Modeling of chemical reactors — XIX†
Transient axial heat and mass transfer in tubular reactors
The stability considerations — I

V. HLAVÁČEK‡ and H. HOFMANN
Institut für technische Chemie, Universität Erlangen-Nürnberg, 8520 Erlangen, West Germany

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Abstract — An approximation is described enabling us to transform distributed parameter systems into lumped parameter systems. The range of applicability of this approximation for axial heat and mass transfer in tubular reactors is investigated. Some interesting results as stability of multiple solutions, occurrence of limit cycles etc. are presented.

1. INTRODUCTION
This paper forms a further communication in the series about instabilities of dynamic systems. It is a continuation of our previous papers XVI[1] and XVII[2] concerning steady state problems of axial heat and mass transfer in tubular reactors.

Great attention was devoted in the literature to studying axial mixing of heat and mass. One can understand this fact because the model including axial mixing can bridge the gap between the stirred tank and plug flow reactors. Raymond and Amundson[3] solved numerically the transient equations for the adiabatic case and pointed out that the lower and upper steady state are asymptotically stable. On the other hand, the middle is always unstable. Ivanov, Beskov and Slinko[4] proved analytically for the case of an adiabatic perturbation that for the adiabatic case both lower and upper steady states are asymptotically stable and that the middle one is unstable. Recently Berger and Lapidus[5] have tried to use the second Ljapunov method but in some cases they did not draw any conclusion about stability on the basis of developed criteria. The applicability of the second Ljapunov method for the analysis of the distributed parameter systems seems to be restricted with respect to up to recently obtained results[5, 6].

Recently, equations describing a laminar flame, which are similar to the equations for axial mixing of heat and mass, have been analyzed from the dynamic point of view by Kirkby and Schmitz[7] and Schmitz[8]. In an excellent study they pointed out that for the case of an adiabatic flame the middle solution is unstable, however, for heat loss from the flame to the surroundings the upper solution (burning state) may be unstable. This solution can be unstable for an adiabatic flame too, but only for a Lewis number LW > 1.

A very powerful approach for the analysis of nonlinear dynamic systems seems to be the method replacing the “distributed parameter systems” by a corresponding “lumped parameter systems”. This “lumping approach”, after taking advantage of the first Ljapunov method, enables one to draw a number of useful conclusions.

In this study the “lumping approach” is utilized. The goal of this communication is to check the accuracy of this approximation for the system in question. This study is not aimed at comprehensively describing all phenomena occurring in axial mixed tubular reactors. In this paper the case of one homogeneous exo-
termic reaction with the same Peclet numbers for heat and mass are dealt with. The extension to more general heterogeneous systems will be presented in one of the next communications of this series.

2. MASS AND ENTHALPY BALANCES

For a homogeneous first order exothermic reaction taking place in tubular flow system the transient equations can be written in the following dimensionless form [1]:

\[
\begin{align*}
\frac{\partial \theta}{\partial \tau} &= \frac{1}{Pe_\theta} \frac{\partial^2 \theta}{\partial \xi^2} - \frac{\partial \theta}{\partial \xi} - \beta(\theta - \theta_c) \\
+ BDa (1 - y) \exp \left( \frac{\theta}{1 + \epsilon \theta} \right) \\
\frac{\partial y}{\partial \tau} &= \frac{1}{Pe_y} \frac{\partial^2 y}{\partial \xi^2} - \frac{\partial y}{\partial \xi} + Da (1 - y) \exp \left( \frac{\theta}{1 + \epsilon \theta} \right)
\end{align*}
\]

subject to boundary conditions:

\[
\begin{align*}
\xi &= 0; \quad \tau > 0: \quad Pe_\theta \frac{\partial \theta}{\partial \xi} = 0 \\
Pe_y \frac{\partial y}{\partial \xi} &= 0 \\
\xi &= 1; \quad \tau > 0: \quad \frac{\partial \theta}{\partial \xi} = 0 \\
\frac{\partial y}{\partial \xi} &= 0
\end{align*}
\]

and initial conditions:

\[
\tau = 0; \quad 0 < \xi < 1: \quad \theta = \theta(\xi); \quad y = y(\xi).
\]

