Steady State Multiplicity and Stability in an Adiabatic Controlled Cycled Stirred Tank Reactor

Steady state multiplicity in exothermic adiabatic reaction systems has previously been demonstrated by a number of authors. Specifically, the work of Root and Schmitz proved the existence of multiple steady states in a loop reactor, but difficulty was encountered in controlling such a reaction system at the intermediate steady states.

Since a close analogy can be demonstrated between loop reactors and controlled cycled reactors (CCTR), it appeared reasonable to attempt to achieve steady state multiplicity in a CCTR. When the chemical reaction of Root and Schmitz was carried out in a CCTR, it proved relatively easy to obtain experimental values of intermediate steady states and to control the reactor at these conditions by means of a simple on-off temperature controller.

This work suggests that chemical systems displaying steady state multiplicity can be experimentally investigated in a CCTR and that cyclic operation may be the best way for controlling such reactions systems.

J. AUSIKAITIS and A. J. ENGEL

Department of Chemical Engineering
Pennsylvania State University
University Park, Pennsylvania 16802

SCOPE

The existence of multiple steady states in exothermic adiabatic reaction systems has been demonstrated both experimentally and theoretically by a number of authors over the past ten years. Briefly, it can be shown that for such reactions in which heat is removed exclusively by the enthalpy of the product leaving the reactor, three steady states are possible for a given set of reaction conditions. Two of these steady states, one at a low temperature and low conversion, the other at high temperature and high conversion, are stable, while the third, at intermediate temperature and conversion, is unstable, insofar as any slight operating disturbance at this state will cause the system to move rapidly to one of the two stable conditions.

Root and Schmitz (1969) first demonstrated the existence of a liquid phase reaction system showing steady state multiplicity: The oxidation of aqueous sodium thiosulfate by hydrogen peroxide in a recycle plug flow reactor (loop reactor). Although these authors successfully explored the unstable steady state region of this reaction, they had difficulty controlling the reaction under such conditions.

It can readily be demonstrated that an almost exact mathematical analogy exists between a loop reactor and a controlled cycled stirred tank reactor (CCTR). The latter is a stirred tank reactor in which part of the reactor contents is periodically dumped and replaced with fresh feed, while operating as a batch reactor between feeding and dumping. Codell and Engel (1971) suggested that such a unit might well be eminently suitable for stable operation under exothermic adiabatic conditions, and thus it appeared promising to attempt to carry out the reaction of Root and Schmitz in a CCTR, with the objective of further exploring the unstable steady state region and to determine if the reaction can be successfully controlled under such operating conditions. This type of operation would be desirable from both the points of view of reactor safety and the ability to determine unstable steady states in new reaction systems.

CONCLUSIONS AND SIGNIFICANCE

The study was carried out in three parts: First, a computer model indicated that the results of Root and Schmitz could, in fact, be duplicated with a CCTR. Second, this hypothesis was verified experimentally with a 1-liter jacketed stirred tank reactor which was operated at nearly adiabatic conditions. A series of runs in which 80% of the reactor contents were dumped each cycle essentially matched Root and Schmitz's data at a corresponding recycle ratio of 20% and further indicated that unstable steady state data could be obtained in a CCTR. However, the unstable steady state could not be maintained for any significant length of time. Therefore, as a third part of the study, an attempt was made to control the reaction in the instability region. This was accomplished by controlling the length of the batch reaction portion of each reactor cycle by means of a thermocouple and an on-off controller. Whenever the reaction temperature reached a preset point, a predetermined fraction of the reactor contents would be dumped and fresh feed added, whereupon the cycle repeated. By these means, the unstable

Correspondence concerning this paper should be addressed to A. J. Engel. J. Ausikaitis is with Union Carbide Corporation, Tarrytown, New York.

steady state was, in fact, completely stabilized so that operation for an indefinite time could continue under these conditions. Moreover, when process disturbances were deliberately introduced, the system would always return to the intermediate steady state rather than seeking the high or low value, as in other studies.

This work has provided, for the first time, experimental verification of multiple steady states in a cyclic reactor. More important, however, it indicates that the unstable steady state found in many exothermic adiabatic reactions can be stabilized safely by the use of a relatively simple control scheme and a CCTR. This further suggests that the CCTR might be a useful device in which to carry out inherently unstable exothermic reactions, particularly for such cases in which the intermediate steady state might be desirable for reasons of product selectivity.

In recent years, the existence of chemical reaction systems having more than one stationary steady state has been the focal point of a number of theoretical studies (Aris and Amundson, 1957, 1958; Bilous and Amundson, 1955; Lin and Palermo, 1967; Luss and Amundson, 1967; Mukherjee and Doraiswami, 1965; Reilly and Schmitz, 1966, 1967; Schmeal and Amundson, 1966). Principally, the phenomenon of steady state multiplicity arises in simple exothermic reactions carried out in adiabatic reactors in which the temperature level at which the reaction proceeds is maintained exclusively by the heat of reaction. Under such conditions, as the temperature rises, the reaction rate increases rapidly in the normal exponential manner, but the heat losses, which consist of the sensible heat of the reaction products and some leakage to the surroundings due to the nonadiabacity, will increase approximately linearly with temperature. This combination of circumstances can, under the appropriate conditions, lead to as many as three steady state temperatures for the reaction system when the heat production and consumption just balance and all other variables remain fixed. It is usually the case, however, that when steady state multiplicity occurs, the high and the low steady states are stable, while the intermediate steady state is highly unstable, so that when it is even slightly perturbed in temperature, the system will rapidly reestablish one of the two extreme steady states. Since the control of chemical reactors is of vital importance in determining the total operation of a chemical plant, the need for understanding and controlling unstable reactors is obvious, particularly in the case of highly exothermic reactions in which uncontrolled temperature rises could prove disastrous.

