An Experimental Study of Unstable States in a Loop Reactor

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An adiabatic loop reactor was operated at naturally unstable steady states in experiments employing the reaction between sodium thiosulfate and hydrogen peroxide in aqueous solution. The unstable states, the intermediate states in a multiple state regime, were stabilized by manual manipulation of the recycle ratio. Resulting temperature data agreed well with those predicted from a plug-flow model. Observations of the transient response to small disturbances from the intermediate states verified that they were indeed unstable as had previously been predicted theoretically. Cursory attempts to stabilize the system by means of automatic feedback control employing a three-mode controller were unsuccessful.

Following our earlier experimental studies (*1*) of stable steady states in the multiple state regime of an adiabatic loop reactor, we conducted a series of experiments focusing on the unstable intermediate states. This paper is a disclosure of the results of our experiments in which we stabilized the reactor by means of manual control at some unstable states and observed the nature of the reactor behavior in the vicinity of these states. Some observations from cursory attempts to stabilize an unstable state by means of automatic feedback control will also be described. Automatic control, however, is not of major concern here; it is the subject of further studies that are currently in progress. There have been no prior reports of experiments with reaction systems at naturally unstable conditions, though numerous theoretical studies have predicted their existence. The stabilization of unstable states by means of automatic control has been studied theoretically for lumped parameter systems (*2*, *3*), but the control of unstable distributed parameter processes such as the loop reactor has not been pursued.

Throughout this paper we shall follow the terminology introduced in the earlier paper (*1*).

EXPERIMENTAL EQUIPMENT

The experimental apparatus described in the earlier paper was modified for the present objectives by the insertion of a pneumatically actuated, stainless steel control valve in the recycle line in place of the needle valve. The control valve was introduced in the unit to permit convenient and reproducible manipulation of the recycle ratio. It received a 3 to 15 lb./sq.in. air pressure signal from a cascaded system consisting of a Leeds and Northrup three-mode, current adjusting type of controller and an electropneumatic converter. The controller operation could be switched either to automatic or manual. In automatic or closed-loop operation, the controller accepted a thermocouple signal (measuring the reactor outlet temperature in our experiments) and produced an output which depended on the difference between the thermocouple signal and a selected set point. In open-loop or manual operation, the air pressure signal to the valve, hence the stem position and the recycle ratio, was conveniently manipulated by means of a dial on the controller.

The presence of the control valve increased the volume of the recycle line to 62.3 ml. All other equipment description and dimensions are the same as those described in reference *1*.

Experiments here, as did those in the earlier study, employed the liquid-phase reaction between sodium thiosulfate and hydrogen peroxide in aqueous solution.

DISCUSSION OF THE UNSTEADY STATE

The solid curves of Figures 1 and 2 represent the predicted steady state outlet and inlet temperatures, respectively, for a plug-flow model with a fresh feed flow rate of 3,600 ml./min. and for the fresh feed concentrations and temperature shown in Figure 1. The curves were obtained from the batch reactor data presented in Figure 1 of reference *1*. Methods for obtaining the curves were discussed in that paper as were the assumptions involved.

The unstable states in Figures 1 and 2 are the intermediate temperature states on those ranges of recycle ratios for which three steady states are possible. The high and low temperature states in the adiabatic system are always stable as are any unique states. In Figures 1 and 2 there are two intervals of the recycle ratio for which three steady states are predicted. One is the interval $0.045 < r < 0.055$, and the other is the interval $0.125 < r < 0.47$. Our experiments centered on the latter interval, the former being too small and involving recycle ratios too low for experimental study in our apparatus.

As the curves of Figures 1 and 2 are traced beginning at a recycle ratio of zero, the region lying to the left is one throughout which changes in temperature with time are negative; in the region lying to the right, they are positive. This requires further clarification. If the instantaneous temperature T' of a plug of fluid at the reactor outlet lies to the left of the curve of Figure 1, then the temperature of the first descendant plug, the plug of fluid formed by mixing a fraction of the plug at the outlet (following its passage through the recycle line) with the fresh feed, will be lower than T' when that plug reaches the outlet position. Applying these considerations in inquiring into the effect of disturbances from a steady state, one can readily arrive at the conclusion that the intermediate state is unstable because in the succession of descendant plugs even the smallest perturbation would grow, and that the other states are stable at least for sufficiently small disturbances.