On the basis of previously presented approximations [1] the system of Eqs. (1)–(5) can be replaced by another system of equations:

\[
\begin{align*}
\frac{d\theta}{d\tau} &= -\left( \frac{\lambda_1^2 + Pe_\theta}{4} \right) \theta - \beta(\theta - \theta_c) \\
+ BDa (1 - y) \exp \left( \frac{\theta}{1 + \epsilon \theta} \right) \\
\frac{dy}{d\tau} &= -\left( \frac{\lambda_2^2 + Pe_y}{4} \right) y + Da (1 - y) \exp \left( \frac{\theta}{1 + \epsilon \theta} \right)
\end{align*}
\]

subject to initial conditions:

\[
\tau = 0: \quad \theta = \theta_0, \quad y = y_0.
\]
catalyst[9]. In Figs. 3 and 4 a comparison of the sizes of the limit cycles is presented. For the given parameters in the one-dimensional approximation, the limit cycle disappears in the interval $Pe = 1.1-1.2$. On the other hand, in the two-dimensional model it disappears for $Pe = 1.6-1.8$. It is interesting to compare the period of one oscillation for the limit cycles with both models. This comparison is reported in Table 1. On the basis of these results we can observe that the simple approximation describes the characteristic features quite well, only the disappearance of the limit cycles at lower Peclet number values can be expected.

(b) Utilizing the approximation for a parametric study

The approximation model forms a set of ordinary nonlinear differential equations, which
interesting cases are presented in Figs. 5–9. In Figs. 5 and 6 nonisothermal-nonadiabatic cases \((\beta = 2.0)\) for \(Pe = 2\) and \(Pe = 3\) respectively are depicted. The solid line \((\Delta = 0)\) bounds the multiplicity, the dashed line \((Q = 0)\) the transient instabilities. One can observe that for higher values of the cooling parameter \(\beta\), as for a CSTR, and for lower Peclet numbers a loop on the dashed line exists, which lies outside of the regions of multiplicity. For the values of the Damköhler number \(Da\) and Peclet number \(Pe\), which are inside this loop (region II) only limit cycles may exist. After increasing the Peclet number the size of the loop decreases, and the entire loop shifts towards the region of multiplicity. In the analogous way as for a CSTR one can draw conclusions about the stability

Table 1. A comparison of the period of limit cycles evaluated from both models. \((B = 11.0; Da = 0.2; \theta_c = 0.0; \beta = 2.0; \epsilon = 0.0)\)

<table>
<thead>
<tr>
<th>(Pe)</th>
<th>One-dimensional model</th>
<th>Two-dimensional model</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>2.77</td>
<td>2.78</td>
</tr>
<tr>
<td>1.0</td>
<td>2.10</td>
<td>2.64</td>
</tr>
<tr>
<td>1.1</td>
<td>1.97</td>
<td>2.61</td>
</tr>
<tr>
<td>1.4</td>
<td>—</td>
<td>2.50</td>
</tr>
<tr>
<td>1.6</td>
<td>—</td>
<td>2.27</td>
</tr>
</tbody>
</table>

are analogous to the set of equations describing dynamic behaviour of a stirred tank reactor. It is obvious that the methods which can be used for the localization of multiple states, limit cycles etc., which were described in our previous paper [10], may be well utilized in this particular case too.

Let us plot the dependence of the Damköhler number \(Da\) against the dimensionless adiabatic temperature rise \(B\) which can be determined on the basis of the conditions \(Q = 0\) and \(\Delta = 0\) [10]. We obtain the analogous type of curves which we studied for the CSTR [10]. In this case a different phenomenon is described. Some

"Da—B"---, bounds of multiplicity; ----, bounds of transient instability.