Recent experience with controlled cycled process operations has suggested to a number of investigators (Codell and Engel, 1967; Douglas, 1967; Fang, 1966; McWhirter, 1962; Schrodt, Sommerfeld, and Martin, 1967) that this mode of operation offers a considerable improvement in operating stability over conventional steady state processes. (By controlled cycling is meant a square-wave, on-off type of operation, as contrasted with sinusoidal or pulsing types of behavior.) A number of theoretical and experimental studies on controlled cycled extraction and distillation columns, gas absorbers, and particle separators (McWhirter, 1962; Robertson and Engel, 1967; Robinson and Engel, 1967) has suggested that unwanted disturbance in the system, beyond those deliberately induced, can be easily controlled by the cycled system while similar perturbations often cause extreme control difficulties in the corresponding steady state operation. Although a considerable amount of effort has been expended on investigating controlled cycled stirred tank reactors (Codell and Engel, 1971; Fang, 1966; Silverman, 1969), experimentation in this area has been somewhat hindered by the scarcity of well defined chemical reactions for which the kinetics are sufficiently understood to make cycled reactor analysis feasible.

The motivation for this work was, therefore, a direct result of previous successful work in two areas. Root and Schmitz (1969) and Vejtasa and Schmitz (1970) for the first time showed experimentally the presence of multiple steady states in a liquid phase exothermic reaction with both a loop reactor and a continuous stirred tank reactor (CSTR). Codell and Engel (1971) presented a mathematical study of a controlled cycle tank reactor (CCTR) using hypothetical rate expressions and claimed that the CCTR was often less sensitive to disturbances than either the CSTR or plug flow reactor. In addition, they claimed that CCTR's should be of particular advantage for exothermic reactions under adiabatic conditions.

STEADY STATE MULTIPLICITY

Root and Schmitz (1969) successfully demonstrated that the characteristics of an adiabatic loop reactor could be determined without complete knowledge of chemical kinetics. For the first time, they showed experimentally the existence of multiple steady states in a liquid phase exothermic reaction. Immediately following this work, Vejtasa and Schmitz (1970) using the same reaction and the same kinetic information, showed that from just the data obtained from an adiabatic batch reaction, intermediate as well as stationary steady states could be predicted with accuracy. The reaction used and initial conditions for the batch reaction are as follows:

$$2\,Na_2S_2O_3 + 4\,H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4\,H_2O$$

Initial Conditions:

$$1.2M\ H_2O_2, \qquad 0.8M\ Na_2S_2O_3, \qquad T_i = 0°C$$

In order to use the information obtained from the adia-

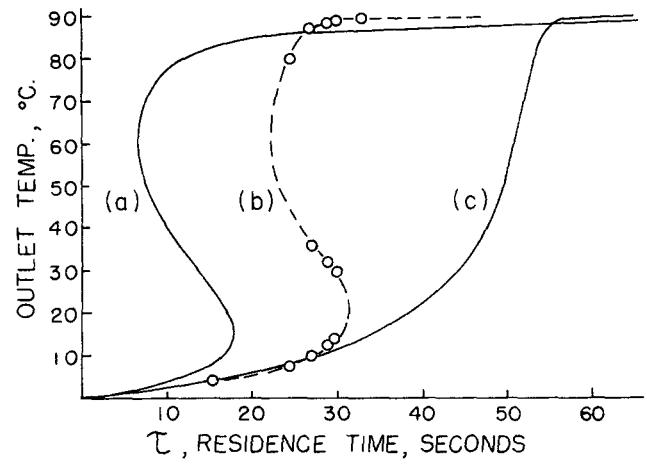

Fig. 1. Steady state temperature vs. residence time: (a) Vejtasa's (1969) adiabatic CSTR; (b) Root's (1968) adiabatic loop reactor with recycle ratio of 0.2; and (c) Root's (1968) adiabatic batch reactor data.

batic batch reaction for prediction of steady state characteristics in Root's adiabatic loop reactor, in Vejtasa's adiabatic CSTR, and in the adiabatic CCTR under investigation here, the inlet conditions of the fresh feed streams must correspond to those initial conditions given above. Some of the predicted steady state curves as determined from the results of Root and Vejtasa as well as the adiabatic batch data are shown in Figure 1.

CONTROLLED CYCLED TANK REACTOR

Codell and Engel (1967) carried out a theoretical investigation of a controlled cycled tank reactor (CCTR) for various types of reaction mechanisms and compared the CCTR's performance to the more conventional continuous stirred tank reactor (CSTR) and plug flow reactor. The operation of the CCTR can be described as follows:

1. During the fill time t_F the stirred tank is filled with fresh feed as rapidly as possible until the desired total volume V_T is reached.
2. During the batch time t_B the reaction is carried out at constant total volume.
3. During the dump time t_D the reactor contents are dumped as rapidly as possible until a fraction F of the original total volume remains.

The preceding sequence is started over again from Step 1 and there is no time delay between the end of one step and the beginning of the next.