Though the above analysis of transient responses is useful in gaining insight into the unsteady behavior of the loop reactor, it is not without limitations, and in fact is not correct in detail. It is implied in the analysis that the only independent perturbations are those in temperature, since the curves of Figures 1 and 2 are based on the assumption that all concentrations are related, independently of time, to the temperature through the stoichiometry of the reaction and through the assumption that the system enthalpy is constant. If these assumptions are not valid throughout the transient state, there is no way of predicting the nature

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of the transient response from Figures 1 and 2. In an experimental situation, independent perturbations in concentration and enthalpy could be introduced, for example, through disturbances in the fresh feed state, but not through disturbances in flow rates alone. While we have no assurance that changes in the fresh feed state were insignificant in our experiments, we shall make that assumption for convenience in discussing manipulative action for control at the unstable state in the next section. When disturbances were introduced deliberately during the course of our experiments, they were created by perturbing the recycle flow and thus brought about little or no independent changes in concentrations and enthalpy. Hence, the arguments concerning the qualitative nature of the time dependent behavior on the basis of steady state pictures, such as those in Figures 1 and 2, are probably meaningful in our experiments.

PROCEDURE FOR MANUAL CONTROL

Once the system had been coerced to the vicinity of an unstable state (a task which will be discussed shortly), our policy for manual manipulation of the recycle ratio to maintain operation near that state followed from the considerations of the previous section. We observed recordings of the outlet temperature and increased or decreased the recycle flow by manipulating the air pressure signal to the pneumatic valve in a manner which depended primarily on the sign of the deviation of the outlet temperature from its desired value. If, for example, the desired operating outlet temperature was 25°C., and if the temperature drifted above that value, the recycle flow was decreased in order to bring the system into a region where temperature changes were negative. After gaining experience through several runs, each of about 90 min. duration, we were generally able to hold a desired unstable state with very fine manipulations of the recycle flow for as long as 7 min. (about thirty residence times) with outlet temperature fluctuations not exceeding 1°C. Furthermore, we were able to reproduce unstable states with suitable precision. As we might have expected, our experiences showed that generally when a manipulation was made to correct an offset, the initial effect of the corrective action was to increase rather than decrease the deviation from the desired state. For example, if the outlet temperature rose above its desired value, our action was to decrease the recycle ratio. But since this action caused an increase in residence time in the reactor, the temperature of the reaction mixture already contained in the reactor would be even greater when it reached the outlet. That is to say that the desired or expected response to the control action was delayed by about one residence time because of the transportation lag in the tubular reactor. In order to achieve successful control, we found it necessary to postpone further corrective action for approximately one residence time. This type of control problem would not be expected in a stirred reactor.

As described above, we worked with the outlet temperature as the measured variable. This location for temperature measurement would seem to be a natural choice, though in our case it was an arbitrary one. No thorough examination of various possible locations was undertaken. One can see, however, from Figure 2 that the inlet temperature would not be a suitable choice as a measured variable, since its steady intermediate value is very insensitive to changes in the recycle ratio.

