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Mathematical modelling of a reverse flow reactor
with catalytic surface dynamics

by

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Mathematical modelling of a reverse flow reactor with catalytic surface dynamics

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Abstract. This paper studies a system of partial differential equations modelling the behaviour of a reverse flow reactor. For the parameters appropriate for the oxidation of ammonia on a Pt/Al₂O₃ catalyst in a typical laboratory set-up, the reactor may be split into regions where approximate formulas that determine its behaviour are deduced. Numerical calculations are presented and can be used to compare with the analytical formulas. The physical insight gained from the asymptotic analysis suggests a new switching strategy which is the subject of numerical experiments. The switching strategy is found to be efficient at minimising the ammonia exiting the reactor after reversal.

Keywords: Reverse flow, mathematical modelling, nonlinear dynamics.

1 Introduction

In this paper, we consider the reverse flow operation of a fixed bed reactor, where the direction of flow through the reactor is changed from forward to backward and vice versa after certain time intervals. Applications include commercially significant processes such as the oxidation of valuable organic compounds Boreskov et al. (1977), the oxidation of SO₂ Matros et al. (1984), the reduction of NO₂ by ammonia Bobrova et al. (1988), sulphur production by the Claus method Matros and Zagoruiko (1987), the conversion or partial oxidation of methane Blanks et al. (1990) and the synthesis of methanol Busche et al. (1993) and ammonia Gerasev and Matros (1991).

This process differs from standard auto-thermal operation, because the heat recovery can take place by regeneration instead of the recuperative heat exchange. The heat recovery is facilitated by the inert parking material at both ends of the fixed bed, which act as recuperative heat exchangers. High energy efficiency may be achieved in reverse flow reactors, since part of the reaction heat is retained inside the fixed bed, thus allowing lower feed temperatures than currently applied. Concentrations and temperatures vary considerably in the fixed bed, depending on design parameters, such as length of both the catalyst and inert bed, the overall bed porosity, as well as operating parameters such as the feed concentration, the gas flow rate and the flow switching frequency. Simulations have been mainly performed by assuming quasi steady-state balance for gas concentrations and temperature steady-state reaction kinetics. It was shown experimentally Noskov et al. (1993) that the catalyst state dynamics, occurring on a time-scale comparable with cycle duration, influence the process and therefore this has to be taken into account in the mathematical model to explain the phenomena observed.

The purpose of this paper is to gain a better understanding of the rôle played by chemical and thermal effects. However, as well as analysing the reactor operation, we shall propose a new switching strategy to minimise the ammonia exiting the reactor after reversal. We present the results of a mathematical study of a reverse flow reactor with the dimensions of a typical laboratory set-up. A dynamic model of the simple two-stage reaction mechanism, which comprises a reversible adsorption stage and a stage describing the

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exothermic reaction on the catalyst surface, is used for the analysis, namely

\[ A + [ \_ ] \leftrightarrow [A], \]

\[ [A] \rightarrow B + [\_]. \]

The kinetic parameters of these stages were determined on the hypothesis that oxidation of ammonia occurs on the Pt/Al₂O₃ catalyst. The oxidation of ammonia is known to involve several simultaneous reactions and is characterised by its intricate multiplicity Il’chenko and Golodets (1975). In our model, the main behaviour of the reaction on this type of catalyst is taken into account, that is the high adsorption probability of ammonia with mostly weakly bounded species, the high adsorption capacity of the catalyst surface Popova et al. (1998a,b) and the strong reactivity of the catalyst for ammonia decomposition De Laney and Manogue (1973). These features seem to be defining the catalyst state dynamics for the ammonia oxidation, which may strongly influence the reactor dynamics as a whole.

A mathematical model is introduced in Section 2 and non-dimensionalised in Section 3, enabling the dominant balances to be identified. Section 4 describes an asymptotic analysis, whereby the governing equations are reduced to simpler systems in various regions of the device. In Section 5, numerical solutions are obtained. The new switching strategy is proposed and numerical experiments are conducted to assess its performance. Finally, Section 6 gives a brief discussion of the results.

