Effective approach to cyclic steady state in the catalytic reverse-flow combustion of methane

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Abstract

Computer-based simulations of a reverse-flow reactor should be carried out till the attainment of the so-called cyclic steady state. Usually this state is achieved by the method of direct dynamic simulations. In the paper of Unger et al. (Comput. Chem. Eng. 21 (1997) 5167.) special approaches, making use of various minimization algorithms based most often on Newton algorithms, are proposed. In the present paper one deals with a comparison and an appraisal of these methods, applied to the reverse-flow catalytic combustion of methane that occurs in coal-mine ventilation air.

1. Introduction

The most often applied technique for the study of reverse-flow reactors is mathematical modeling of the process under consideration (see e.g. Matros, 1989). In the paper of Aube and Sapoundiev (2000) the mathematical model was verified by experiments performed for the oxidation of lean methane emissions, i.e. the case similar to the present study. The most interesting are results for the state, in which the process behavior in successive reversion cycles becomes repeatable. Such a state is called the cyclic steady state (CSS). The usual approach is direct dynamic simulation (DDS), consisting in successive solution of the partial differential equations of the material and energy balance i.e. by calculating the transient from a certain initial start up to attainment of CSS. To accelerate convergence to CSS often instead of DDS iterative shooting methods, first proposed by Gupta and Bhatia (1991) are used (see also e.g. Khinast and Luss, 1997, or Unger et al., 1997). The common feature of these methods is the absence of simulation of the whole transient process. One of these methods is the global discretization by finite element method (e.g. Salinger and Eigenberger, 1996a). However, the major drawback of this method is that it generally leads to a large system of nonlinear equations. An approach similar to the one presented by Unger et al. (1997) was applied in the present work.

2. Definition of cyclic steady state

2.1. Definition based on the repeatability of the process behavior

In the paper of Unger et al. (1997) the definition of CSS is given first in a rather sketchy form “… From a practical point of view the state where the process repeats itself after one cycle … is called the cyclic steady state”. Further, the authors give a formal definition of CSS as an algebraic problem with respect to the initial condition for the successive cycle. If one assumes that the vector of the state variable at the end of cycle τ is a smooth function of the initial values xo:

\[ x(\tau) = X(x_0) \]  

then CSS will occur when

\[ R(x_0) \equiv X(x_0) - x_0 \equiv 0. \]
Usually this formula cannot be accurately fulfilled. Some residual remains which is minimized in the process of searching the cyclic steady state, until a certain given accuracy \( \varepsilon_{\text{per}} \) is attained.

\[
R(x_0) = ||x(\tau) - x_0|| < \varepsilon_{\text{per}}.
\]  

(3)

In the quoted paper a few ways of such minimization are analyzed. However, a full reversal cycle consists of two half-cycles. In the first one the reaction mixture in the reactor flows in one direction, whereas in the second half-cycle the flow in the opposite direction takes place. The moment at which the flow direction returns to the initial one is the end of the full reversal cycle. The notion “process repeats itself” requires precision. Namely, profiles of all state variables of the reactor, temperatures and concentration of reactants and products, will be repeated.

2.2. Thermodynamic definition

The steady state of any process occurs when the variations of mass and energy accumulation in this process vanish. In the case of processes occurring in a forced unsteady state, the fulfillment of this principle is for average values at some time intervals. Burghardt (2003) derives formally, for the one-dimensional continuous two-phase model the criterion of autothermicity, based on this principle including both one- and multireaction system. The author assumes also heat exchange with surroundings. The condition in question, resulting from the first law of thermodynamics may thus be reduced to the following form:

\[
\Delta T_{\text{ad}} \times X_{\text{average}} = \left( \frac{1}{n \pi/2} \right) \int_{T_{\text{inlet}}}^{T_{\text{outlet}}} T_{\text{outlet}}(t) \, dt - T_{\text{inlet}} + \Delta T_S. 
\]  

(4)

Condition (4) is not necessarily fulfilled in each reversal half-cycle (\( n \) is not necessarily unity, i.e. \( n \geq 1 \)). In particular, it indicates that the successive half-cycle may not necessarily constitute a mirror copy of the preceding half-cycle. Gosiewski and Wramuzinsky (2002, 2003) present examples of simulations with various conditions of heat extraction from the reactor. They show that at the CSS asymmetry of profiles in successive half-cycles occurs. For an asymmetric cycle the thermodynamic condition (4) can be fulfilled only for the full reversal cycle (i.e. for \( n = 2 \)).

