A Theoretical Study of a Controlled-cycled Stirred-Tank Reactor

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A mathematical study was carried out for a stirred reactor in which the feed and product streams were periodically interrupted. The cycled reactor proved superior to a continuous stirred-tank reactor for first- and second-order reactions, and surpassed a plug-flow reactor for those cases in which the reaction rate passes through a maximum, such as autocatalytic and exothermic adiabatic reactions. Temperature-programmed cycled reactors were also studied, but appeared to have little advantage over conventional reactors.

Cyclic processes have stirred up great interest among chemical engineers because of their ability to improve the performance of various conventional unit operations such as distillation, absorption, and extraction. However, cyclic operation of reactors has led to some confusion with some reports indicating process improvement while others indicate the opposite.

The confusion regarding cyclic reactors stems entirely from a problem of nomenclature. The terms pulsed, cycled, and periodic have been applied to such systems, sometimes having similar and sometimes quite different meaning. Those cyclic or pulsed operations in which sinusoidal or square-wave disturbances are superimposed on the steady feed rate to a continuous stirred-tank reactor (CSTR) (5) are to be differentiated from those treated here, in which the constant feed rate is periodically interrupted, resulting in short batch reaction steps (*6*). The two systems present entirely different experimental and mathematical problems and cannot be compared in any simple way. A third type of system, a backmix reactor with steady feed and naturally occurring internal oscillations (chemical oscillators), should also be clearly differentiated.

The present study is an elaboration of that by Fang and Engel (*6*) in which the feed and product streams of a stirred reactor were periodically turned on and off, resulting in cyclic behavior (controlled cycling).

GENERAL

One of the chief advantages of a backmix reactor over batch and plug-flow reactors is its ability to avoid sensitive reactant and product concentrations lying between the initial and final concentrations. The controlled-cycled stirred-tank reactor (CCTR) has this same capability because it operates in a series of short batch reaction steps under such desired operating conditions that the initial and final concentrations during a batch step will meet the required concentration criteria. At the end of each batch reaction, part of the reactor contents is dumped and fresh feed is added to reestablish the normal reactor volume. After several such operating cycles, the CCTR will achieve pseudo steady state conditions where each reaction cycle is a duplicate of the previous one.

In general, a distributed feed plug-flow reactor can also avoid certain critical concentration ranges, and there is a superficial similarity between distributed feed reactors and the CCTR. However, it should be clear that although adjacent segments of a distributed feed reactor may have identical concentration patterns of a given reactant, they will also have progressively increasing concentrations of product, whereas the CCTR has identical concentration-time profiles of reactants and products for each cycle.

It is the purpose of this paper to demonstrate the feasibility of CCTR operation and also to show that the CCTR is frequently superior in conversion or size to other reactor systems.

THEORY

Consider the reaction

$$A + B + \cdots \xrightarrow{k} R + S + \cdots$$

whose kinetics are defined by the general rate expression

$$r = f(k, C_A, C_B, C_R, C_S, \cdots)$$

The reaction takes place in a perfectly mixed tank in the following manner:

1. During time t_1, the reactant is charged to the tank at constant volumetric rate q until filled to volume V.
2. During time t_2, the reaction proceeds at constant volume.
3. During time t_3, the reactor contents are discharged at rate q equal to the charge rate until a fraction δ of the reactor volume has been removed.

The preceding sequence is now repeated from step 1.

After correcting for the variation in reactor volume, it can be shown that the system is represented by the set of equations:

$$\begin{aligned} \frac{dC_A}{dt} &= \frac{q}{v}(C_{AF} - C_A) - r \quad \text{during charge period } t_1 \\ \frac{dC_A}{dt} &= -r \quad \text{during reaction period } t_2 \\ \frac{dC_A}{dt} &= -r \quad \text{during discharge period } t_3 \end{aligned} \tag{1}$$

During the discharge step, the average reactant concentration in the reactor and the effluent stream $\overline{C}_A$ is given by

$$\overline{C}_A = \frac{\int_0^{t_3} qC_A\,dt}{\int_0^{t_3} q\,dt} = \frac{\int_0^{t_3} C_A\,dt}{t_3} \tag{2}$$

The above reactor system has been described by Fang (*6*) and named controlled cycling stirred-tank reactor, or CCTR.