Fig. 5. Parametric plane.
of the upper steady state[10]. In the region III the instability of the upper solution can be expected, on the other hand, in region IV this state seems to be stable.

For the adiabatic case interesting phenomena can be predicted. For $Pe_\theta > Pe_u$ in some cases (see Fig. 8) limit cycle can be expected. For lower values of the relation $Pe_\theta/Pe_u$ the existence of the limit cycles is suppressed (see Fig. 7). For the case $Pe_\theta < Pe_u$ and for adiabatic conditions the limit cycles do not exist. In this case, however, the region of multiplicity is shifted toward the lower values of $B$. For an equality of Peclet numbers we have described that the sufficient and necessary condition for unicity is determined by the value $B$ which is, in numerical value, exactly the same as for a CSTR (e.g. for $\epsilon = 0.05$, $B^* = 5.0$ or for $\epsilon = 0$, $B^* = 4.0$ etc.)[10]. From Fig. 9 the critical value $B^* = 2.8$ can be extracted. For the inequality $Pe_\theta > Pe_u$ the critical value of $B$ shifts toward higher values, e.g. from Fig. 8 we can extract $B^* = 9.45$.

5. SOME TYPICAL FEATURES OF EQS. (1)-(5)
(a) Limit cycles

We can extend the concept of limit cycles into the distributed parameter system. In these systems the entire profile $\theta(\xi)$ and $y(\xi)$ exhibits oscillations. For the descriptive purposes we can plot in the phase plane e.g. the points at the given axial coordinate $\xi$, or just the integral
mean values $\theta$ and $\gamma$ because these correspond to the simple description. It is necessary to stress that the mathematics for nonlinear partial differential equations is not satisfactorily developed or does not exist. For the ordinary differential equations Bendixon proved that if the trajectory $C$ remains in a finite domain without approaching any singularities, then $C$ is either a closed trajectory or approaches such a trajectory. As far as we know this theorem has not been proved for the functional space. In the case of the distributed parameter systems where a single profile exists, which is unstable, then one can intuitively expect and on the physical basis assume that the profiles will oscillate around the steady state profile. This statement can be verified numerically[9]. From Figs. 10–15 we can extract some characteristic features of this phenomenon. Figures 10–13 make it possible to observe the temperature oscillations of the mean value as well as point values at the axial distance $\xi = 1.0$ and $\xi = 0.2$ respectively. On the basis of these figures we may observe that near the inlet the oscillations are higher than at the reactor outlet. The dashed line is a steady state integral mean value. In the

Fig. 8. Parametric plane. "Da – B". ——, bounds of multiplicity ——, bounds of transient instability.

Fig. 9. Parametric plane. "Da – B". ——, bounds of multiplicity ——, bounds of transient instability.

Fig. 10. Time dependence of temperature. Mean values. Undamped oscillations.
following figure we can observe the time dependence of the temperature profiles. Let us notice that although this case may be localized quite well by means of the approximation, the reactor does not work as a "slightly perturbed" reactor. The same dependences for the concentration are in Figs. 14 and 15. As can be extracted from these figures concentrations as well as temperatures do oscillate in broad region. Let us note that the maximum conversion is almost the total conversion, (e.g. see coordinates \( \tau = 0.65 \) and \( \tau = 3.29 \) in Fig. 15).

