switching off the total flow and feed pumps for a measured length of time. Thus during the duration of the disturbance the only flow through the reactor was by gravity. Figure 13 shows the outlet temperature responses to such disturbances for two experiments. In the first, the pumps were left off for a period of 30 sec. during which time the temperature of the nearly stagnant mixture in the system rose rapidly. As shown in Figure 13, the temperature perturbation damped out after the pumps were switched back on. The transient temperature was oscillatory, due to the repeated recycling of the perturbation. In a second experiment with the same initial state, the pumps were left off for 45 sec. In this case, as shown in Figure 13 the perturbation did not decay, and the system approached the high temperature state. Thus the low temperature state at a recycle ratio of 0.35 was found to be unstable to a 45 sec. disturbance of this nature. The transient temperature curve for the second experiment shows very large oscillations which are a result of the recycling of the perturbation. Rotameter readings, and hence flow rates, were found to oscillate during the transient period though attempts were made to hold them constant by manual adjustment.

Observations were made also of the stability of the high temperature states to large disturbances. Again with operation at a recycle ratio of 0.35 but this time at the high temperature state, an upset was created by turning off the total flow pump. Feed flows were maintained as constant as possible during the disturbance, and at its termination the recycle ratio was quickly readjusted to 0.35. Figure 14 shows the responses to disturbances of 30 and 45 sec. durations. As shown, the outlet temperature returned to its initial state in the former case, but became steady at the low temperature state in the latter.

CONCLUSION

The principal results of this work are (a) the attainment of experimental data showing steady state multiplicity in a chemical reactor, (b) the experimental observations of instability of a continuous flow reactor when subjected to sufficiently large temporary upsets, and (c) the demonstration of the capability of a simple model for predicting, quantitatively as well as qualitatively, the main features of the steady state performance of the loop reactor.

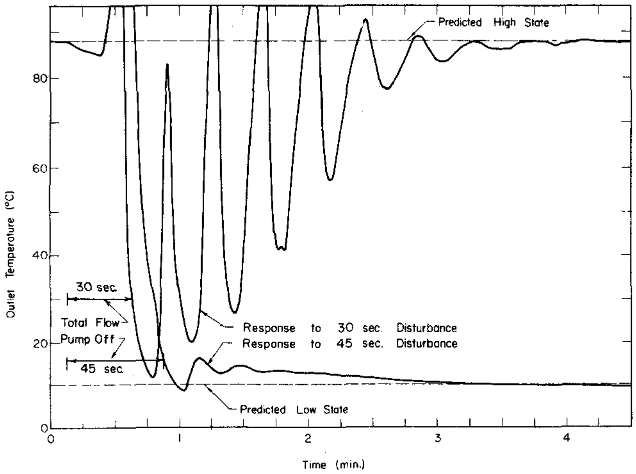


Fig. 14. Responses to large disturbances from high-temperature state for $Q_F = 3{,}800$ ml./min. and $r = 0.35$.

To our knowledge this is the first published report of experiments pertaining to steady state multiplicity and stability in a chemical reactor involving a liquid phase reaction, although many theoretical investigations of these characteristics for various types of chemical reactors have appeared in the literature through the past fifteen years.

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NOTATION

$\mathbf{A}$ = matrix of stoichiometric coefficients in Equation (1) and vector of stoichiometric coefficients in Equation (1*a*)
C_p = heat capacity
H = total enthalpy relative to atomic state
ΔH = heat of reaction
I = function defined by Equations (4) and (5)
M_F = total mass flow rate of fresh feed
Q_F = total volumetric flow rate of fresh feed
r = recycle ratio defined as the fraction of the total reactor stream which is recycled
R = reaction rate expression for single-step kinetic model
$\mathbf{R}, R_i$ = vector of rates of formation by chemical reaction and the *i*th component of the vector
t = time
Δt = interval of time
Δt_r = residence time in the recycle line
Δt_R = residence time in the reactor
T = temperature
V_r = volume of recycle line
V_R = volume of reactor
$\mathbf{x}$ = vector of mass fractions
ρ = density
θ = dummy variable of integration in Equations (4), (8), and (9)

Subscripts

F = fresh feed
I = reactor inlet
o = reactor outlet
r = recycle

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