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Fang, however, assumed negligible reaction during the charge and discharge steps.

This study attempts to account for reaction over the full cycle and apply the concepts of the CCTR to various reaction systems. In all the calculated cases, δ is assumed to be less than unity, which causes transient conditions to exist not only in the various steps during a single cycle, but also from one cycle to the next until pseudo steady state operation is achieved. In most of the work presented here, a number of case studies were made because generalized relationships were impossible to obtain.

ISOTHERMAL IRREVERSIBLE REACTIONS

Consider the n^{th} order irreversible reaction

$$nA \xrightarrow{k} R$$

During the charge step (t_1)

$$\frac{dC_A}{dt} = \frac{q}{v}(C_{AF} - C_A) - kC_A^n \qquad (3)$$

During the batch step (t_2)

$$C_{A2} = C_{A1}e^{-kt_2} \qquad \text{(first-order reaction, } n = 1) \qquad (4)$$

or

$$C_{A2} = \frac{C_{AF}}{\dfrac{C_{AF}}{C_{A1}} + kt_2C_{AF}} \qquad \text{(second-order reaction, } n = 2) \qquad (5)$$

During the discharge step (t_3)

$$C_{A3} = C_{A2}e^{-kt_3} \qquad \text{(first-order reaction)} \qquad (6)$$

or

$$C_{A3} = \frac{C_{AF}}{\dfrac{C_{AF}}{C_{A2}} + kt_3C_{AF}} \qquad \text{(second-order reaction)} \qquad (7)$$

The average reactant concentration over the discharge step is

$$\overline{C}_A = \frac{C_{A2}}{kt_3}(1 - e^{-kt_3}) \qquad \text{(first order)} \qquad (8)$$

$$\overline{C}_A = \frac{C_{A2}}{kt_3C_{AF}}\ln(1 + kt_3C_{AF}) \qquad \text{(second order)} \qquad (9)$$

The dimensionless residence time of the reaction mixture in a CCTR is given by

$$\theta = \frac{t_1 + t_2 + t_3}{\delta}kC_{AF}^{n-1} \qquad (10)$$

Equations (3) through (10) were solved recursively on a digital computer for as many cycles as necessary to obtain pseudo steady state reactor operation, and for a variety of combinations of δ and k. The residence times needed to achieve the same conversion at the same volumetric flow rate as the CCTR were then calculated for a plug-flow and backmix reactor. For these reactors the residence time is defined as

$$\theta = \frac{V}{q}kC_{AF}^{n-1} \qquad \text{(See Appendix)} \qquad (11)$$

These results were compared with those of the CCTR and are shown in Figures 1 and 2 for first- and second-order reactions, respectively. It can be seen that the CCTR gives shorter reaction times than the backmix reactor, but approaches plug-flow reactor operation only in the limit when the dumping fraction δ approaches unity. Figure 2 shows that at low conversions, the CCTR is less efficient than the backmix reactor. This is caused by an excessive amount of the reaction time being spent in filling and dumping the reactor.

One of the chief advantages of a CCTR is its ability to avoid sensitive reactant concentrations lying between the

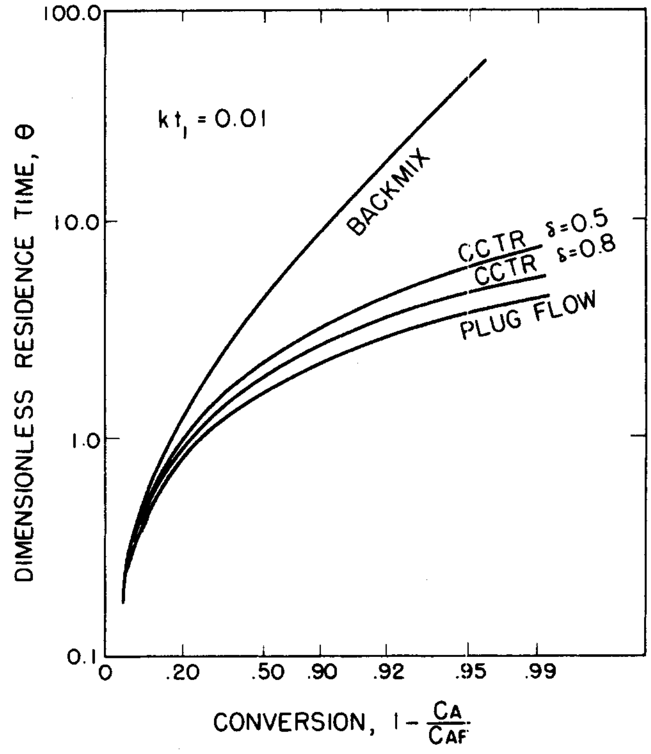

Fig. 1. Residence time to achieve a given conversion. First-order isothermal irreversible reaction.