The problem of asymmetric solutions is not new. Such solutions for a reactor with gas phase cooling has been shown in the work of Rehacek et al. (1992) and also by Salinger and Eigenberger (1996b) or Khinast et al. (1999). Matsos (1989) found mirror symmetry only for the adiabatic process, i.e. without heat exchange with surroundings. One cannot claim, however that the symmetry exists only for such cases. Many studies (cf., e.g. Rehacek et al., 1992; Gosiewski and Wramuzinsky, 2002, 2003) show that heat exchange with surroundings promotes asymmetric solutions.

2.3. Methods of attainment of the CSS in simulation of reverse-flow reactors

Unger et al. (1997) classify methods of attainment of CSS for various cyclic processes, called regenerative ones, as:

- direct dynamic simulation (DDS),
- special (shooting) methods, shortly named here iterative ones.

These two approaches are described below.

3. Attainment of CSS by direct dynamic simulations

Taking into account that, at the moment of reversal the zero point of the axial coordinate changes, the initial conditions of temperature for the next half-cycle will be the reversed temperature profile at the end of the preceding cycle, according to the following formula:

\[
T_{c}^{j+1}(z, 0) = T_{c}^{j}(L - z, \tau/2).
\]  

(5)

Such computations are from the numerical viewpoint just the method of direct substitution, i.e. so-called Pickard iteration.

It follows from the thermodynamic condition (4) that the appearance of CSS may be determined for various number of half-cycles \( n \). The advantage of DDS lies in the fact that the way of achievement of CSS does not require explicitly the determination of a value of \( n \) for which condition (4) should be fulfilled, since Pickard iteration (of direct substitutions) does not require, either, checking the value of an objective function in each step of iteration. On the other hand, their weakness is the long time necessary to attain/achieve CSS. The determination of the objective function (residual) is necessary, in principle, only to check the terminal condition for the computations. One may, after all, calculate a number of steps (in this case: half-cycles) and then compute the terminal condition. In such a situation various objective functions can be computed after executing the given number of steps. They can be compared a posteriori to determine if desired accuracy has been achieved. The two following measures of the accuracy of attainment of CSS in a reverse-flow reactor are defined:

\[
\delta T(z) = |T_{c, j}^{\text{start}}(z) - T_{c, j-1}^{\text{start}}(z)| 
\]  

(6)

and

\[
\delta T_{\text{twin}}(z) = |T_{c, j}^{\text{start}}(z) - T_{c, j-2}^{\text{start}}(z)|. 
\]  

(7)

Measure (6) corresponds to assumption of the value \( n = 1 \) in Eq. (4) i.e. the assumption that successive half-cycles constitute the mirror copy of the preceding cycle, the average heat balance of the reactor being fulfilled already for a single half-cycle. On the other hand, the measure (7) assumes that \( n = 2 \), which means that the repeatability occurs only for the full cycles and only for the full cycle is the average heat
balance of reactor fulfilled. In this way two functions of assessment of obtained process profiles by DDS were used:

\[ I_{\text{single}} = \Delta T_{\text{av}} = \frac{1}{k} \sum_{i=1}^{k} \delta T(z_i) \]  
\[ I_{\text{twin}} = \Delta T_{\text{twin}}^{\text{av}} = \frac{1}{k} \sum_{i=1}^{k} \delta T_{\text{twin}}(z_i), \]

where \( k \) is an arbitrarily selected number of “control points” along the reactor bed length. The values of both functions were checked frequently during the process of DDS.