Consider the reaction

$$A + B \ldots \rightarrow R + S + \ldots$$

whose kinetics and general rate expression can be expressed as

$$r = f(k, C_A, C_B, \ldots)$$

The CCTR reaction system can now be represented by the following set of equations:

$$\frac{dC_A}{dt} = \frac{q}{v}(C_{Af} - C_A) - r \quad \text{during } t_F$$

$$\frac{dC_A}{dt} = -r \quad \text{during } t_B$$

$$\frac{dC_A}{dt} = -r \quad \text{during } t_D$$

It may be noticed from the above equations that during t_B and t_D the CCTR is performing essentially as a batch reactor and that only during t_F does the CCTR resemble a backmix reactor. During the dump time, product leaves the CCTR over a finite amount of time, and its average outlet concentration is given by

$$\overline{C}_A = \frac{\int_0^{t_D} qC_A dt}{\int_0^{t_D} q dt} = \frac{\int_0^{t_D} C_A dt}{t_D}$$

Experimentally, it is often significantly easier to monitor temperature versus time than it is to monitor concentration versus time in a reactor. This, however, hinges upon the constraint that we can get enough information needed from the temperature alone. Therefore we might make use of the fact that for a simple exothermic adiabatic reaction the temperature of the reactor contents is directly proportional to conversion, provided the heat capacity of the reactants and the heat of reaction remain constant

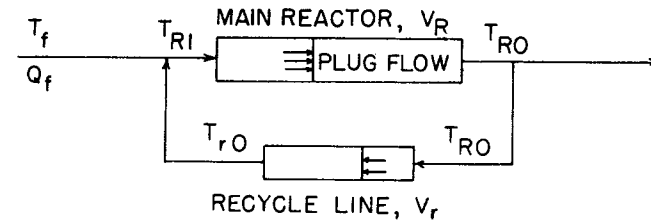

Fig. 2. Schematic loop reactor.

over the temperature range under consideration. With these assumptions made for this type of mechanism we can rewrite the describing CCTR equations in terms of temperature:

$$\frac{dT}{dt} = \frac{q(T_f - T)}{v} + \frac{(-\Delta H)r}{\rho C_p} \quad \text{during } t_F$$

$$\frac{dT}{dt} = \frac{(-\Delta H)r}{\rho C_p} \quad \text{during } t_B$$

$$\frac{dT}{dt} = \frac{(-\Delta H)r}{\rho C_p} \quad \text{during } t_D$$

Similarly, during the dump time, product is discharged at some average temperature $\overline{T}_O$, given by

$$\overline{T}_O = \frac{\int_0^{t_D} T_O dt}{t_D}$$

COMPARISON OF THE CCTR TO THE LOOP REACTOR

Although not readily apparent, the CCTR with instantaneous feed time is an exact mathematical analog of the loop reactor. The schematic of the loop reactor is depicted in Figure 2. The similarities in the describing equations for a batch reactor and a plug flow reactor is not a new concept, and, since the loop reactor is essentially two plug flow reactors, that is, one for the main reactant stream and the other for the recycle line, the reaction path in both sections follows that of a batch reactor. The analogies between the CCTR and the loop reactor now become more apparent. First, the holdup time in the main reactor section corresponds exactly to t_B of the CCTR. Also the temperature at the outlet of the main reactor T_{RO} corresponds to the temperature just at the end of the batch time T_B. Second, the holdup time in the recycle line corresponds to t_D of the CCTR. Also the temperature at the recycle line outlet T_{rO} corresponds to the temperature at the end of the dump time T_D. Last, the recycle ratio r in the loop reactor corresponds to the quantity $(1 - F)$ in the CCTR.

The only difference in the two reactor types, besides physical appearance, is that the CCTR requires a finite period of time t_F to reestablish the original total volume. The loop reactor, on the other hand, has instantaneous mixing of fresh feed and recycled product.

Another interesting aspect of the CCTR is that in the limits as F approaches 0 and 1, the CCTR approaches the operation of a CSTR and batch reactor respectively, while the same can be said of a loop reactor when the recycle ratio approaches 1 and 0.

COMPUTATIONAL METHOD FOR CCTR

Some of the assumptions Root (1968) used in his loop reactor will also hold for the CCTR. An adiabatic batch reactor is a system of constant enthalpy. Because a single

step kinetic model is assumed, the reaction path (a state curve of concentration versus time) can be represented by the proportional state curve of temperature versus time. This state curve is the adiabatic batch reaction curve of Figure 1. The temperature changes in the CCTR during each step are calculated by an iterative stepping procedure along this curve, for which the time steps for the batch and dump periods may be described mathematically as

$$T - T_i = \int_{t(T_i)}^{t(T_i)+\Delta t} \frac{(-\Delta H)r}{\rho C_p}\, dt$$

and during the feed period as

$$T - T_i = \left[F \int_{t(T_i)}^{t(T_i)+\Delta t} \frac{(-\Delta H)r}{\rho C_p}\, dt \right] - \left[\frac{(1-F)}{\Delta t} \int_0^{\Delta t} \frac{(-\Delta H)r}{\rho C_p}\, dt \right]$$

With the values of V_T, F, $(-\Delta H)$, ρ, C_p, t_F, t_B, and t_D set at constant values, the iterative calculations are allowed to proceed until a quasi steady state is achieved at a residence time given by

$$\tau = \frac{t_F + t_B + t_D}{F}$$

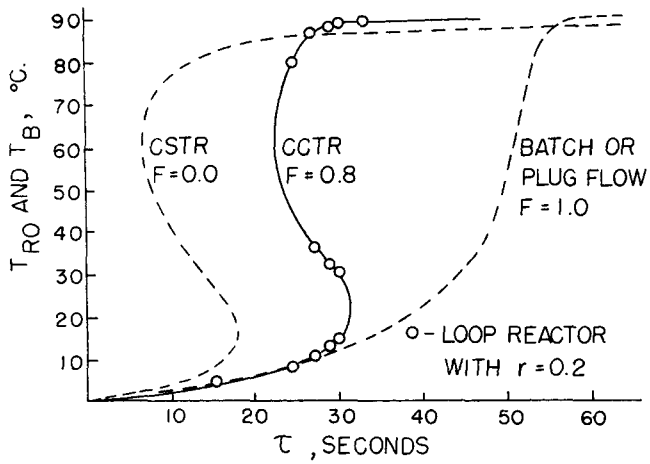

Fig. 3. Comparison of theoretical quasi steady states of CCTR model to corresponding steady state points of Root's (1968) loop reactor.