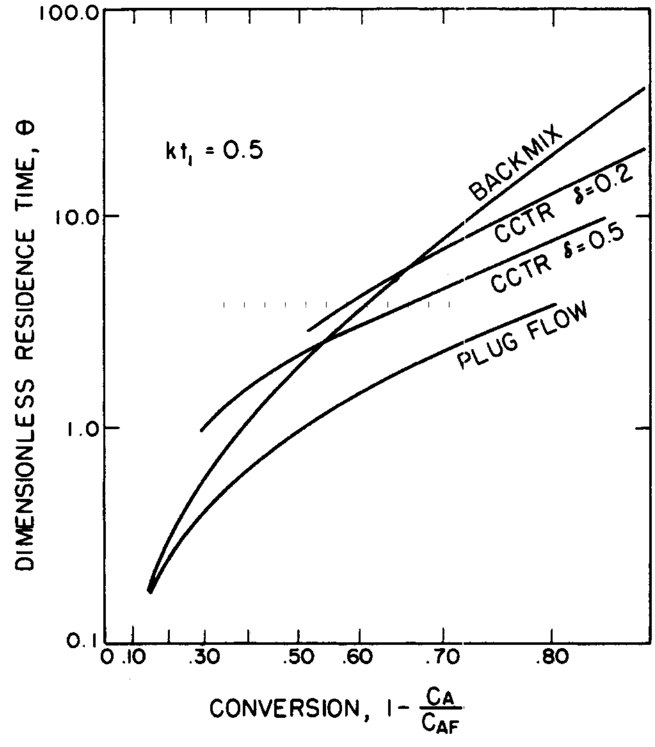

Fig. 2. Residence time to achieve a given conversion. Second-order isothermal irreversible reaction.

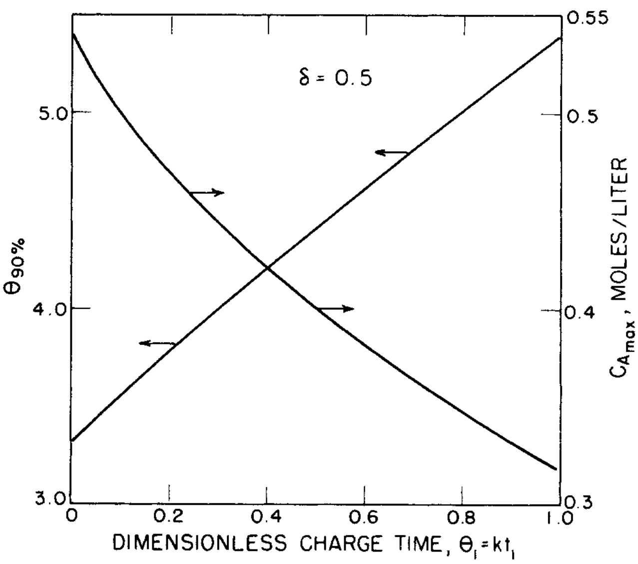

Fig. 3. Maximum concentration in reactor and time required to reach 90% conversion in a CCTR. First-order isothermal irreversible reaction.