As we have shown in this paper an occurrence of limit cycles is rapidly suppressed as a result of increasing value of the Peclet number. After inspection of the loop domain in Figs. 5 and 6 this fact may be verified by taking advantage of the numerical simulation of Eqs. (1)–(5). For lower values of the Peclet number the approximation describes quite well the behaviour of the partial differential system. Roughly speaking, in the vicinity of the lower branch of the loop (e.g. in Fig. 5 in the region
II for a given value of $B$ the corresponding lower value of $Da$ a slowly winding spiral may exist instead of limit cycles (i.e. the singular point in the phase plane is of the focus type and the change of the mean radius after one revolution is small). Furthermore, in the region inside the loop, for low values of $B$, the limit cycles do not exist. After the first preliminary numerical inspection of the distributed systems the loop (dashed curve) seems to be shifted toward higher values of $B$. For example from Fig. 6 for $B = 9$ we can determine that for $Da = 0.23, 0.24$ and $0.25$ limit cycles can exist. The numerical simulation of Eqs. (1)-(5) shows that for the first two values the singular point of the focus character exists, but for $Da = 0.25$ the limit cycle can be computed. The exact determination of the stability bounds for a distributed parameter system is quite a difficult task because, if a stable singular point of the focus type starts to exist then the trajectory in the phase plane is almost identical with a "limit cycle" and the change in mean radius of the spiral is very small. A similar phenomenon was observed by Luus and Lapidus[11] for a CSTR. In these cases it is difficult to discriminate between the limit cycle and a focus and it seems to be necessary to check the steady state profiles for stability [7, 9]. But a lot of additional troubles can arise again, because of the eigenvalues of the set of linear ordinary differential equations arising after linearization of transient equations in the vicinity of the steady state solution. If the size of this linear system is small (mesh size for discretization in the axial direction has only a few points) the determination of the governing eigenvalues is not exact enough. On the other hand, for a large system of linear equations there are computational difficulties in estimation of the eigenvalues.

The effect of the parameters on the period of limit cycles can be extracted from Tables 1 and 2.

### Table 2. Effect of the Damköhler number $Da$ on the period of limit cycles. The exact model; $(\beta = 2.0; \theta_e = 0.0; \varepsilon = 0.0; Pe = 2.0; B = 10.0)$

<table>
<thead>
<tr>
<th>$Da$</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>4.70</td>
</tr>
<tr>
<td>0.20</td>
<td>4.05</td>
</tr>
<tr>
<td>0.21</td>
<td>3.55</td>
</tr>
</tbody>
</table>

(b) **Multiple solutions**

(i) **Adiabatic case.** In an adiabatic case for the equality $Pe_\theta = Pe_v$ the dashed line ($Q = 0$) remains in the domain of multiplicity ($\Delta = 0$) and does not exhibit the loop character. Therefore, one can expect only the saddle-type instabilities. In an adiabatic case, upper and lower steady states can be assumed to be asymptotically stable. This fact was verified analytically[4] as well as numerically[3, 7]. The character of the time profiles in an adiabatic case may be observed in Fig. 16. A quite complicated situation may exist for $Pe_\theta \neq Pe_v$. Since neither of the steady state equations have been analyzed we intend to discuss this case in a forthcoming communication.

(ii) **Nonadiabatic case.** In a nonadiabatic case as well as for conditions of a nonequality of Peclet numbers, the problems of multiplicity are tedious. In this case the systematic analysis has not been performed and, therefore, we restrict
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6. DISCUSSION

In this paper some definitions have been used which are common in nonlinear mechanics where sets of nonlinear ordinary differential equations are studied. However, utilizing these definitions may be useful for functional space too. An extension of the first Ljapunov method to functional space, which is of great importance in theoretical reaction engineering, seems to be possible. Therefore, a term “point”, which has been used in this paper, should be understood as a point in functional space.

This and some preliminary analysis have shown that the correspondence between sets of ordinary and partial differential equations is broad, e.g. one can prove rigorously for a CSTR that the middle steady state is of saddle character and, therefore, is always unstable. This statement is valid in functional space too and the middle profile is always supposed to be unstable. As we have shown, the same analogy is valid for a case where only one unstable solution exists. For a CSTR an oscillation of temperature and conversion may be observed. On the other hand, in distributed parameter systems the whole profile, \( \theta(\xi) \) and \( \psi(\xi) \), oscillate. A similar correspondence for multiplicity may be constructed if more than one unstable solutions of the steady state equations exist.

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REFERENCES

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