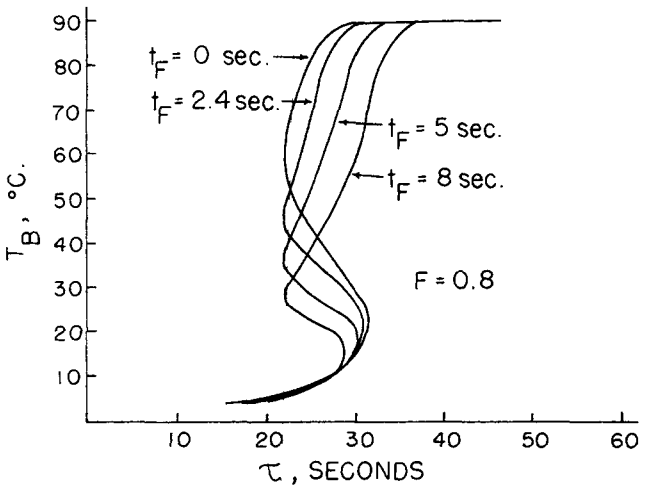

Fig. 4. Predicted quasi steady state temperature for increasing durations of the feed time in the CCTR.

During the operations of the CCTR one of the variables q is set equal to zero for a finite period of time (t_B). Because of this, an analytical solution was not attempted, since this sort of problem requires singular perturbation techniques which were considered beyond the scope of this work.

THEORETICAL RESULTS

If the CCTR is actually the mathematical analog of the loop reactor, it might be useful to show how the model for the CCTR compares with values taken from the predicted theoretical curves for Root's loop reactor. The temperature used for this direct comparison were T_{RO} of the loop reactor and T_B of the CCTR. Root presented his predicted steady state outlet temperatures versus recycle ratio for constant feed rates Q_f. For this comparison only cross-plotted values for $r = 0.2$ were used. With this value of r and Q_f we can calculate the holdup time in each section from the values given for V_r and V_R. The result of this comparison is shown in Figure 3. It can be seen that the agreement is excellent, which indicates that the analogy does indeed exist.

For the comparison presented in Figure 3, t_F (as explained previously) must be set equal to zero in order for the analogy to hold, while experimentally, t_F must be some finite value in the CCTR. Because the total cycle time ($t_F + t_B + t_D$) will range from 5 to 30 seconds, the value of t_F is significant. The effect of increasing the duration of t_F was predicted computationally and is shown on Figure 4.

It may be seen that increased values of t_F, everything else remaining constant, result in lower temperatures for a given residence time. Therefore we may conclude that as far as reactor conversion is concerned, the loop reactor will always outperform the CCTR for the same average residence time. As t_F becomes small compared to the total cycle time for slower reactions, this detrimental effect is minimized.

The effect of increasing t_D is less significant. Because the temperature acts intensively during the dump time, the only effect of increasing t_D will be to raise the integration range for calculating the average outlet temperature $\overline{T_O}$. However, $\overline{T_O}$ will be exactly the same for a given residence time where $t_B + t_D$ = constant.

EXPERIMENTAL METHOD

All experimental runs were carried out in a 1000-ml. Plexiglas stirred tank. The tank was surrounded by Pyrex pipe such that the annular space could be evacuated in order to approach adiabatic operation. Flow of fresh feed into the reactor and product out of the reactor were controlled with solenoid valves actuated by automatic cycle timers. Two 17-liter feed tanks were filled with 2.4M H_2O_2 and 1.6M $Na_2S_2O_3$. Both tanks were cooled to -3°C before beginning a run. Just before each reactant entered the CCTR, each feed line passed through an ice bath maintained at 0°C so that fresh feed entered the CCTR at exactly 0°C. The temperature in the CCTR was monitored continuously with a copper-constantan thermocouple and a strip chart recorder. The values of t_F and t_D and the pressure on the two feed tanks were preset such that the proper fraction would be dumped and filled in the CCTR. For each run, t_B was set and the CCTR allowed to come to a pseudo steady state before t_B was reset. The reactor and supporting equipment are presented in Figure 5.

Experimental runs were carried out for a dumping fraction of $F = 0.8$. The total volume V was set at 500 ml in order to avoid splashing of reactant. The values of $t_F = 2.5$ s and $t_D = 2.35$ s were predetermined for proper operation. For each

data point, t_B was set at a value between 0 and 25 s and the CCTR was allowed to come to a quasi steady state before t_B was altered. Since the CCTR is never really at steady state, a quasi steady state is one in which the new recorded temperature swings are exactly the same as the previous cycle's. The CCTR took about 1 to 2 min. to reach this condition from start up or t_B change. Typical experimental temperature versus time data for start up to quasi steady state are depicted in Figure 6.

EXPERIMENTAL RESULTS

In operating an experimental adiabatic reactor under transient conditions, the sensible heat of those parts of the apparatus in direct contact with the reaction mixture become a significant part of the total heat load of the system. These parts include the reactor walls, agitator, and thermowells. In the case of Root's loop reactor and Vejtasa's CSTR, the equipment temperature lagged behind that of the reaction mixture, but eventually, when steady state was achieved, these temperatures became uniform. In the present work, however, equipment temperatures always lagged reaction temperatures because of the inherent transient operation of the CCTR. Since the rigorous analysis of transient heat transfer through the reactor walls and other components was beyond the scope of this work, a simplified model was assumed.