Fig. 1 presents development of both objective functions for the reverse-flow catalytic combustion of methane containing 0.4 vol% (with the utilization of heat of combustion by means of 8% of hot gas withdrawal similarly as in Nieken et al. (1994), from the central zone of the reactor) during DDS as a function of successive numbers of half-cycles. As may be seen, the value of function (8), after almost 50 half-cycles stabilizes at a rather high mean temperature difference, equal to ca. 10 K, whereas function (9) diminishes monotonically, reaching the value of ca. 10^{-4} K, i.e. of order of accuracy of numerical computations after 100 computed half-cycles. It shows that a small but stable asymmetry is formed, since it does not diminish in the process of further simulations.

4. Application of iterative methods with constraints of decision variables for finding the CSS in the reverse-flow reactor

4.1. Concise discussion of the numerical methods employed

The dynamic simulations of the catalytic combustion of hydrocarbons constitute, in general, a difficult numerical problem, since large heat release from the combustion reaction cause high temperature and concentration gradients in the reactor. This creates stability problems for the numerical process. So, one is forced to use a dense numerical grid and sophisticated numerical methods in order to obtain stable and reasonably accurate results.

The mathematical model of catalytic combustion of methane in a reactor with fixed catalyst bed was already described by Gosiewski and Warmuzinski (2002, 2003). It is a one-dimensional, two phase model, both for heat and for mass transfer. It takes into account the effective thermal conductivity in the solid phase and dispersion in the gas phase. Owing to strong non-linearities occurring in the model, the numerical package PDEX1M (Nowak et al., 1996) for integration of parabolic differential equations was employed. The advantage of the package is adaptation of the size of the time step of numerical integration, as well as adaptation of size of the spatial grid to obtain accurate computations. Such an adaptation causes that the nodes of spatial grid appear at different points in individual time steps. Moreover, in some regions this is a dense grid, whereas in other regions it becomes sparse. Thus the initial distribution of state variables after each reversal may be determined at different points and for a different number of these points. For this reason the \( k \) control points along the bed length, at which one calculates the values of state variable, used for calculation of residual (3), were selected at points, which did not necessarily constitute the nodes of the numerical grid. Besides, the number of these points was much smaller than the number of nodes. Moreover, the control points were uniformly distributed in space, whereas the adaptive package PDX1M generates the numerical network with the nodes distributed non-uniformly. For this reason, in order to determine the uniformly distributed points for the minimization of residual (3) use has been made of interpolation procedures by the method of spline functions. Similar procedure was employed for determination of catalyst temperatures \( T_c \) at \( m_{\text{in}} \) points of the numerical network from control points of the temperature distribution, calculated by the minimization procedure and usually

\[ k \ll m_{\text{in}} \]  

and conversely, from the temperature distribution at \( m_{\text{fin}} \) points of network, calculated at the end of a half-cycle, the temperature values at \( k \) uniformly distributed points were computed in order to determine the objective function of minimization and also

\[ m_{\text{fin}} \gg k. \]

It should be remembered, that

\[ k = \text{const}; \quad m_{\text{in}} = \text{var}; \quad m_{\text{fin}} = \text{var}. \]  

The number \( k \) of uniformly distributed control points is assumed arbitrarily. This number \( k \) was selected as a compromise between the accuracy of representation of the profile of...
the state variable and CPU-time necessary for computations of gradient matrix (sensitivity matrix), indispensable for operation of the majority of the minimization procedures. Usually, gradient-oriented procedures perform updating of the gradient matrix every few steps of computations. In reverse-flow reactors there is in principle no possibility of supplying a procedure to calculate the gradient analytically. This means that the minimization procedure aimed at updating the gradient matrix, performs $k$ or sometimes $2 \times k$ (when the gradient is determined on the basis of trial steps, made in two directions) auxiliary “ineffective” steps which do not tend to a minimum. In the present work, however, use has been made of standard optimization procedures of the IMSL library, which update the gradient matrix quite often.