As mentioned earlier, the first task in operating at or near an unstable state concerned the start-up problem, the problem of bringing the state of the reactor close to the desired state so that manipulative action could be initiated. It was imperative that the system be brought very near the desired state because any large deviations were difficult to handle by manipulations with the recycle flow. As judged from Figure 1, if the outlet temperature were very far above its desired value at an intermediate state, the recycle ratio would have to be decreased below 0.12 to bring about negative temperature changes with time. If the outlet temperature were considerably below its desired value, the recycle ratio would have to be increased above 0.52 to cause positive temperature changes. We found that the most satisfactory procedure was to bring the outlet temperature near its desired value by adjusting the fresh feed flow rate with the total flow fixed roughly at a value corresponding to the desired state as determined from the predicted steady state curve. Once the outlet temperature was within 1° or 2°C. of its desired value, the feed rate was set at 3,600 ml./min., and manipulations of the recycle flow began. Even then we were not always successful in keeping the outlet temperature near its desired value for longer than several seconds; in fact, failures were as frequent as successes. In some cases the start-up procedure had to be repeated several times before the desired state was achieved. This was probably due to the fact that forcing the outlet temperature to the vicinity of its desired steady value did not guarantee that the entire temperature profile was in the proximity of the corresponding desired profile, and, as a result, large deviations quickly appeared in the outlet when the feed rate was finally adjusted to 3,600 ml./min. We considered a steady state as having been observed whenever we could sustain operation for at least 3 min. (about twelve residence times) with amplitudes of fluctuations in all recorded temperatures not exceeding 2°C. and corresponding recycle manipulations not covering a range greater than 0.02.

RESULTS AND DISCUSSION

Experimental outlet and inlet temperatures, which include measurements at some stable as well as unstable states, are shown in Figures 1 and 2, respectively. The dashed curve represents a rough fit of the data which show good agreement with predicted temperatures. Possible reasons for discrepancies were discussed in reference *1*. The data points shown for the intermediate states indicate the reproducibility of those states. Attainment of intermediate states for recycle ratios between 0.13 and 0.26 was not attempted because of the insensitivity of the steady outlet temperature to changes in the recycle ratio on that range.

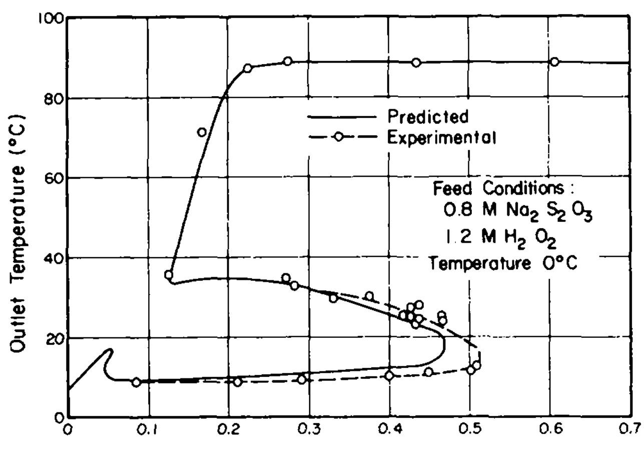

Fig. 1. Predicted and experimental outlet temperatures for Q_F = 3,600 ml./min.

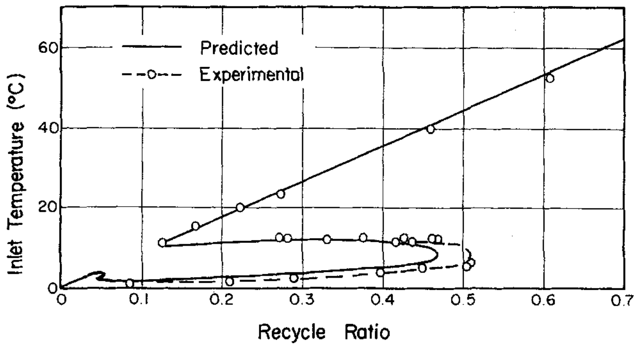

Fig. 2. Predicted and experimental inlet temperatures for Q_F = 3,600 ml./min.

Some observations of the reactor behavior in the vicinity of an unstable state are worth relating. We found that the system showed no strong tendency to depart suddenly from an unstable state once it had arrived sufficiently close to that state. This would be expected, since time derivatives become vanishingly small near the steady state, and, as a result, transients should be slow. In fact, we found that in many cases the unstable state in quest would become so steady that we could cease all manual manipulations for 2 or 3 min. with no noticeable change in temperatures.