## 2 Problem formulation

In this section, we introduce a one-dimensional mathematical model for the reverse flow reactor. The spatial coordinate is denoted by \( x \) and \( t \) is time. The fixed bed consists of two inert packed beds (\( 0 < x < x_1 \) and \( x_2 < x < x_3 \)) separated by the catalyst bed (\( x_1 < x < x_2 \)). The inert and catalyst bed are assumed to be connected so that heat flux is continuous between these regions. The parameters are defined and values are given in Table 1. The values of kinetic parameters were estimated on the basis of results published elsewhere Il’chenko and Golodets (1975)-Matros and Bunimovich (1996). The initial boundary value problem for the ammonia concentration in the bulk gas phase \( C_f \), the ammonia concentration in the catalyst pore gas phase \( G_e \), the temperature of the bulk gas phase \( T_f \), the temperature of the solid phase \( T_s \) and the surface coverage of ammonia \( \theta \) is

\[
\phi_f \frac{\partial C_f}{\partial t} + \phi_f u \frac{\partial C_f}{\partial x} = -\beta_0 a_v \phi_f (C_f - C_c) \quad \text{for} \quad x_1 < x \leq x_2, \tag{1}
\]

\[ (1 - \phi) \frac{\partial C_c}{\partial t} = \beta_0 a_v \phi_f (C_f - C_c) - \rho_f (r_{ads} - r_{des}) \quad \text{for} \quad x_1 \leq x \leq x_2, \tag{2} \]

\[ \phi_f c_f \frac{\partial T_f}{\partial t} + \phi_f c_f u \frac{\partial T_f}{\partial x} = \alpha_0 a_v (T_s - T_f) \quad \text{for} \quad 0 < x < x_3, \tag{3} \]

\[ (1 - \phi) \rho_c c_t \frac{\partial T_s}{\partial t} = (1 - \phi) \lambda_c \frac{\partial^2 T_s}{\partial x^2} - \alpha_0 a_v (T_s - T_f) - (H_{react} r_{react} + H_{ads} r_{ads} + H_{des} r_{des}) \quad \text{for} \quad x_1 \leq x \leq x_2, \tag{4} \]

\[ (1 - \phi) \rho_c c_t \frac{\partial T_s}{\partial t} = (1 - \phi) \lambda_c \frac{\partial^2 T_s}{\partial x^2} - \alpha_0 a_v (T_s - T_f) \quad \text{for} \quad 0 < x < x_1 \quad \text{and} \quad x_2 < x < x_3, \tag{5} \]

\[ L_1 \frac{\partial \theta}{\partial t} = r_{ads} - r_{des} - r_{react} \quad \text{for} \quad x_1 \leq x \leq x_2, \tag{6} \]

where the reaction rates are given by

\[ r_{ads} = k_{ads} C_c (1 - \theta) \exp(-E_{ads}/RT_s), \quad r_{des} = k_{des} \theta \exp(-E_{des}/RT_s), \quad r_{react} = k_{react} \theta \exp(-E_{react}/RT_s), \]

the boundary conditions are

\[ C_f = C_a \quad \text{on} \quad x = x_1, \quad T_f = T_a, \quad \frac{\partial T_s}{\partial x} = 0 \quad \text{on} \quad x = 0 \quad \text{and} \quad \frac{\partial T_s}{\partial x} = 0 \quad \text{on} \quad x = x_3 \tag{7} \]
and the initial conditions are

\[ C_f = C_c = \theta = 0, \quad T_f = T_s = T_{\text{initial}} \quad \text{at} \quad t = 0. \]  

(8)

The reaction rates of adsorption, desorption and reaction are given by \( r_{\text{ads}}, r_{\text{des}} \) and \( r_{\text{react}} \), respectively. Equations (1) and (2) represent conservation of mass for the ammonia concentration. Equations (3), (4) and (5) correspond to conservation of energy. The surface coverage is modelled by (6). We have only stated the model for the gas traversing the domain from left to right, the model corresponding to gas traversing the domain from right to left is similar.