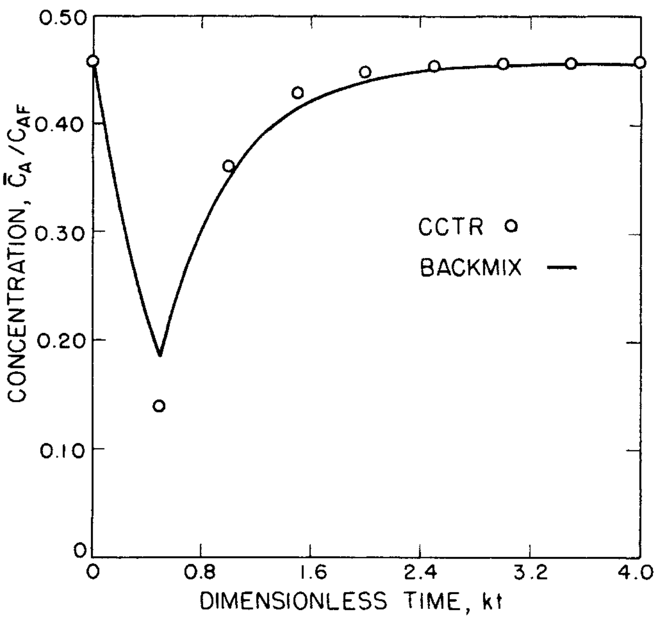

Fig. 4. Perturbation recovery. First-order reaction. −100% concentration disturbance for one cycle. $\delta = 0.5$; $V = 1$ liter; $q = 1$ liter/kt.

feed and the product concentrations, as shown in Figure 3. Here the maximum reactant concentration in the CCTR is plotted as a function of dimensionless charging or dumping time. Also shown is the dimensionless residence time to achieve 90% conversion. Short charging and dumping times lead to higher efficiency (lower residence time), but also entail higher reactant concentrations. Thus, for those reactions in which high reactant concentrations must be avoided, long charge times should be used. In all cases, however, it was shown that for a corresponding maximum reactant concentration, the CCTR was more efficient than the backmix reactor.

THE SENSITIVITY OF A CCTR AND BACKMIX REACTOR TO A CONCENTRATION DISTURBANCE

Several authors have claimed that cyclic processes are inherently less sensitive to disturbances than continuous processes (*6*, *8*). Fang (*6*) observed experimentally an apparently complete return to steady state, after a concentration disturbance, in only one or two cycles of a CCTR. However, he performed no quantitative studies on this phenomenon.

In the present work, a CCTR and backmix reactor of equal conversions and output were studied for first- and second-order irreversible isothermal reactions. When both reactors were at steady state, a concentration disturbance of ±100% was superimposed on the feed composition for the length of one CCTR cycle. Figure 4 illustrates a typical case. In general, when the reaction was first order for both positive and negative disturbances, the average outlet concentration from the CCTR was initially deflected more, but recovered more quickly than that from the backmix reactor. The same was true for the second-order reaction case with negative perturbation. However, when the reaction was second order and the disturbance positive, the CCTR showed a lesser deflection than the backmix reactor and also recovered more quickly.

The area under the concentration-time curve is perhaps a more meaningful analysis of reactor response, since it relates the displacement in product throughput to the disturbance. Figure 5 is the eventual displacement of unreacted reactant throughput caused by the disturbance. A lower absolute value indicates better performance.

In the first-order case the CCTR always does poorer than the backmix reactor. The second-order case leads to just the opposite conclusion. For positive disturbances and high dumping fractions, the CCTR excels, although it also does well for negative disturbance. These advantages accrue from the smaller volume needed in a CCTR for a given conversion and, in the positive disturbance case, the much higher reactant concentration during the charge step than in the backmix reactor. Both these effects are less important for the first-order case.

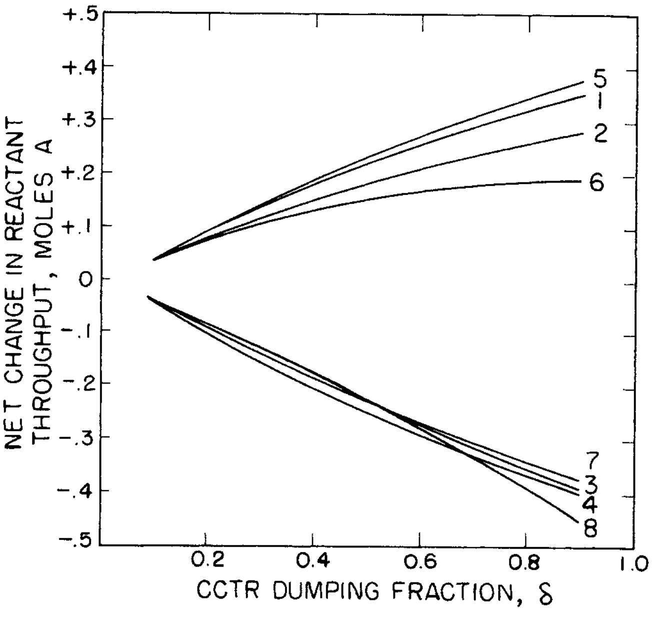

Fig. 5. Throughput of unconverted reactant. One-cycle disturbance.