An empirical heat transfer coefficient of 5.68 kw/m² °K (1,000 B.t.u./hr. ft.² °F) was estimated for the convection of heat from the liquid contents to the walls of the reactor. Therefore, one can assume negligible resistance in the liquid film. One can also assume that the walls of the reactor and all other equipment in contact with the reaction mixture have infinite thermal conductivities. With these assumptions, one can state that the equipment temperature will always follow exactly that of the reaction mixture if the system is indeed adiabatic. Therefore, instead of considering a dumping fraction based on volume, it might be best to base the dumping fraction on total enthalpy. Physically, this means that when fresh feed is charged to the reactor during t_F, the cold feed must lower the temperature of the reactor walls and other components as well as the liquid contents. Since it was estimated that the latent heat of the equipment and liquid contents was 1.28 times that of the liquid contents alone, one can do the appropriate calculations for $F = 0.8$ (which is based on volume) and arrive at an effective dumping fraction of $F' = 0.6$ based on enthalpy. Therefore in Figure 7, data are plotted for an experimental dumping fraction of $F = 0.8$ and these points are compared to the predicted quasi steady states from the CCTR computer model using $F' = 0.6$. The agreement is quite good considering the severity of the assumptions and that the thermal conductivity of Plexiglas is in fact quite low.

In Figure 7, the data plotted as circles corresponds to both low and high stable quasi steady state points. Because the intermediate portion of the hysteresis loop corresponds to that region that is inherently unstable, no operation may be expected there for any extended period time. In order to obtain data in this region the intermediate must be approached as closely as possible and then the response of the system noted. This method, used first

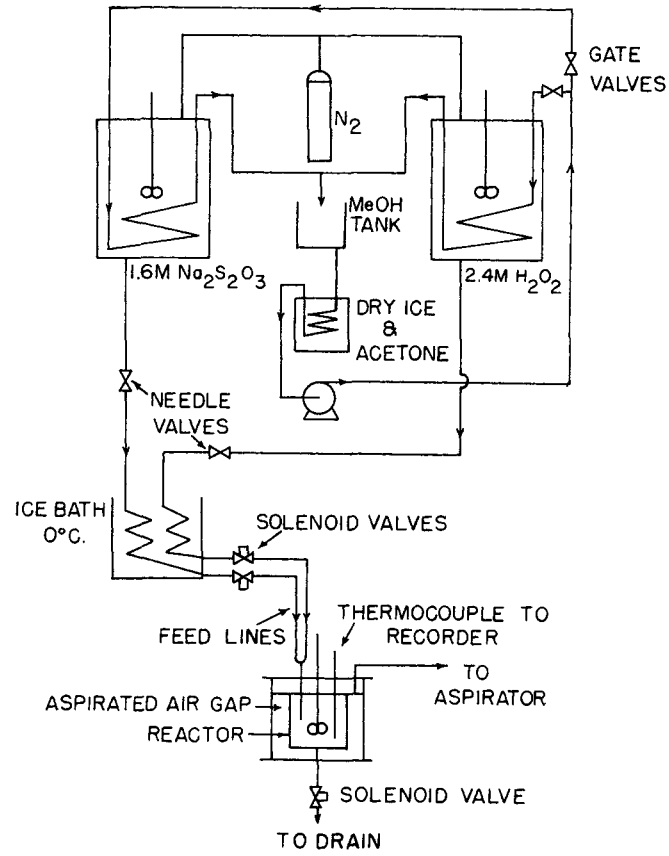

Fig. 5. Experimental feed and reactor system.

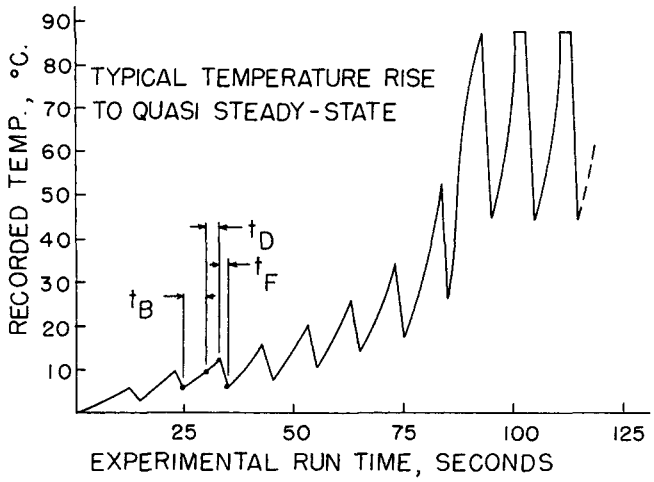

Fig. 6. Recorded temperature vs. time for CCTR startup to quasi steady state.

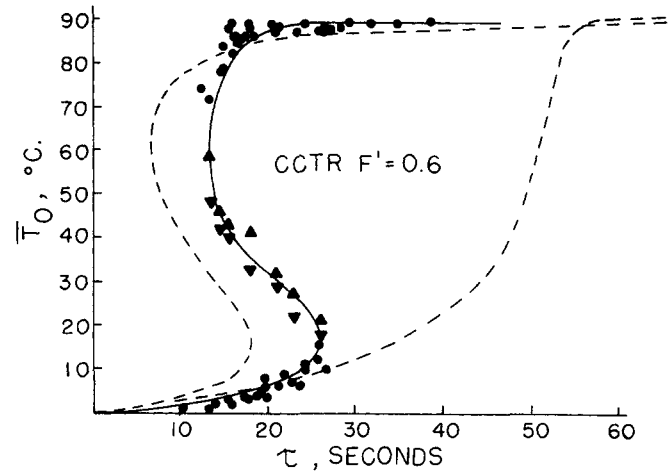

Fig. 7. Experimental CCTR quasi steady states vs. residence time. $V = 500$ ml., $t_F = 2.5$ sec., $t_D = 2.35$ sec., $F = 0.8$: ● = steady state; ▲ = approached from below; and ▼ = approached from above.