The following minimization criterion was used:

$$J_{\text{single}} = \frac{1}{k} \sum_{i=1}^{k} (\delta T(z_i))^2 = \min,$$  \hspace{1cm} (13)

i.e. assuming the process repeatability after each half-cycle of the reversal. The model for the reversal process contains a significant accumulation term in only one balance equation, accumulation of heat in the solid phase of reactor packing. Thus it has been assumed that the temperature profile $T_{\text{solid}}$ in the solid phase is the parameter that determines the state of the reactor. Only the temperature profiles in the bed were treated as state variable. The following constraint of control variables for minimization

$$T_{\text{inlet}}^\text{start} \leq T_{\text{c, j}}(z) \leq T_{\text{bound}}$$  \hspace{1cm} (14)

was implemented.

The value of admissible maximum temperature $T_{\text{bound}}$ was selected at an adequately high level so practically it was the non-active constraint in the entire computational process. On the other hand, the lower constraint, assumed as the value of temperature of the gas inlet to the reactor was often active for the points close to the inlet and outlet from reactor. This efficiently limited the search range for catalyst temperature in the process of minimization.

4.2. Results

In Fig. 2, development of index (8) during the process of iterative minimization of this criterion was presented for the same reverse-flow reactor data, for which the transients shown in Fig. 1 were obtained. The iterative computations have been carried out making use of the two minimization routines with simple bounds of the control variables:

- routine DBCONF using the quasi-Newton algorithm and a finite-difference gradient,
- routine DBCLSF using Levenberg–Marquardt algorithm with approximation of a finite-difference Jacobian.

When applying the first routine the direct minimization of criterion (13) is implemented directly, whereas in the second case the computation of the minimization criterion is somewhat more complex. One computes the vector $F(x)$ according to the following relationship:

$$F(x) = F(T_{\text{c, start}}),$$  \hspace{1cm} (15)

and afterwards the minimization is accomplished using the formula

$$\min_{x \in \mathbb{R}^k} \frac{1}{2} F(x)^T F(x) = \frac{1}{2} \sum_{i=1}^{k} f_i(x)^2,$$  \hspace{1cm} (16)

where $f_i(x) = (\delta T(z_i))^2$ is a component of the vector $F(x)$.

Presentation of the results of minimization by means of these special iterative methods as functions of number of steps performed in the search direction is misleading since it does not indicate the computational effort for updating the gradient. For this reason the graphs in Fig. 2 show all half-cycles computations (i.e. both “effective” and “ineffective” ones). The moments at which the routine performed the effective steps are indicated on the graph as crosses. As may be seen, both routines, after executing a certain number of computation of half-cycles (steps) stabilize index (8) at the value of ca. 20 K, later there is no improvement of the value, although in the best case there is slow creeping reduction of the objective function (residual). The application of Levenberg–Marquardt routine leads to the stabilization of this value after performing the computation of ca. 80 half-cycles, whereas in the case of quasi-Newton routine this occurs after twice as large (about 160) number of steps. Strictly speaking, this is not the stabilization of the value of residual, since after setting up the criteria for termination of computations in such a manner that the quasi-Newton routine should perform many more steps (710 half-cycles, among which there are only 53 effective steps) this error was still reduced to ca. 10 K.

Fig. 3 illustrates an analogous development achieved for the inlet methane concentration equal to about 1 vol% (with...
the utilization of heat by 30% of hot gas withdrawal). The deviations for both routines after computation of about 120 half-cycles are in this case somewhat larger (about 30 K), nevertheless both transients are similar. In the case of the assumption that criterion (9), describing the full reversion cycle, is the object of minimization, the computational effort for each iteration step and also for updating the gradient would be twice as high, since two half-cycles should be computed in each step. In this case the numerical effectiveness is probably smaller.

