evaluate $\nu_{0.5}$. This may not be possible with some of the poorer drag reducing polymers. For example, guar gum in water was studied (*6*) at concentrations up to 100 ppm by mass and 50% drag reduction was not achieved. As a result, the system could not be correlated without data at higher concentrations where non-Newtonian behavior is approached.

The last point of consideration is the use of the parameter $\nu_{0.5}$ as opposed to a value of $\nu$ at some value of $f/f_{pv}$ other than 0.5. The data for the polyethylene oxides (PEO-coagulant and PEO WSR-301) dissolved in water were used to examine this possibility. The results indicated that scatter about the correlating curve increased when the subscript on $\nu$ was increased incrementally from 0.5 to 0.8. Recall that the subscript on $\nu$ refers to the value of $f/f_{pv}$ at which $\nu$ is evaluated. The value of $\nu$ at $f/f_{pv}$ equal to 0.45 was tested ($\nu_{0.45}$) and showed some indication of decreasing this scatter. But the results were inconclusive because some data had to be extrapolated to obtain the value of $\nu_{0.45}$. The extrapolation was very susceptible to error, and values of $\nu_{0.45}$ varied greatly for different degrees of the polynomial used to fit the data for the plot of $f/f_{pv}$ versus $\nu$. Hence from a practical standpoint $\nu_{0.5}$ is probably the best parameter.

## NOTATION

$C$ = concentration, ppm by mass
$D$ = tube inside diameter, ft.
$f$ = Fanning friction factor
$f_{pv}$ = Fanning friction factor for purely viscous fluids
$N_{Re}$ = Reynolds number
$U$ = bulk average velocity, ft./sec.
$\nu$ = characteristic frequency, $U/D\ N_{Re}^{0.75}$, sec.$^{-1}$
$\nu_{0.5}$ = value of $\nu$ for which $f/f_{pv} = 0.5$, sec.$^{-1}$

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# Multiple Limit Cycles in a Continuous Stirred-Tank Reactor

**P. V. HEBERLING, N. Y. GAITONDE, and J. M. DOUGLAS**
**Department of Chemical Engineering**
**University of Massachusetts, Amherst, Massachusetts 01002**

In their classical paper on the stability and control of continuous stirred-tank reactors (CSTR), Aris and Amundson (*1*) presented an example where there appeared to be multiple limit cycles. When they solved the nonlinear equations describing the CSTR on an analog computer for a particular set of parameters, they found a case where a stable limit cycle seemed to surround a stable equilibrium point. This kind of behavior can occur only when an unstable limit cycle lies between the stable singular point and the stable limit cycle, so that it acts as a source of trajectories for these two kinds of sinks. However, a more extensive analysis of this same problem by Luus and Lapidus (*8*) revealed that a stable limit cycle does not exist, that is, the real part of the root is sufficiently small that the trajectories appear to be closed, but actually they approach the stable equilibrium point very, very slowly.

It is possible to develop approximate analytical solutions for multiple limit cycles. One approach is simply to retain up to the fifth-order terms in the Taylor series expansions of the nonlinear functions presented in an earlier paper (*2*) so that one of the expressions for the secular terms becomes

$$C_4 A^4 + C_2 A^2 + C_0 A^2 = 0 \qquad (1)$$

where $A$ represents the amplitude of the limit cycle, $C_0$, $C_2$, and $C_4$ are known constants which can be related to the CSTR design parameters, and $C_4$ depends on the fifth-order terms in the Taylor series expansions. Then, for certain values of the system parameters Equation (1) has two real roots, which hopefully correspond to the amplitudes of two limit cycles.