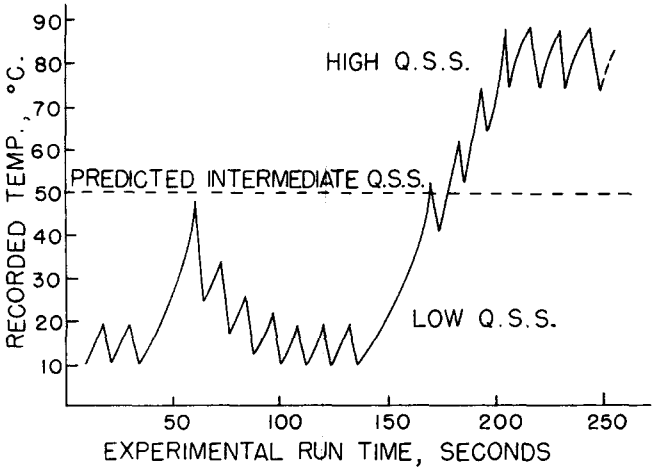

Fig. 8. Typical approach by the CCTR to the unstable intermediate steady state.

by Vejtasa (1969), consisted of perturbing the temperature into the intermediate region. While operating the CCTR at the low quasi steady state, the automatic timers are shut off during t_B, allowing the temperature in the reactor to rise into the region of the predicted intermediate state. At the precise moment when the desired temperature is reached, the timers are again actuated to assume normal operation as before. Therefore, the downward pointing triangles of Figure 7 represent, for a specified residence time, the highest temperature perturbation allowed by the CCTR for return again to the low stable state. The upward pointing triangles, similarly, represent the lowest temperature perturbation allowed before return to the high stable state. With successive experimental perturbations the region of the unstable intermediate existence may be narrowed down to that region between the upward and downward pointing triangles. Any perturbations in the regions where only unique stable states exist will always result in the return of the CCTR to the original state from which the perturbation originated. Figure 8 depicts such perturbations in the multiple state regime.

OPERATION IN THE UNSTABLE REGION

Vejtasa made no attempts to operate his CSTR in the intermediate unstable region with automatic control. However, after gaining experience, Root was able to manually control the loop reactor for a maximum of seven minutes in the unstable region. Several attempts were made to stabilize the system using automatic feedback control. A three-mode controller was used in the loop reactor to sense the outlet temperature and to vary the amount of recycle with a control valve. The results of these unsuccessful attempts are shown in Figure 9.

The easiest and most accessible control variable in the CCTR is t_B. If the value of t_B can be adjusted continually such that the CCTR will dump product at a temperature in the intermediate unstable state region, then we can successfully operate in this region. Since the CCTR always exhibits transient internal temperatures, then if the temperature can be sensed just before the intermediate steady state is reached, the dump cycle can be actuated at the proper moment. All that is required experimentally is an on-off temperature controller that trips a relay to actuate the dump cycle as soon as the reaction mixture has reached the preset temperature. A Honeywell R7161B Indicating Potentiometer Controller proved to be quite adequate. Therefore the new cycle becomes:

1. Fill (t_F and v held constant)
2. Batch operation until set point is reached (variable t_B)
3. Dump (t_D and F held constant)

During the operation of the CCTR with automatic temperature control the requirements for quasi steady state behavior became different. Rather than waiting for repetitive temperature cycles, now the lengths of each cycle must be equal and repetitive. Also the residence time must be calculated from the length of the quasi steady state cycle time (as recorded) and the fraction dumped. Figure 10 depicts a typical experimental result for start up to quasi steady state in the CCTR with automatic temperature control.

This form of automatic control was completely successful. The CCTR was able to operate in the entire intermediate unstable region with relative ease. In fact, obtaining data in this manner was so simple that another curve for $F = 0.6$ was also verified. The data are shown on Figure 11.

Deviations from the intermediate state during experimental operation did not amount to more than ±2°C in $\overline{T_O}$ for a dumping fraction $F = 0.8$, while at $F = 0.6$, deviations were ±5°C. It was also noticed that for opera-

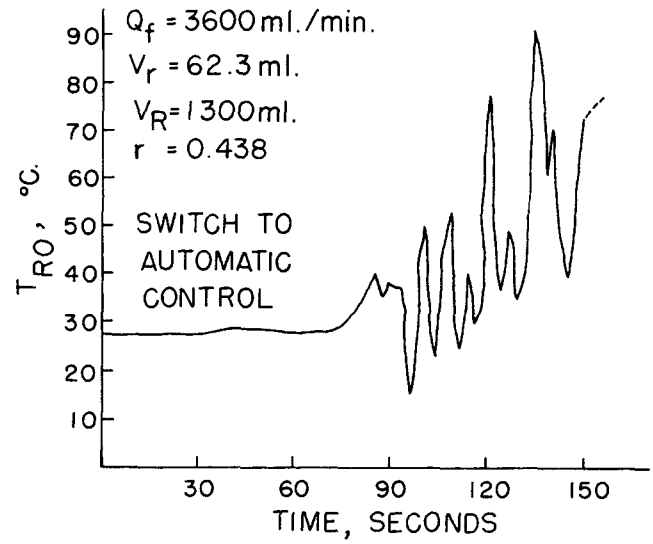

Fig. 9. The effect of automatic control on an intermediate steady state in Root's (1968) loop reactor.