3 Non-dimensionalisation

3.1 Introduction

The reactor may attain one of two stable steady states. The stable steady state of practical interest corresponds to significant chemical reaction taking place, henceforth known as the hot solution branch. The other steady state is associated with extinction (cold solution branch). We only briefly summarise the appropriate non-dimensionalisation for the cold solution branch. We transform to dimensionless variables via \( C_f = C_0 \check{C}_f, \quad C_c = C_0 \check{C}_c, \quad T_f = T_0 + \Delta^* \check{T}_f, \quad T_s = T_0 + \Delta^* \check{T}_s, \quad r_{\text{ads}} = \check{r}_{\text{ads}} r_{\text{ads}}, \quad r_{\text{des}} = \check{r}_{\text{des}} r_{\text{des}}, \quad r_{\text{react}} = \check{r}_{\text{react}} r_{\text{react}}, \quad t = \check{t} \) (\( \tau \) is the period of switching) and \( x = L \hat{x} \) \((L = x_2 - x_1)\). The * denotes either the cold (\( C \)) branch of solutions or the hot (\( H \)) branch of solutions.

3.2 Hot solution branch

A representative value of the temperature rise is given by a balance of the reaction term and transport of heat between fluid and solid in (4), namely the larger of the two positive real roots of

\[ \frac{a_0 a_v \Delta^H}{|H_{\text{react}}| k_{\text{react}}} = \exp \left( \frac{-E_{\text{react}}}{R(T_0 + \Delta^H)} \right). \]

This value may then be employed to obtain characteristic values for the reaction rates

\[ r_{H_{\text{ads}}} = k_{\text{ads}} C_a \exp \left( \frac{-E_{\text{ads}}}{R(T_0 + \Delta^H)} \right), \quad r_{H_{\text{des}}} = k_{\text{des}} \exp \left( \frac{-E_{\text{des}}}{R(T_0 + \Delta^H)} \right), \quad r_{H_{\text{react}}} = k_{\text{react}} \exp \left( \frac{-E_{\text{react}}}{R(T_0 + \Delta^H)} \right). \]

Making the transformation to dimensionless variables, equations (1)-(8) become

\[ \sigma \frac{\partial \check{C}_f}{\partial \check{t}} + A \delta \frac{\partial \check{C}_c}{\partial \check{x}} = -(\check{C}_f - \check{C}_c) \quad \text{for} \quad \check{x}_1 < \check{x} \leq \check{x}_2, \]

(9)

\[ \nu \frac{\partial \check{C}_c}{\partial \check{t}} = D(\check{C}_f - \check{C}_c) - \frac{B}{\epsilon} \check{r}_{\text{ads}} + \frac{1}{\epsilon} \check{r}_{\text{des}} \quad \text{for} \quad \check{x}_1 < \check{x} \leq \check{x}_2, \]

(10)

\[ \epsilon \sigma \frac{\partial \check{T}_f}{\partial \check{t}} + A \delta \frac{\partial \check{T}_f}{\partial \check{x}} = \check{T}_s - \check{T}_f \quad \text{for} \quad 0 < \check{x} \leq \check{x}_3, \]

(11)

\[ \delta \frac{\partial \check{T}_s}{\partial \check{t}} = K \delta \frac{\partial^2 \check{T}_s}{\partial \check{x}^2} - (\check{T}_s - \check{T}_f) - \left( - \frac{\check{r}_{\text{react}}}{\epsilon} \check{r}_{\text{ads}} + \frac{\check{r}_{\text{des}}}{\epsilon} \right) \quad \text{for} \quad \check{x}_1 < \check{x} \leq \check{x}_2, \]

(12)

\[ \delta \frac{\partial \check{r}_{\text{ads}}}{\partial \check{t}} = L \delta \frac{\partial^2 \check{r}_{\text{ads}}}{\partial \check{x}^2} - (\check{T}_s - \check{T}_f) \quad \text{for} \quad 0 < \check{x} < \check{x}_1 \quad \text{and} \quad \check{x}_2 < \check{x} < \check{x}_3, \]

(13)

\[ \check{G} \delta \frac{\partial \theta}{\partial \check{t}} = B \frac{\check{r}_{\text{ads}}}{\epsilon} - \frac{1}{\epsilon} \check{r}_{\text{des}} - \check{r}_{\text{react}} \quad \text{for} \quad \check{x}_1 < \check{x} \leq \check{x}_2, \]