5. Comparison of reactor parameters in the CSS attained by various computational methods

In practice, numerical effectiveness as well as attaining similar reactor operation parameters in CSS is important, even if various approaches to the state are used. Hence the problem arises as to whether or not making use of different computational techniques for attainment of CSS as to gave the same final state. Fig. 4a presents the catalyst temperature profiles during half-cycle calculated for methane concentration equal to 0.4 vol% by the direct simulation method. Similar profiles for the application of Levenberg–Marquardt algorithm, are shown in Fig. 4b. Analogous profiles obtained by a quasi-Newton method are indicated in Figs. 4c and d. In the case of Fig. 4c, 250 half-cycles were computed whereas in the case of Fig. 4d, 710 half-cycles. The comparison shows that all these profiles differ significantly. It may be seen from Fig. 4 that computations of several hundreds of half-cycles are necessary to get some similarity between the shape of temperature profiles obtained by iteration with the quasi-Newton algorithm to that obtained by direct simulation.

The comparison of other parameters essential for estimation of the reliability of the computational methods is given in Table 1.

When the value of the average deviation of temperature profiles (residual) is large, then the approximate error of reactor heat balance, calculated from Eq. (4) may be used as an estimate of the reliability of the results. This error might often be significant because of averaging dynamically changing transients, particularly in the case of heat extraction by the central withdrawal of hot gas. On the other hand, one can take this error as an auxiliary assessment of CSS obtained. This means that determining the deviation of average temperature rise in reactor from the adiabatic rise \( \Delta T_{\text{ad}} \) theoretically calculated indicate whether or not the results show attainment of the CSS. In the case of DDS, although the relative deviation of this increase from \( \Delta T_{\text{ad}} \) is still significant (11%), the results look reliable and, moreover, require the smallest computational effort. The value of \( I_{\text{win}} \) i.e. the measure of repeatability of the temperature profile after calculating a full cycle, is in this case very small (somewhat above 0.0001 K). For the results by the Levenberg–Marquardt algorithm, the heat balance error is not acceptable (114%), although the convergence to the value of temperature error \( I_{\text{single}} \approx 20 \text{ K} \) was achieved at the computational effort almost half that of when using the quasi-Newton algorithm.

6. Summary

For the cases considered, application of special iterative methods to the simulation of a reverse-flow catalytic combustion of methane does not provide computational advantage. Our findings, however, cannot be taken as a total disqualification of these methods. Their failure in our case was probably the result of

- non-uniform numerical network and, difficulties of determining accurate values of state variables by interpolation using spline functions.
- large temperature gradients along the reactor length caused by the large heat of combustion.

In the routines applied a large computational effort was spent on frequent updating the gradient matrix. In the examples investigated the number of effective steps was not large, but the majority of the CPU-time was used to execute the ineffective steps. Even if routines with reduced number of updates actually reduce the CPU-time, errors resulting from inaccurate interpolation of state variables would remain. Summing up, in complex cases, special iterative methods may not provide an improvement of the computational process. It seems that shooting methods are advantageous for the cases when global discretization can be effectively used.

Two advantages of the method of direct dynamic simulations should be mentioned:

- If initial profiles of state variables correspond to the actual initial state of reactor, then the method of direct simu-
Fig. 4. Temperature profiles during an half-cycle for methane concentration of 0.4% for CSS attained using various methods: (a) Direct dynamic simulations; (b) Levenberg–Marquardt; (c) quasi-Newton (after 250 half-cycles); and (d) quasi-Newton (after 710 half-cycles).