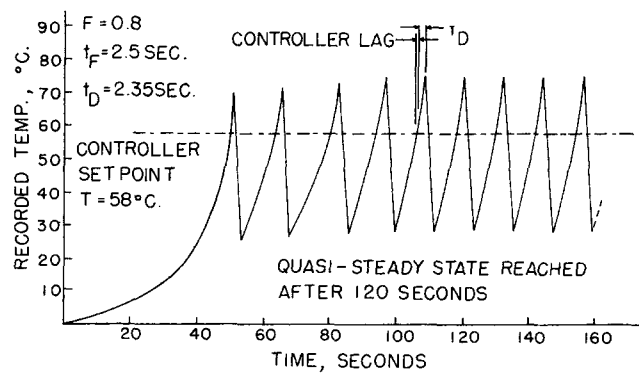

Fig. 10. Approach of the experimental CCTR with automatic temperature control to quasi steady state from initial startup.

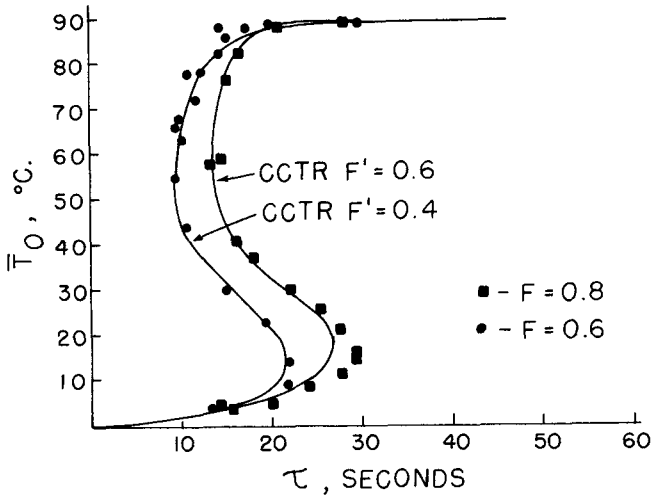

Fig. 11. Experimental quasi steady states in the CCTR with automatic temperature control.

tions with $F = 0.6$ the CCTR showed some decrease in stability. This can be expected since the amount dumped and replaced is actually the controlling mechanism. One run was made to see if the CCTR would drift from the set point for a run of long duration. Therefore, the CCTR was started up and operated at one set point until the fresh feed was exhausted. The CCTR held completely steady in the intermediate region for 29 min. which represents nearly 80 CCTR cycles. There was no reason to believe that the CCTR could not have operated at this unstable point indefinitely.

Another interesting factor was the transient response of the CCTR to disturbances. Since this is essentially what was done to obtain data in the unstable region without automatic control, a large amount of information regarding response was accumulated. In all cases, without automatic control, the CCTR responded to disturbances by recovering to the original stable state approximately four times faster than either the CSTR or loop reactors. For those cases where automatic control was used, the CCTR took a maximum of 3 to 5 cycles (20 to 45 s) to recover.

CONCLUSIONS

This work has provided for the first time experimental verification of multiple steady states in a cyclic reactor configuration with a liquid phase, homogeneous, exothermic reaction. It has also provided experimental confirmation of the theoretical CCTR model, which to date has been lacking as has most experimental work on other types of cyclic reactors. Most importantly, it has been shown for this reaction system that the CCTR with the most basic control system could operate in the intermediate unstable region with relative ease by eliminating the control problem. Recoveries from disturbances were also moderately better than those reported for the experimental operation of the continuous loop reactor and CSTR.

This work further suggests that inherently unstable reactions might be best carried out in cyclic reactors. Even under the condition where an operating point might be locally stable but not globally stable, the ability to make all operating points globally stable may mean the difference between successful operation of a reactor or disaster caused by runaways.

NOTATION

C = reactant concentration
$\overline{C}$ = average product concentration
C_p = heat capacity
F = fraction of reactant dumped
F' = effective fraction dumped
ΔH = heat of reaction
k = reaction rate coefficient
Q = flowrate
q = flowrate
r = reaction rate
r = recycle ratio
T = temperature
$\overline{T}$ = average product temperature
t = time
V_T = total volume
v = instantaneous volume

Greek Letters

ρ = density
τ = residence time

Subscripts

A, B = reactants
Af = reactant A in feed
B = batch
D = dump
F = feed
f = feed
i = initial
O = outlet
R, S = products
R = main reactor
RI = main reactor inlet
RO = main reactor outlet
r = recycle line
rO = recycle line outlet

LITERATURE CITED

Aris, R., and N. R. Amundson, "Stability of Some Chemical Systems Under Control," *Chem. Eng. Progr.*, **53**, 227 (1957).

———., "An Analysis of Chemical Reactor Stability and Control—I. The possibility of Local Control, with Perfect or Imperfect Control Mechanisms," *Chem. Eng. Sci.*, **7**, 121 (1958).

Bilous, O., and N. R. Amundson, "Chemical Reactor Stability and Sensitivity," *AIChE J.*, **1**, 513 (1955).

Cannon, M. R., "Controlled Cycling Improves Various Processes," *Ind. Eng. Chem.*, **53**, 926 (1961).

Codell, R. B., "A Theoretical Study of the Controlled Cycling Stirred Tank Reactor (CCTR)," M.S. thesis, Pennsylvania State Univ., University Park (1967).