(14)
where
\[ \hat{r}_{\text{ads}} = \hat{C}_c (1 - \theta) \exp \left( \frac{\beta_{\text{ads}}(\hat{T}_s - 1)}{1 + \gamma \hat{T}_s} \right), \quad \hat{r}_{\text{des}} = \theta \exp \left( \frac{\beta_{\text{des}}(\hat{T}_s - 1)}{1 + \gamma \hat{T}_s} \right), \quad \hat{r}_{\text{react}} = \theta \exp \left( \frac{\beta(\hat{T}_s - 1)}{1 + \gamma \hat{T}_s} \right), \]
with the boundary conditions
\[ \hat{C}_f = 1 \quad \text{on} \quad \hat{x} = \hat{x}_1, \quad \hat{T}_f = 0, \quad \frac{\partial \hat{T}_s}{\partial \hat{x}} = 0 \quad \text{on} \quad \hat{x} = 0 \quad \text{and} \quad \frac{\partial \hat{T}_s}{\partial \hat{x}} = 0 \quad \text{on} \quad \hat{x} = \hat{x}_3, \]
and the initial conditions
\[ \hat{C}_f = \hat{C}_c = \theta = 0, \quad \hat{T}_f = \hat{T}_s = \hat{T}_{\text{initial}} \quad \text{at} \quad \hat{t} = 0. \]

The dimensionless constants \( \sigma, A\delta, \nu, D, B/\epsilon, 1/\epsilon, \epsilon \sigma, A\epsilon \delta, \delta, K\delta^2, F, H\delta, L\delta^2, G\delta, \gamma, \beta_{\text{ads}}, \beta_{\text{des}}, \beta, \hat{T}_{\text{initial}}, \hat{x}_1, \hat{x}_2 \) and \( \hat{x}_3 \) are defined in Table 2; the constraints \( \sigma \ll \delta \ll 1, \nu \ll 1, \epsilon \ll 1 \) typically hold for this catalyst. The small parameters are \( \sigma \), representing the ratio of time-scale for variations in ammonia concentration in the bulk gas phase to time-scale for switching, \( \nu \), the ratio of time-scale for variations in ammonia concentration in the catalyst pore phase to time-scale for switching, \( \epsilon \), the ratio of time-scale for desorption to time-scale for reaction and \( \delta \), which represents the ratio of length-scale for the reaction region to the length-scale for the catalyst part of the reactor. The small parameter \( \delta \) also represents the ratio of time-scale for reaction to time-scale for switching which is equivalent to the original definition on multiplying both time-scales by the thermal wave speed (see below). We have taken \( |H_{\text{ads}}| = |H_{\text{des}}| \), this equality must hold to a good approximation for (10), (12) and (14) to be consistent at leading order.

### 3.3 Cold solution branch

In this case the typical temperature rise is very much less than the input fluid temperature, so the characteristic values for reaction rates are
\[ r_{\text{ads}}^C = k_{\text{ads}} C_a \exp(-E_{\text{ads}}/RT_a), \quad r_{\text{des}}^C = k_{\text{des}} \exp(-E_{\text{des}}/RT_a), \quad r_{\text{react}}^C = k_{\text{react}} \exp(-E_{\text{react}}/RT_a). \]
A representative value of the temperature rise is now obtained from a balance of the reaction term and rate of temperature change in (4), namely
\[ \Delta C = \frac{\tau |H_{\text{react}}| r_{\text{react}}^C}{(1 - \phi) \rho c_{\text{cc}}}. \]
We will not consider this solution branch below as it is of no practical importance.

### 4 Asymptotic analysis

#### 4.1 Introduction

In this section we consider (9)-(16) in two asymptotic limits. The reactor is split into regions as shown in Figure 1, namely a preheat region (inert part adjacent to the reaction region), a reaction region (catalyst part where reaction takes place), inert region, burnt region (catalyst part where no ammonia is present), an adsorbed ammonia region (discussed below), a boundary layer at input and output. These regions, as shown in Figure 1, exist for a time interval after a switch has taken place; this being the time interval of most interest. In order to avoid an excessive number of suffices, the same notation \( C_0, C_0', \theta_0, T_0' \) and \( T_0' \) will be used in the leading order problems in each of the regions; these quantities are defined anew in each subsection. Similar comments apply to \( T_1', T_1' \) and so on.
After a switch has taken place, there is inevitably some ammonia adsorbed in the catalyst bed. This would represent an additional region until this ammonia had either reacted or desorbed and left the reactor. We will not consider this region in this section.