However, as has been shown before (*3*), different methods of approximating the process nonlinearities will lead to somewhat different solutions. Also, alternative generating solutions will correspond to different results. Hence, the region in parameter space where Equation (1) will predict multiple limit cycles will vary with the particular details of the solution technique. Regions of this type corresponding to three different approximate analytical solutions are shown in Figures 1 and 2 for two sets of system parameters. The first approximate solution is the one mentioned in the previous paragraph and is referred to as Gaitonde's method (*4*). The second is taken from the work of Gilles (*5*) and Hlaváček (*7*) et al. This solution is obtained by approximating the Arrhenius expression by the function $e^{aT}$, assuming a periodic solution for the reactor composition and temperature, using the series expansion for exp (cos $\omega t$) which contains Bessel functions as the coefficients in the series, and then undertaking a harmonic balance. The third approximate solution was developed by Heberling (*6*), who used the equations describing a curtate cycloid as a generating solution, rather than the more conventional trigonometric functions. All three solutions give a secular equation having the same form as Equation (1), and the

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N. Y. Gaitonde is with Esso Research and Engineering, Florham Park, New Jersey.

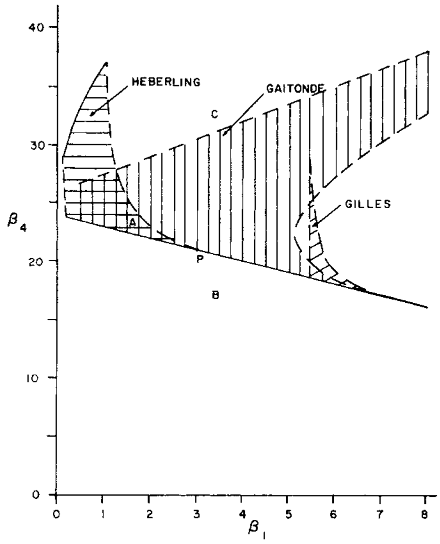

**Fig. 1. Region for multiple limit cycles, $\beta_3$ = 80, $\beta_5$ = 0.3125.**

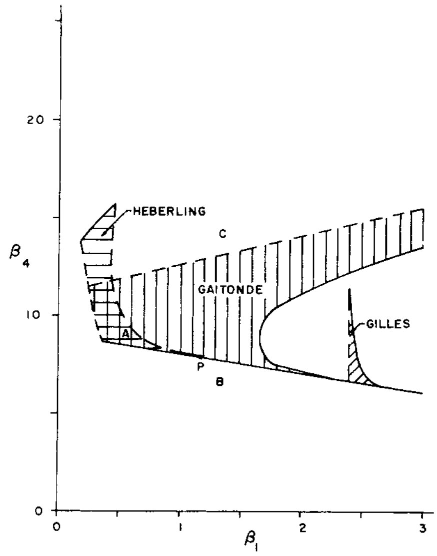

**Fig. 2. Region for multiple limit cycles, $\beta_3$ = 40, $\beta_5$ = 0.25.**

coefficients in this expression for the three cases are listed in Table 1 in terms of the nomenclature appearing in previous papers (2, 3).

It is apparent from these graphs that the predictions obtained from the three approximate solutions do not agree very well with one another. In fact, not all the regions even overlap. In order to see which result is correct, or most nearly correct, it is necessary either to numerically integrate the nonlinear equations or to extend the theory to higher order correction functions. Since it would have been a very tedious matter to determine additional terms from the theory and since we were interested in comparing the numerical and theoretical estimates of the time averaged value of the reactor conversion, we solved the equations numerically for several sets of parameters.

Phase plane plots for three sets of parameters are shown in Figures 3 through 5. The dashed curves on these graphs were computed by reversing the direction of time in the numerical integration, a procedure which makes the unstable limit cycle become stable. Based on a number of integrations of this type, we believe that the region of parameter space which actually corresponds to multiple limit cycles is in the lower right-hand corner of area *A* in Figures 1 and 2. Both Gaitonde's and Heberling's solutions predict that multiple limit cycles should exist for these cases, but Gilles' solution is quite different.