Table 1
Comparison of reactor parameters in the CSS obtained by various computational methods

<table>
<thead>
<tr>
<th>Computational method</th>
<th>Number of half-cycles computed</th>
<th>Final value of criterion $I_{\text{single}} = \Delta T_{\text{av}}$</th>
<th>Approximate error of the heat balance of half-cycle</th>
<th>Maximum temperature $T_{\text{max}}$</th>
<th>Effective conversion in reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct simulations</td>
<td>100</td>
<td>10.8 ($^a$)</td>
<td>+11</td>
<td>1129</td>
<td>95.6</td>
</tr>
<tr>
<td>Levenberg–Marquardt algorithm</td>
<td>134</td>
<td>22.6</td>
<td>+114</td>
<td>1218</td>
<td>99.8</td>
</tr>
<tr>
<td>Quasi-Newton algorithm</td>
<td>250</td>
<td>20.7</td>
<td>+14</td>
<td>1106</td>
<td>97.1</td>
</tr>
<tr>
<td></td>
<td>710</td>
<td>12.0</td>
<td>−14</td>
<td>1059</td>
<td>90.15</td>
</tr>
</tbody>
</table>

$a$ For direct simulations the value of criterion $I_{\text{tw}}$ is equal only to 0.000137 (K).

- An objective function for minimization does not need to be evaluated. It is sufficient to calculate values to see if CSS has been attained. Criterion (8) for repeatability in each half-cycle and criterion (9) for repeatability in each full cycle can be examined simultaneously without affecting either the simulation or the computational time. By contrast in the special iterative methods, it must be assumed in advance which criterion is to be minimized.

In the case studied making use of the two iterative minimization methods, only criterion (8) was used as the objective function; whereas both criteria (8) and (9) were used with direct simulations. Application of criterion (9) for the special iterative (shooting) methods would increase the CPU-time at least twofold.
### Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$</td>
<td>gass heat capacity, J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$l_{\text{single}}$</td>
<td>assessment of deviation from CSS according to Eq. (9), K</td>
</tr>
<tr>
<td>$l_{\text{twin}}$</td>
<td>assessment of deviation from CSS according to Eq. (10), K</td>
</tr>
<tr>
<td>$J_{\text{single}}$</td>
<td>minimization criterion, K$^2$</td>
</tr>
<tr>
<td>$k$</td>
<td>number of control points along the reactor length</td>
</tr>
<tr>
<td>$L$</td>
<td>total reactor length, m</td>
</tr>
<tr>
<td>$m_{\text{fin}}$</td>
<td>number of numerical grid points at the end of the half-cycle</td>
</tr>
<tr>
<td>$m_{\text{in}}$</td>
<td>number of numerical grid points at the beginning of the half-cycle</td>
</tr>
<tr>
<td>$n$</td>
<td>number of the half-cycles averaged for the heat balance control</td>
</tr>
<tr>
<td>$t$</td>
<td>time, s</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, K</td>
</tr>
<tr>
<td>$T_{\text{bound}}$</td>
<td>admissible maximum temperature, K</td>
</tr>
<tr>
<td>$T_{\text{max}}$</td>
<td>maximum catalyst bed temperature, K</td>
</tr>
<tr>
<td>$x$</td>
<td>vector of state variables subset</td>
</tr>
<tr>
<td>$X$</td>
<td>vector of state variables subset at the end of reversal cycle, dimensionless</td>
</tr>
<tr>
<td>$y$</td>
<td>mole fraction in gas phase, dimensionless</td>
</tr>
<tr>
<td>$z$</td>
<td>axial coordinate in reactor, m</td>
</tr>
</tbody>
</table>

### Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta T$</td>
<td>starting temperature deviation in consecutive half-cycles, K</td>
</tr>
<tr>
<td>$\delta T_{\text{twin}}$</td>
<td>starting temperature deviation in consecutive full cycles, K</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>heat of reaction, J mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta T_{\text{ad}}$</td>
<td>adiabatic temperature rise, K</td>
</tr>
<tr>
<td>$\Delta T_s$</td>
<td>temperature difference due to heat transfer to surroundings, K</td>
</tr>
<tr>
<td>$\tau$</td>
<td>full cycle time of reversal, s</td>
</tr>
</tbody>
</table>

### Acknowledgements

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### References