The first parameter regime is characterised by the key small parameters \( \epsilon \ll 1 \) and \( \delta \ll 1 \) which corresponds to much shorter desorption/adsorption time-scales than reaction time-scale and the reaction taking place over much shorter distances than the length of the catalyst part of the reactor, respectively. The second parameter regime also has the constraints \( \beta \gg 1 \) and \( T_{in} - 1 = O(1) \) and positive. These additional restrictions correspond to large activation energy for reaction and high temperature at the input of the preheat region.

### 4.2 \( \epsilon \ll 1 \) and \( \delta \ll 1 \)

#### 4.2.1 Preheat region

The preheat region is in the inert region immediately adjacent to the reaction region. In (11) and (13) we scale \( \hat{z} = \hat{z}_1 + \delta X \) \((X < 0 \text{ in the preheat region})\) to give

\[
\begin{aligned}
\mathcal{E}_0 \frac{\partial \hat{T}_s}{\partial t} + \mathcal{A}_0 \frac{\partial \hat{T}_s}{\partial X} &= \hat{T}_s - \hat{T}_f, \\
\mathcal{H}_0 \frac{\partial \hat{T}_s}{\partial t} &= \mathcal{L}_0 \frac{\partial \hat{T}_s}{\partial X^2} - (\hat{T}_s - \hat{T}_f),
\end{aligned}
\]

with the matching conditions \( \hat{T}_s \to T_{in} + O(\delta) \) and \( \hat{T}_f \to T_{in} + O(\delta) \) as \( X \to -\infty \) (where the notation \( O(q) \) means of the order of \( q \)); the input temperature of the preheat region being denoted by \( T_{in} \) at leading order. This input temperature is determined by the inert region (see below). We obtain

\[
\hat{T}_s = T_{in} + C_p \exp(\lambda_+ X) + O(\delta), \quad \hat{T}_f = T_{in} + \frac{\mathcal{L}_0}{\mathcal{A}_0} \lambda_+ C_p \exp(\lambda_+ X) + O(\delta)
\]

where \( \lambda_+ = \left( -1 + \sqrt{1 + 4(\mathcal{A}_0)^2} \right) / 2 \mathcal{A}_0 \) and \( C_p \) is the constant to be obtained by continuity with the reaction region at \( X = 0 \). We note that the time-scale in the preheat region (and also the reaction region below) is shorter than the time-scale for switching. The preheat and reaction regions are at pseudo steady state in this analysis.

The temperature rise in the preheat region is caused mainly by thermal conduction through the inert bed from the reaction region. The inert bed then transfers energy to the cooler fluid. This region is responsible for high temperatures at the start of the reaction region \((X = 0)\). This region has to be taken into consideration in the development of the new switching strategy, because of the thermal conduction from the reaction region.

#### 4.2.2 Reaction region

In the reaction region we adopt the scalings \( \hat{z} = \hat{z}_1 + \delta X \) \((X \geq 0 \text{ in the reaction region})\), \( \hat{C}_f \sim C_f^0 \), \( \hat{C}_c \sim C_c^0 \), \( \theta \sim \theta_0 \hat{T}_f \sim T_f^0 \), and \( \hat{T}_s \sim T_s^0 \) to give the leading-order balance in (9)-(12) and (14), namely

\[
\begin{aligned}
\mathcal{A} \frac{\partial C_f^0}{\partial X} &= -(C_f^0 - C_c^0), \\
\mathcal{D}(C_f^0 - C_c^0) &= \theta_0 \exp \left( \frac{\beta(T_s^0 - 1)}{1 + \gamma T_s^0} \right), \\
\mathcal{A}_0 \frac{\partial T_f^0}{\partial X} &= T_f^0 - T_s^0,
\end{aligned}
\]

\[\]
The boundary conditions with the preheat region may be obtained by considering the solution in the preheat region at \( X = 0 \). The boundary conditions become

\[
\begin{align*}
on X = 0 & \quad \frac{\partial T_0}{\partial X} = \lambda_+ (T_0 - T_{in}), \quad \mathcal{L} \lambda_+ (T_0 - T_{in}) = \mathcal{E} (T_0^f - T_{in}), \quad C_0^f = 1, \\
\text{and the matching condition} & \quad T_0^f - T_{in} \to 0 \text{ as } X \to \infty.
\end{align*}
\]

