# Enhancing the Performance of Spontaneously Oscillatory Chemical Reactions

**K. Otawara**

*Technical Management and Systems Department, Kureha Chemical Industry, 16 Ochiai, Nishiki, Iwaki, Fukushima 974, Japan*

**L. T. Fan***

*Department of Chemical Engineering, Kansas State University, Manhattan, Kansas 66506*

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Oscillations are often deemed undesirable when chemical reactions are carried out in practice because they tend to give rise to operational complexities. It is demonstrated that such oscillations need not always be avoided. In fact, the yield of the desired product from an autocatalytic reaction in a continuous stirred-tank reactor can be, at least, quadrupled.

## Introduction

Oscillations or deterministic chaos in chemical reactions have attracted the interest of various researchers.[1−4] Such oscillations have often been deemed undesirable because they cause operational complexities. Nevertheless, there are indications that this is not always the case. For example, Lazar[5] has shown that the mean concentration of the product of a biochemical reaction is enhanced by forced oscillations. It appears, however, that relatively little has been done in practice to take advantage of spontaneously oscillating chemical reactions. In this note, it is demonstrated that spontaneous concentration oscillations of an autocatalytic reaction need not always be circumvented and that under some situations, these oscillations can be highly beneficial in terms of the yield or selectivity of the desired product.

## Oscillatory Autocatalytic Reaction in the Continuous Stirred-Tank Reactor (CSTR)

Under certain circumstances, a three-variable autocatalator oscillates in either a closed[6] or open system.[2,7] This reaction comprises the following six steps.

$$\mathrm{P} \rightarrow \mathrm{A} \tag{1a}$$

$$\mathrm{P} + \mathrm{C} \rightarrow \mathrm{A} + \mathrm{C} \tag{1b}$$

$$\mathrm{A} \rightarrow \mathrm{B} \tag{1c}$$

$$\mathrm{A} + 2\mathrm{B} \rightarrow 3\mathrm{B} \tag{1d}$$

$$\mathrm{B} \rightarrow \mathrm{C} \tag{1e}$$

$$\mathrm{C} \rightarrow \mathrm{D} \tag{1f}$$

The corresponding reaction rates are

$$-r_a = k_0 C_P \tag{2a}$$

$$-r_b = k_C C_P C_C \tag{2b}$$

$$-r_c = k_U C_A \tag{2c}$$

$$-r_d = k_1 C_A C_B^{\,2} \tag{2d}$$

$$-r_e = k_2 C_B \tag{2e}$$

$$-r_f = k_3 C_C \tag{2f}$$

**Closed System.** When the pool chemical approximation is adopted for the autocatalator and $C_P$ is regarded constant at $C_{P0}$ in eqs 2a through 2f, the governing equations of a closed system, i.e., batch reactor, in which this system of reactions proceeds, can be written as

$$\frac{dx}{d\theta} = a(b + z) - x - xy^2 \tag{3a}$$

$$\frac{dy}{d\theta} = \frac{1}{c}(x + xy^2 - y) \tag{3b}$$

$$\frac{dz}{d\theta} = \frac{1}{d}(y - z) \tag{3c}$$

where

$$x = \left(\frac{k_1 k_U}{k_2^{\,2}}\right)^{1/2} C_A \tag{4a}$$

$$y = \left(\frac{k_1}{k_U}\right)^{1/2} C_B \tag{4b}$$

$$z = \left(\frac{k_1 k_3^{\,2}}{k_U k_2^{\,2}}\right)^{1/2} C_C \tag{4c}$$

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are the dimensionless concentrations,

$$\theta = k_U t \tag{5}$$

is the dimensionless time, and

$$a = \left(\frac{k_C}{k_3}\right) C_{P_0} \tag{6a}$$

$$b = \left(\frac{k_0 k_3}{k_C k_2}\right)\left(\frac{k_1}{k_U}\right)^{1/2} \tag{6b}$$

$$c = \frac{k_U}{k_2} \tag{6c}$$

$$d = \frac{k_U}{k_3} \tag{6d}$$

The system exhibits spontaneous oscillations; moreover, for certain sets of parameters, it behaves chaotically.[2]

**Open System.** The model described above resorts to the pool chemical approximation. The closed system, however, is incapable of indefinitely oscillating because the consumption of reactant P is not negligible in reality. For chemical oscillations to continue, therefore, the reactor need be fed continuously, thus resulting in an open system, i.e., continuous stirred-tank reactor (CSTR), whose governing equations are

$$\frac{dw}{d\theta} = -ew(b + z) + f(a - w) \tag{7a}$$

$$\frac{dx}{d\theta} = w(b + z) - x - xy^2 - fx \tag{7b}$$

$$\frac{dy}{d\theta} = \frac{1}{c}(x + xy^2 - y) - fy \tag{7c}$$

$$\frac{dz}{d\theta} = \frac{1}{d}(y - z) - fz \tag{7d}$$

where

$$f = \frac{F}{Vk_u} \tag{8}$$

is the dimensionless feed rate to the reactor, and

$$e = \frac{k_c k_2}{k_3}\left(\frac{1}{k_u k_1}\right)^{1/2} \tag{9a}$$

$$w = \left(\frac{k_c}{k_3}\right) C_P \tag{9b}$$

$F$ and $V$ in eq 8 are the flow rate and reactor volume, respectively. Equations 7−9 have been numerically solved by the fifth-order, Runge−Kutta−Verner method with a dimensionless sampling time of $1 \times 10^{-4}$.