No.	Reactor	Reaction order	Disturbance, %
1	Backmix	1	+100
2	Backmix	2	+100
3	Backmix	2	−100
4	Backmix	1	−100
5	CCTR	1	+100
6	CCTR	2	+100
7	CCTR	1	−100
8	CCTR	2	−100

AUTOCATALYTIC REACTIONS

For the autocatalytic reaction

$$A + R \xrightarrow{k} R + R \quad \text{(isothermal, irreversible)}$$

the reaction rate depends on both the product and reactant concentration. This leads to an unusual condition where the rate passes through a maximum with increasing conversion.

The design equations for the CCTR becomes

$$\frac{dC_A}{dt} = -kC_A(C_F - C_A) + \frac{q}{v}(C_{AF} - C_A) \tag{12}$$

where $C_F = C_{AF} + C_{RF}$.

During the charge step (t_1) Equation (12) was solved numerically, while during the batch and discharge steps, the following analytic solutions were used:

Batch step (t_2):

$$C_{A2} = \frac{C_F}{\left(\frac{C_F - C_{A1}}{C_{A1}} e^{kt_2C_F}\right) + 1} \tag{13}$$

Discharge step (t_2):

$$C_{A3} = \frac{C_F}{\left(\frac{C_F - C_{A2}}{C_{A2}} e^{kt_3C_F}\right) + 1} \tag{14}$$

The average product concentration is

$$C_R = \frac{1}{kt_3} \ln \frac{1 + \frac{C_F - C_{A2}}{C_{A2}} e^{kt_3C_F}}{1 + \frac{C_F - C_{A2}}{C_{A2}}} \tag{15}$$

The dimensionless residence times for a particular conversion are

CCTR: $$\theta = \frac{t_1 + t_2 + t_3}{\delta} kC_F \tag{16}$$

Plug flow: $$\theta = \ln \frac{C_{AF}(C_F - C_A)}{C_A(C_F - C_{AF})} \tag{17}$$

Backmix: $$\theta = \frac{C_F(C_{AF} - C_A)}{C_A(C_F - C_A)} \tag{18}$$

where

$$\theta = \frac{V}{q} kC_F$$

Figure 6 is an evaluation of the three reactors for an autocatalytic reaction with a 99 : 1 ratio of A to R in the feed. The CCTR is clearly the best choice for this application.

In the low to intermediate range of conversions, the plug-flow reactor does poorly since there is very little R present to initiate the reaction. Conversely, the backmix reactor does very well in this range, but performance deteriorates badly in the high conversion range because the average concentration of reactant is only the low output concentration.

The CCTR combines the features of both the backmix and plug-flow (or batch) reactors. In the low conversion range, fresh reactant is immediately mixed with product from the previous cycle, so that the reaction is rapidly initiated. During the batch step, however, the reaction occurs without inefficient backmixing, and therefore the average reactant concentration is higher than the backmix concentration.

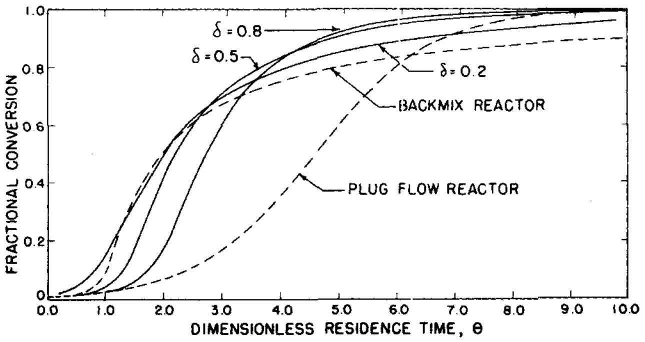

Fig. 6. Autocatalytic reaction. $C_{AF}/C_{RF} = 99$.