Table 1. Terms in Equation (1)

Gaitonde and Douglas Solution

$$C_0 = -(1 + \beta_1 + \beta_4 - \beta_3\beta_5)$$

$$C_2 = -\frac{\beta_3\beta_5^2}{2}\left[(\beta_3 - 2)(2 + 3\beta_1 + C_0) - \beta_5(\beta_3^2 - 6\beta_3 + 6)\right]$$

$$C_4 = -\frac{\beta_3\beta_5}{12}(4 + 5\beta_1 + 2C_0)(\beta_3^3 - 12\beta_3^2 + 36\beta_3 - 24)$$

Heberling and Douglas Solution

$$C_0 = -(1 + \beta_1 + \beta_4 - \beta_3\beta_5)$$

$$C_2 = \frac{1}{4}\left[\frac{1}{2}\beta_1\beta_3(2 - \beta_3) - 2\beta_3\beta_4 + 3\beta_3\beta_5\right] - \frac{1}{32}\beta_3(\beta_1\beta_3 + 2\beta_3\beta_5 - \beta_3\beta_4)$$

$$C_4 = -\frac{\beta_3}{192}\left[96\beta_4 - 120\beta_5 + \beta_1(\beta_3^3 - 12\beta_3^2 + 36\beta_3 - 24)\right] + \frac{\beta_3^2}{192}\left[18\beta_4 - 24\beta_5 - \beta_1(6 - 6\beta_3 + \beta_3^2)\right]$$

Gilles and Hlaváček et al. Solution

$$C_0 = -(1 + \beta_1 + \beta_4 - \beta_3\beta_5)$$

$$C_2 = \frac{1}{8}(\beta_3\beta_5 - 3\beta_1 - 2)$$

$$C_4 = \frac{1}{192}(\beta_3\beta_5 - 5\beta_1 + 2)$$

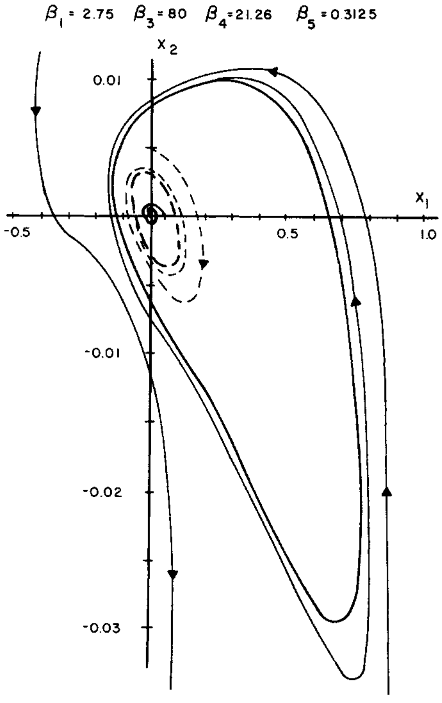

**Fig. 3. Multiple limit cycles, $\beta_1$ = 2.75, $\beta_3$ = 80, $\beta_4$ = 21.26, $\beta_5$ = 0.3125.**

The point labeled *P* on Figures 1 and 2 can be called a trifurcation point, because it separates regions where there are two limit cycles (area *A*), one limit cycle (area *B*, which corresponds to steady states which are unstable focii), and no limit cycles (area *C*, which corresponds to steady states which are stable focii). If we use Heberling's solution and our meager computer results to generalize the location of this trifurcation point, we obtain the curves shown in Figure 6. With this graph it is a fairly simple matter to estimate combinations of parameters which will lead to multiple limit cycles.

It is interesting to note that the parameters used to construct Figure 3 correspond to the optimum steady state design of Case 3 studied by Gaitonde and Douglas (3). Actually, we did not expect to obtain multiple limit cycles for this case, but they were predicted by our analytical solution. The stable, steady state operating point will never be reached unless the initial conditions for the start up of the reactor lies within the unstable limit cycle. In terms of the original system parameters this means that the initial composition must be between 0.000171 and 0.00328 g.-mole/cu.cm. and the initial temperature must be in the range 596° and 605°K. This seems to be a fairly rigid requirement since the feed composition is 0.01 and the feed temperature is 289. For other start-up conditions the reactor will generate periodic outputs corresponding to the stable limit cycle. The numerical solutions indicate that the time average outlet composition for the oscillating system is 21% lower than the optimum steady state value (which means that the conversion is higher) and that the time average temperature is 0.12% above the steady state value. Moreover, the oscillator has a 5% lower operating cost than the optimum steady state plant. These values are almost identical to those obtained when we used a positive feedback control system to make the stable reactor become unstable, so that a single limit cycle was observed.