A simple consequence of (19)-(22) is

\[
K \frac{\partial^2 T_0^s}{\partial X^2} - (T_0^s - T_0^f) + (1 + F) \theta_0 \exp \left( \frac{\beta (T_0^s - 1)}{1 + \gamma T_0^s} \right) = 0,
\]

(22)

\[
BC_0^f (1 - \theta_0) \exp \left( \frac{\beta \alpha (T_0^s - 1)}{1 + \gamma T_0^s} \right) = \theta_0 \exp \left( \frac{\beta \alpha (T_0^s - 1)}{1 + \gamma T_0^s} \right).
\]

(23)

The boundary conditions with the preheat region may be obtained by considering the solution in the preheat region at \( X = 0 \). The boundary conditions become

\[
on X = 0 & \quad \frac{\partial T_0}{\partial X} = \lambda_+ (T_0 - T_{in}), \quad \mathcal{L} \lambda_+ (T_0 - T_{in}) = \mathcal{E} (T_0^f - T_{in}), \quad C_0^f = 1, \\
\text{and the matching condition} & \quad T_0^f - T_{in} \to 0 \text{ as } X \to \infty.
\]

A simple consequence of (19)-(22) is

\[
K \frac{\partial^2 T_0^s}{\partial X^2} - \mathcal{E} T_0^f - AD (1 + F) C_0^f = - \mathcal{E} T_{in} - AD (1 + F),
\]

(24)

which represents a balance between chemical and thermal energy in the reaction region. This conservation law is of greatest significance as \( X \to \infty \) and as \( X \to -\infty \) in the preheat region, because the derivative of the solid temperature is negligible in these limits and the overall temperature rise is predicted.

Analytical solutions of (19)-(23) can only be obtained in limiting cases (see below). We adopt a numerical approach to examine the variation of the output temperature of the reaction region \( (T_{out}) \) as a function of the input temperature of the preheat region \( (T_{in}) \). The equations (19)-(23) are not a differential algebraic system because it is possible to rearrange (20) and (23) to obtain unique values for \( \theta_0 \) and \( C_0^f \) in terms of \( \lambda_+ \) and \( T_{in}^f \). Therefore, we have a highly nonlinear boundary value problem with parametric time dependence through \( T_{in} \). The AUTO bifurcation package was selected to solve this problem.

In Figure 2, the final temperature obtained in the reaction region \( (T_{out}) \) is plotted as a function of input temperature to the preheat region \( (T_{in}) \). At low input temperatures negligible thermal energy is generated by the chemical reaction, so that \( T_{out} = T_{in} \). At high temperatures all the chemical energy has been turned into thermal energy, so that \( T_{out} = T_{in} + T_{ch} \) where \( T_{ch} \) is independent of \( T_{in} \). The temperature rise \( T_{ch} \) is in agreement with the temperature rise predicted by the conservation law (24), namely \( T_{ch} = \mathcal{D} (1 + F) / \mathcal{E} \). Finally at intermediate temperatures only a fraction of the chemical energy has been converted into thermal energy.

4.2.3 Inert/burnt region

The inert region is mainly responsible for the regenerative heat exchange in the reverse flow reactor. In the inert region the chemistry plays no rôlé and the system of equations (9)-(14) reduces to (11) and (13). We introduce expansions of the form \( \tilde{T}_s \sim T_0^s + \delta T_1^s \) and \( \tilde{T}_f \sim T_0^f + \delta T_1^f \) as \( \delta \to 0 \). We obtain \( T_0^s = T_0^f = T_{in}^f \) and the one-way wave equation

\[
\frac{\partial T_0^s}{\partial \tilde{t}} + \mathcal{E} \frac{\partial T_0^s}{\mathcal{H}} - AD (1 + F) C_0^f = - \mathcal{E} T_{in} - AD (1 + F),
\]