The outlet temperature histories shown in Figure 3 present an example of some further experimentation at unstable conditions and illustrate conclusively the natural instability of the steady state. In the particular case shown in Figure 3, we manipulated the recycle flow until the system was sufficiently steady at the desired outlet state of 25°C. so that manipulations could be ceased briefly. Such a period is represented by the first section of curve (a) of Figure 3 which extends for about 65 sec. in time and is indicated by a recycle ratio of 0.43. We then introduced a small perturbation by increasing the recycle ratio to 0.46 until the temperature changed by about 2°C., at which time the recycle ratio was reset at the value of 0.43. If the original steady state at r = 0.43 had been stable to the small disturbance, the outlet temperature would have returned to 25°C., but, as shown by curve (a), the temperature continued to increase. Eventually a stable high temperature state was reached. Curve (b) of Figure 3 shows the effect of a perturbation in the opposite direction from the same steady state. Again it is seen that the perturbation continued to grow in response to the temporary change in the recycle ratio. In this case, however, the disturbance caused a continual decrease in the outlet temperature which eventually led to the low temperature state.

Some points brought out earlier in connection with the discussion of the nature of transient responses are nicely illustrated by the curves of Figure 3. Those curves show, for example, that temperature changes with time are positive in regions to the right of an unstable state of Figure 1 and negative in regions to the left. They show further that the initial and the eventual responses are opposite; for example, on curve (a) the outlet temperature began first to decrease when the change in recycle ratio was made, but it eventually increased with time. The duration of its decrease was approximately one reactor residence time.

As a final item of interest, we discuss briefly our attempts to utilize automatic control at an unstable state. Our procedure in these attempts was to manipulate the system manually to the point where very steady operation was achieved at the set point. We then switched the three-mode controller operation from manual to automatic. The switching caused no bumping of the valve position whatsoever, but invariably automatic control failed to maintain operation near the set point. After a short time, perhaps 20 sec. at most, as the outlet temperature began to drift, control action would cause the control valve to move randomly between the completely open and completely closed positions leading, of course, to large erratic temperature fluctuations. This happened regardless of the control parameters or the modes selected. We shall not delve here into lengthy discussions of the reasons for the failures of automatic control, since our work in this regard was superficial rather than deliberate. The observations reported here are preliminaries for a more thorough study, currently underway, of control of naturally unstable states in this and similar systems which will include computer simulations.

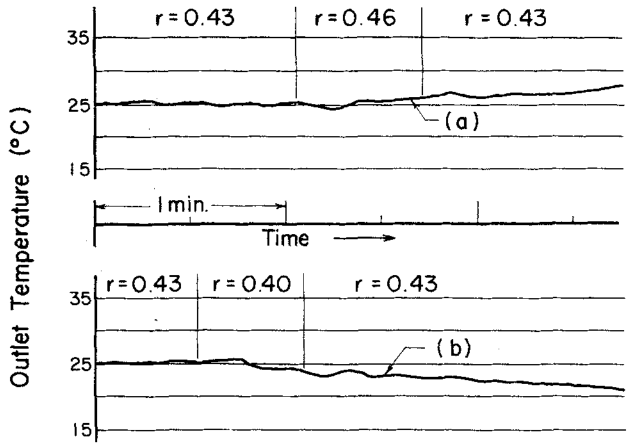

Fig. 3. Reactor behavior near an unstable state.

Aside from lags in the control system response and perhaps undesirable valve characteristics, one certain cause of difficulty in the loop reactor with conventional automatic control, and perhaps the main reason for its failure is the delay in response of the measured variable to the control action. As discussed earlier, the initial effect of control action is an outlet temperature change in the wrong direction. This causes the controller to increase its action even further. In our procedure for manual control, we compensated for this delay in response and for the initial effect when it was observed by delaying further manipulation. It would seem that either a small on-line computer or some electronic or mechanical signal delaying device would be required in the utilization of automatic control.

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NOTATION

Q_F = total volumetric flow rate of fresh feed
r = recycle ratio defined as the fraction of the total reactor stream which is recycled

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