Results are less dramatic when there is a high enough R concentration in the feed to initiate the reaction immediately. For example, for $C_{AF} = 0.90\ C_F$, the CCTR has only a slight advantage over the plug-flow reactor, but still excels over the backmix reactor.

It has been shown (*4*, *7*) that for autocatalytic and exothermic adiabatic reactions, a CSTR followed by a plug-flow reactor constitutes the optimal reactor system. The CCTR, as shown above, approaches this scheme, but is certainly not superior to it. However, the inherent savings of a single stirred tank over a dual reactor system makes the CCTR worth considering for such reactions (also see following section).

Levenspiel (7) points out that, while true autocatalytic reactions are rare, an exothermic adiabatic reaction may be viewed as a special case of an autocatalytic reaction if heat is considered as one of the products. Indeed, the results of the exothermic adiabatic reactor evaluations are surprisingly similar to those for an autocatalytic reaction.

ADIABATIC REACTORS

In industry, isothermal reactors are often undesirable because of the high cost of heat transfer equipment. Instead, many reactors are designed to operate adiabatically (9).

In an adiabatic reaction, the temperature change is proportional to the conversion F, providing that heats of reaction and heat capacities remain constant over the range

$$T = T_F + Fb \tag{19}$$

If the Arrhenius rate expression is used, an adiabatic heat balance gives

$$k = k_F \exp\left(\frac{E}{RT_F}\ \frac{1}{1 + \frac{T_F}{bF}}\right) \tag{20}$$

The design Equation (3) may now be integrated numerically with a variable rate coefficient from Equation (20) and the fact that

$$F = \frac{C_{AF} - C_A}{C_{AF}} \tag{21}$$

The adiabatic CCTR was evaluated and compared to backmix and plug-flow reactors for first- and second-order exothermic and endothermic reactions. The equations for the backmix and plug-flow reactors are

Backmix: $$\theta = \frac{F}{\frac{k}{k_F}(1 - F)^n} \tag{22}$$

Plug flow: $$\theta = \int_0^F \frac{dF}{\frac{k}{k_F}(1 - F)^n} \tag{23}$$

where

$$\theta = k_F C_{AF}^{n-1} \frac{V}{q}$$

Equation (23) was solved numerically.

For the endothermic first- and second-order adiabatic reactions, the relative efficiencies of the reactors appeared to be similar to those of first- and second-order isothermal reactions (Figure 1) with the CCTR efficiency falling between those of the backmix and plug-flow reactor. High values of δ gave improved efficiencies. Since, for an endothermic reaction, the rate coefficient decreases with increased conversion, a reactor with the highest average reactant concentration is desirable (*4*). The plug-flow reactor meets this criterion since the average concentration is between the inlet and outlet concentration, while the backmix reactor operates at the low outlet concentration.

The situation is quite different for exothermic adiabatic reactions. Figures 7 and 8 are for the first- and second-order exothermic adiabatic reactions, respectively. The first-order case is very similar in appearance to the autocatalytic reactor evaluation (Figure 6) and clearly shows the superiority of the CCTR. The same arguments as for autocatalysis may be used to explain the results if heat is considered a product. The second-order case is less dramatic, since high concentration is more important in determining the reaction rate than the increase in rate coefficient due to temperature rise.

YIELD REACTIONS

It is well known that some reactions have optimal time-temperature profiles which fall with increasing conversion. Two such reactions are exothermic equilibrium reactions and consecutive reactions. Both have been well studied for plug-flow reactors (*1*, *2*) and backmix reactors (*1*).

Consider any exothermic reaction occurring in a CCTR equipped with a cooling coil. During the charging step, the temperature will rise because of high reaction rate due to the high reactant concentration. As the reaction proceeds in the batch and discharge steps, the rate of heat input due to reaction will fall as the conversion increases, and the temperature will drop since heat is being removed by the cooling coil.

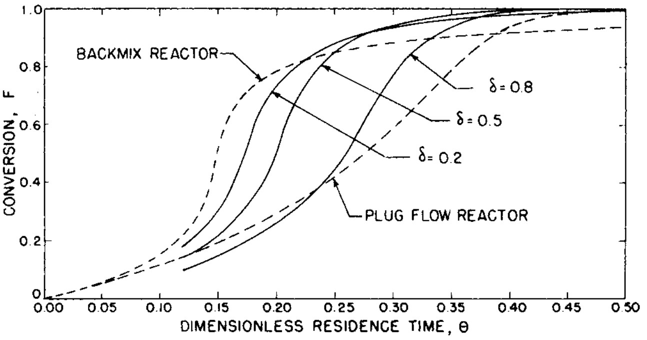

Fig. 7. First-order exothermic adiabatic reaction. $b/T_F = -0.1$. $E/RT_F = 40$.