———., and A. J. Engel, "A Theoretical Study of a Controlled Cycle Stirred Tank Reactor," *AIChE J.*, **17**, 220 (1971).

Douglas, J. M., "Periodic Reactor Operation," *Ind. Eng. Chem. Process Design Develop.*, **6**, 43 (1967).

Fang, M., "A Theoretical and Experimental Investigation of Controlled Cycling Stirred Tank Reactor," M.S. thesis, Penn. State Univ., University Park (1966).

Lin, K. H., and J. A. Palermo, "Kinetics and Reaction Engineering, I" *Ind. Eng. Chem.*, **59**, 51 (1967).

Luss, D., and N. R. Amundson, "Stability of Loop Reactors," *AIChE J.* **13**, 279 (1967).

McWhirter, J. R., "Theoretical and Experimental Analysis of a Controlled Cycling Distillation Column," Ph.D. thesis, Penn. State Univ., University Park (1962).

Mukherjee, S. P., and L. K. Doraiswamy, "Reaction Kinetics and Reactor Design," *Brit. Chem. Eng.*, **10**, 93 (1965).

Reilly, M. J., and R. A. Schmitz, "Dynamics of a Tubular Reactor with Recycle—Part I. Stability of the Steady State," *AIChE J.*, **12**, 153 (1966).

———., "Dynamics of a Tubular Reactor with Recycle—Part II. Nature of the Transient State," *ibid.*, **13**, 519 (1967).
Robertson, D. C., and A. J. Engel, "Particle Separation by Controlled Cycling," *Ind. Eng. Chem. Process Design Develop.*, **6**, 2 (1967).
Robinson, R. G., and A. J. Engel, "An Analysis of Controlled Cycling Mass Transfer Operations," *Ind. Eng. Chem.*, **59**, 22 (1967).
Root, R. B., "An Experimental Study of Steady State Multiplicity in a Loop Reactor," Ph.D. thesis, Univ. Illinois, Urbana (1968).
———., and R. A. Schmitz, "An Experimental Study of Steady State Multiplicity in a Loop Reactor," *AIChE J.*, **15**, 607 (1969).
Schrodt, V. W., J. T. Sommerfeld, and O. R. Martin, "Plant Scale Study of Controlled Cyclic Distillation," *Chem. Eng. Sci.*, **22**, 766 (1967).
Schmeal, W. R., and N. R. Amundson, "The Effect of Recycle on a Linear Reactor," *AIChE J.*, **12**, 1202 (1966).
Silverman, R. P., "Theoretical and Experimental Investigation of a Staged, Controlled-Cycling, Stirred Tank Reactor System," M.S. thesis, Penn. State Univ., University Park (1969).
Vejtasa, S. A., "An Experimental Study of Steady State Multiplicity in an Adiabatic Stirred Reactor," Ph.D. thesis, Univ. Illinois, Urbana (1969).
———., R. A. Schmitz, "An Experimental Study of Steady State Multiplicity in a Adiabatic Stirred Reactor," *AIChE J.*, **16**, 410 (1970).

Manuscript received June 14, 1973; revision received and accepted November 5, 1973.

An Empirical Correlation of Second Virial Coefficients

A new correlation of second virial coefficients of both polar and nonpolar systems is presented. It uses the Pitzer-Curl correlation for nonpolar compounds, but in a modified form. The second virial coefficient of nonhydrogen bonding compounds (ketones, acetaldehyde, acetonitrile, ethers) and weakly hydrogen bonding compounds (phenol) is fitted satisfactorily with only one additional parameter per compound, which is shown to be a strong function of the reduced dipole moment. Two parameters are needed for hydrogen bonding compounds (alcohols, water), but for alcohols, one parameter has been kept constant and the other expressed as a function of the reduced dipole moment. The extension of the correlation to mixtures is satisfactory, direct, and involves only one coefficient per binary.

CONSTANTINE TSONOPOULOS

Esso Reseach and Engineering Company
Florham Park, New Jersey 07932

SCOPE

Vapor-phase nonideality should properly be taken into account in the analysis and correlation of vapor-liquid equilibria, especially at superatmospheric pressures. For reduced densities up to ¼ (roughly speaking, up to pressures of 15 atmospheres), the effect of vapor-phase imperfection can be reliably calculated using only the second virial coefficient B of the pure components and cross-coefficients for each binary (for example, see Prausnitz, 1969).

A very successful correlation of the B of nonpolar gases has been proposed by Pitzer and Curl (1957); see Equation (6). The soundness and reliability of the Pitzer-Curl correlation make its use as the basis of a correlation of the B of polar systems highly desirable. The objective of this study was to extend the Pitzer-Curl correlation to the following polar compounds of interest: ketones, aldehydes, acetonitrile, ethers, alcohols, phenol, and water.

A similar approach has been taken by O'Connell and Prausnitz (1967) and by Halm and Stiel (1971), but both of these correlations are lacking in several respects, including reliability; they are fully discussed in the Appendix.* The O'Connell-Prausnitz correlation has been used widely (for example, in two important monographs on computer calculations for vapor-liquid equilibria; Prausnitz et al., 1967; Renon et al., 1971); it is therefore used as the basis of comparison with the new correlation.

Another correlation of the B of polar system which, while not using the Pitzer-Curl correlation, is based on a similar idea to ours is that proposed by Black (1958); it is discussed in the Appendix. Other correlations that are not based on the Pitzer-Curl correlation and are not considered here are those of Kreglewski (1969), Nothnagel et al. (1973), O'Connell (1971), and of Polak and Lu (1972).

The Appendix has been deposited as Document No. 02293 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., New York, N. Y. 10017 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.