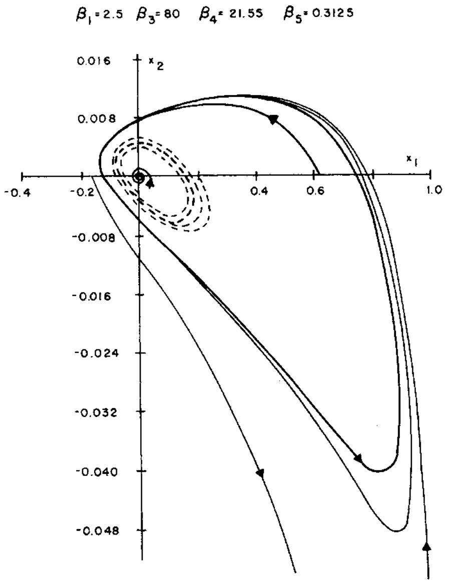

Fig. 4. Multiple limit cycles, $\beta_1 = 2.5$, $\beta_3 = 80$, $\beta_4 = 21.55$, $\beta_5 = 0.3125$.

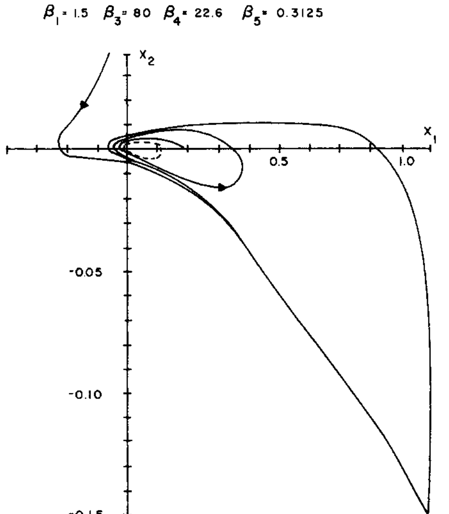

Fig. 5. Multiple limit cycles, $\beta_1 = 1.5$, $\beta_3 = 80$, $\beta_4 = 22.6$, $\beta_5 = 0.3125$.

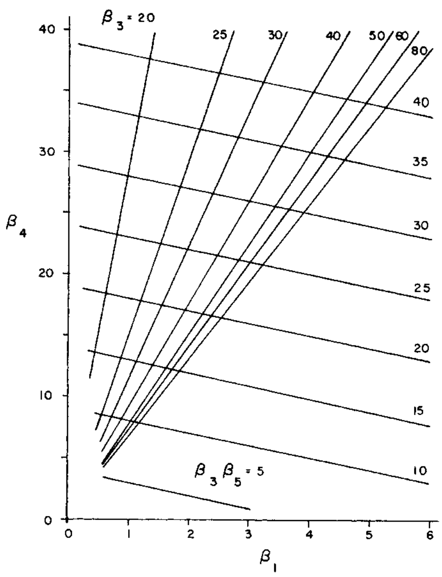

Fig. 6. Location of trifurcation points.

Systems similar to that shown in Figure 3 are called hard oscillators because it is necessary to introduce a fairly large disturbance into a process operating at steady state conditions in order to cause it to oscillate. This is in contrast to soft oscillators, such as those described in previous papers (*1* to *3*) where self-excited oscillations can be obtained from systems initially at rest. Potential start-up problems with hard oscillators are obvious, but the possible advantages of periodic operation have not been recognized until recently.

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