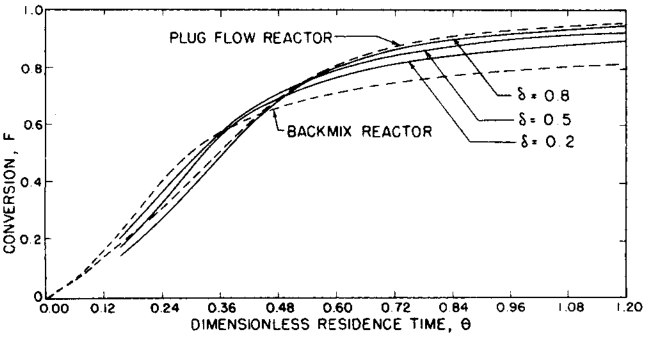

Fig. 8. Second-order exothermic adiabatic reaction. $b/T_F = -0.1$. $E/RT_F = 40$.

The above illustration is the basis for automatic temperature programming of a CCTR, which can sometimes improve the performance of a yield reaction.

The basic material balance for the equilibrium reaction $nA \underset{k_1}{\overset{k_2}{\rightleftharpoons}} nR$ (n order, exothermic) is

$$\frac{dC_n}{dt} = -k_1 C_A^n + k_2 (C_F - C_A)^n + \frac{q}{v} (C_{AF} - C_A) \tag{24}$$

where

$$C_F = C_{AF} + C_{RF} = C_A + C_R$$

If the heat transfer from the cooling coil is assumed to be proportional to the liquid level in the tank, and the driving force $(T - T_c)$

$$\frac{dT}{dt} = \frac{(-\Delta H)}{\rho C_p} [k_1 C_A^n - k_2 (C_F - C_A)^n] + \frac{q}{v} (T_F - T) - \frac{U}{\rho C_p} (T - T_c) \tag{25}$$

The rate coefficient is of the Arrhenius form.

Similar equations may be written for the consecutive reaction:

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

$$\frac{dC_A}{dt} = -k_1 C_A + \frac{q}{v} (C_{AF} - C_A) \tag{26}$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R + \frac{q}{v} (C_{RF} - C_R) \tag{27}$$

$$\frac{dT}{dt} = \frac{(-\Delta H_1)}{\rho C_p} k_1 C_A + \frac{(-\Delta H_2)}{\rho C_p} k_2 C_R + \frac{q}{v} (T_F - T) - \frac{U}{\rho C_p} (T - T_c) \tag{28}$$

No thorough study of the temperature-programmed CCTR was undertaken in the present work since the effects of so many parameters were involved. Instead, purely hypothetical examples are presented to show that improvement over isothermal operation is possible. All cases were calculated for a 1-liter CCTR. The average flow rate was 0.1 liter/min. and the flow rate during the charge and discharge steps was 1.0 liter/min. The coolant temperature was 25°C. and heat transfer was assumed proportional to $(T - T_c)$.

The conversion for first- and second-order equilibrium reactions and first-order consecutive reaction in a CCTR was optimized with respect to feed temperature and heat transfer coefficient, and the results compared to those for the optimal isothermal reaction. The best results of this limited evaluation are presented in Table 1.

A small improvement of about 3% was obtained for the temperature-programmed equilibrium reactions, but no improvement for the consecutive reaction was obtained. It is not possible to draw conclusions from the last result since only a very limited study of very particular parameters was conducted.

Although this was not confirmed, it seems reasonable that the temperature-programmed, or the isothermal reactor, would do better than an adiabatic reactor because the temperature in the latter would always increase with increasing conversion for an exothermic reaction.