## Feedback Mechanism

When $a$, $b$, $c$, $d$, and $e$ are chosen to be 0.2, 65, $5 \times 10^{-3}$, $2 \times 10^{-2}$, and $1 \times 10^{-3}$, respectively, the system spontaneously oscillates in a certain range of $f$. Figure 1 displays the temporal history of $y$ when $f$ is chosen to be 0.016 34; note that for a very brief period, the magnitude of $y$ becomes extraordinarily large, thereby rendering it possible to greatly enhance the yield of B, if the input and output rates of flow are increased during this period.

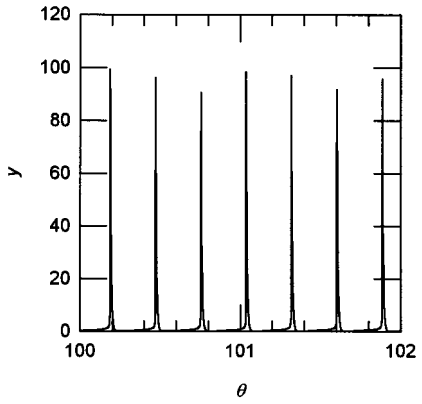


**Figure 1.** Time series of $y$.

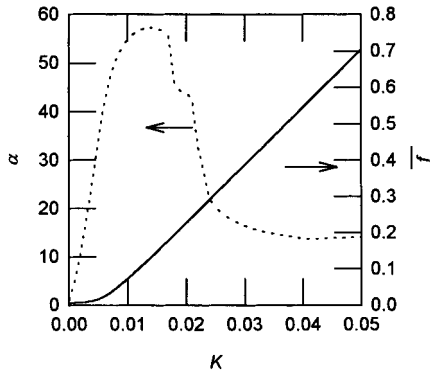


**Figure 2.** Variations of α and $f$ with parameter $K$.

A feedback mechanism is incorporated into the CSTR in the present work. With this mechanism, the greater the $y$, the greater the $f$. Since the system operates at a steady state when $f$ is less than a certain value, defined as $f_{min}$, $f$ should always be larger than $f_{min}$ for the feedback mechanism to be effective: Once the system attains a steady state, oscillations might cease. In this note, $f_{min}$ is estimated to be $6 \times 10^{-3}$ from the bifurcation diagram of the system. Thus, the feedback mechanism can be expressed as

$$f = \max(Ky, f_{min}) \tag{10}$$

where $K$ is the gain.

## Results and Discussion

To demonstrate the efficacy of the proposed feedback mechanism, the following indices are introduced to evaluate the performance of a CSTR.

$$\alpha = \frac{\int_0^\theta fy\, d\theta}{\int_0^\theta f\, d\theta} \tag{11a}$$

$$\beta = \frac{\int_0^\theta fy\, d\theta}{\theta} \tag{11b}$$

Note that α and $\beta$ represent the average dimensionless concentration and flow rate of B, respectively. It has been found that when the feedback mechanism is absent, the smaller the $f$, the smaller the α; moreover, when $f$ is larger than 0.62, the system remains at a steady state. Thus, the condition of small $f$'s, i.e., low feed rates, should be avoided especially when B is the desired product. Nevertheless, when the feedback mechanism

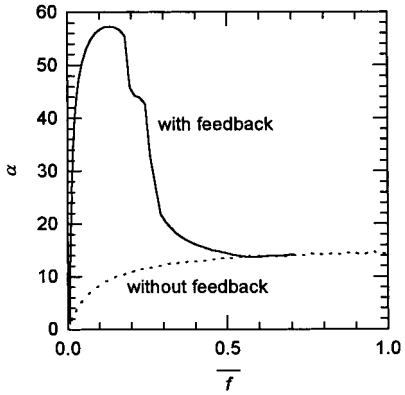


**Figure 3.** Comparison of α's with and without the feedback mechanism.

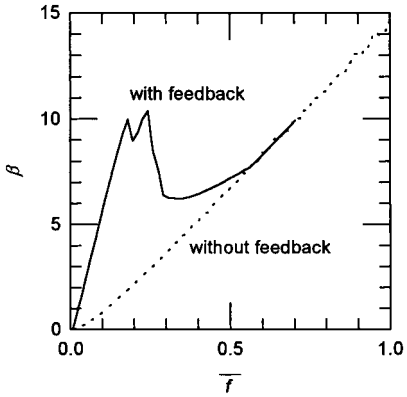


**Figure 4.** Comparison of $\beta$'s with and without the feedback mechanism.

is present, α could become exceedingly large, as illustrated in Figure 2, which also contains the mean value of *f*.

Figure 3 summarizes the results pertaining to α. The value of α with the feedback mechanism is always larger than that without the mechanism; in fact, the feedback mechanism can remarkably magnify α. The feedback mechanism approximately quadruples the maximum value of α. Since the separation of participating chemical species is usually necessary after the reaction, designing and operating the reactor around *f* so as to maximize α would reduce the cost of separation. The values of $\beta$ with and without the feedback mechanism are compared in Figure 4. Note that the former is always much greater than the latter for small *f*.

In this study, all parameters except *f* are fixed; however, varying them may further improve the performance of the system under consideration. In any event, it has been amply demonstrated here that chemical oscillations should not always be circumvented.

## Concluding Remarks

In operating chemical reactors, the practice has been to suppress chemical oscillations. Such oscillations in conjunction with the proposed feedback mechanism, however, might enhance the performance of a continuous stirred-tank reactor. The present study unequivocally demonstrates that it is indeed the case for a reactor with a set of reactions modeled as an autocatalator; the maximum yield of the desired product from this reactor can be, at least, quadrupled.

## References and Notes

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