TABLE 1. SUMMARY OF PARAMETERS AND RESULTS FOR YIELD PROBLEMS

	First-order equil.	Second-order equil.	Consecutive
E_1/R, °K.	$-5{,}840.0$	$-5{,}840.0$	$-9{,}000.0$
E_2/R, °K.	$-14{,}900.0$	$-14{,}900.0$	$-15{,}000.0$
A_1, (moles/liter)$^{1-n}$/min.	3×10^7	3×10^7	0.535×10^{11}
A_2, (moles/liter)$^{1-n}$/min.	2.5×10^{19}	2.5×10^{19}	0.461×10^{18}
$(- \ H_1)/\rho \ C_p$, (°K.)(liter)/(mole)(min.)	$+18.0$	$+18.0$	$+17.0$
$(- \ H_2)/\rho \ C_p$, (°K.)(liter)/(mole)(min.)	—	—	$+28.0$
q = flow rate during charge or discharge steps, liters/min.	1.0	1.0	1.0
t, residence time, min.	10.0	10.0	10.0
T_C, coolant temperature, °K.	293.0	293.0	293.0
C_{AF}, moles/liter	0.9	0.9	0.9
C_{BF}, moles/liter	0.1	0.1	0.1
T^*, isothermal, °K.	316.5	319.0	343.0
T_F^*, °K.	342.0	347.0	352.9
U^*, cal./(min.)(°K.)(liter)	242.0	205.0	75.0
Best isothermal conversion	0.690	0.572	0.589
Best programmed conversion	0.714	0.592	0.589
Improvement	3.4%	3.4%	~0%

CONCLUSIONS

Operating a stirred-tank reactor in an on-off manner often leads to improvement over continuous operation. For reactions where the rate passes through a maximum, the CCTR can be more efficient than either a backmix or plug-flow reactor on a residence time basis.

The CCTR was shown to be more sensitive to a concentration disturbance than a backmix reactor for a first-order isothermal reaction, but usually less sensitive than the backmix reactor for a second-order isothermal reaction.

For reactions which have falling optimal temperatures with increasing conversion, the CCTR can sometimes be operated more efficiently by adding a cooling oil which provides automatic temperature programming.

In general, CCTR operation can be used to increase the capacity of a given CSTR in most cases, the improvement being greater the higher the reaction order. However, each reaction system must be analyzed mathematically by the methods presented here before clear-cut conclusions can be drawn because of the difficulty in generalizing the results of this study.

ACKNOWLEDGMENT

We should like to recognize the pioneering work done on CCTR's by Ming Fang. Also, we thank the Union Carbide Corporation for fellowship support.

NOTATION

A = Arrhenius frequency factor
b = maximum reaction temperature change, °K.
C = reactant concentration, g.-moles/liter
$\overline{C}$ = average product concentration, g.-moles/liter
C_p = heat capacity, cal./(g.-mole)(°K.))
E = activation energy
F = fractional reactant conversion, Equation (21)
ΔH = heat of reaction, cal./g.-mole
k = reaction rate coefficient, 1/sec. (first order) and liters/(g.-mole)(sec.)(second order)
n = reaction order
q = charge rate, liters/sec.
r = reaction rate, g.-moles/(liter)(sec.)
t = reaction time, sec.
T = temperature, °K.
U = heat transfer coefficient, cal./(liter)(sec.)(°K.)
v = instantaneous reactor volume, liters
V = total reactor volume, liters

Greek Letters

θ = dimensionless residence time
δ = fraction of reactor dumped
ρ = density, g.-moles/liter

Subscripts

A, B = reactants
c = coolant
F = feed, fractional conversion
R, S = products
1 = charge step
2 = batch reaction step
3 = discharge step

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APPENDIX

In comparing the CCTR with backmix and plug-flow reactors it was necessary to calculate a dimensionless holdup time for all three reactors. That for the CCTR is given in Equation (10). For plug-flow and backmix reactors having the same conversion and average volumetric throughputs as the CCTR, the general residence time is given by

$$\theta = \frac{V}{q} \, k \, C_{AF}^{n-1} \tag{11}$$

Specifically, this equation reduces to the following forms:

Plug-flow reactor:

First order: $$\theta = \ln \frac{C_{AF}}{C_A}$$

Second order: $$\theta = \frac{C_{AF} - C_A}{C_A}$$

Backmix reactor:

First order: $$\theta = \frac{C_{AF} - C_A}{C_A}$$

Second order: $$\theta = \frac{(C_{AF} - C_A) C_{AF}}{C_A^2}$$

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