(25)

where \( \mathcal{E} / \mathcal{H} \) corresponds to the dimensionless wave speed. There is a boundary layer at the input (in this case \( \tilde{x} = 0 \)) and at the output (in this case \( \tilde{x} = \tilde{x}_3 \)) which we consider below. If we restrict our attention to the region \( \tilde{x} > \mathcal{E} \tilde{t} / \mathcal{H} + O(\delta) \) and take the initial condition \( T_0^s(\tilde{x}, 0) = f(\tilde{x}) \), we obtain the solution \( T_0^s = f(\tilde{x} - \mathcal{E} \tilde{t} / \mathcal{H}) \). At next order (11) and (13) give

\[
\begin{align*}
\frac{\partial T_1^s}{\partial \tilde{t}} + \mathcal{E} \frac{\partial T_1^s}{\mathcal{H}} - (\mathcal{L} + \mathcal{A}^2 \mathcal{E}^2) \frac{\partial^2 T_0^s}{\partial \tilde{x}^2}, & \quad T_1^f = T_1^s - \mathcal{E} \frac{\partial T_0^s}{\partial \tilde{x}}.
\end{align*}
\]

We take the initial condition to be of the form \( T_1^s(\tilde{x}, 0) = 0 \), to obtain

\[
T_1^s = \left( \frac{\mathcal{L} + \mathcal{A}^2 \mathcal{E}^2}{\mathcal{H}} \right) f'' \left( \tilde{x} - \mathcal{E} \tilde{t} / \mathcal{H} \right), \quad T_1^f = \left( \frac{\mathcal{L} + \mathcal{A}^2 \mathcal{E}^2}{\mathcal{H}} \right) f' \left( \tilde{x} - \mathcal{E} \tilde{t} / \mathcal{H} \right) - \mathcal{E} f' \left( \tilde{x} - \mathcal{E} \tilde{t} / \mathcal{H} \right).
\]
The solid temperature decreases where $f$ is concave ($f'' < 0$) and increases where $f$ is convex ($f'' > 0$). This diffusion mechanism takes place even if $L = 0$; this leading to the unusual situation of convection terms creating a diffusive effect. We note that this effect becomes more significant the longer the wave is allowed to propagate. The fluid temperature is slightly larger than the solid temperature on the descending slope of the wave when $f$ decreases ($f' < 0$) and slightly smaller on the ascending slope when $f$ increases ($f' > 0$). The temperature rise in the reaction region was $O(1)$, whilst the maximum temperature only falls in the $O(\delta)$ correction term. This paradox is resolved by taking the length of the reactor to be $O(1/\delta)$.

If the length of the reactor is $O(1/\delta)$, then a multiple-scales approach is required. Space will now be described by the short length-scale $\tilde{x}$ and the long length-scale $\xi = \delta \tilde{x}$. Time is described by the short time-scale $\tilde{t}$ and the long time-scale $\mu = \delta \tilde{t}$. We define new expansions of the form $\tilde{T}_s \sim T^s_0 + \delta T^s_1$ and $\tilde{T}_f \sim T^f_0 + \delta T^f_1$ as $\delta \to 0$. We obtain $T^s_0 = T^f_0$ and the one-way wave equation (25). We adopt a solution of the form $T^f_0 = f(\tilde{x} - \delta \tilde{t}) + \tilde{f}(\mu, \xi, \tilde{x} - \delta \tilde{t} \tilde{t})$. At next order (11) and (13) give

$$\frac{\partial T^f_1}{\partial \tilde{t}} + \frac{\partial \delta T^f_1}{H \partial \tilde{x}} = \left( \frac{\partial + \delta^2 \tilde{t}^2} {H} \right) \frac{\partial T^f_0}{\partial \mu} - \frac{\partial T^f_0}{H} \frac{\partial \delta T^f_1}{\partial \xi}. \quad (26)$$

The right-hand side of (26) is secular. Thus to maintain the asymptotically of the expansion, we have the condition

$$\frac{\partial T^f_0}{\partial \mu} + \frac{\partial \delta T^f_1}{H \partial \xi} = \frac{(\mathcal{L} + \delta^2 \tilde{t}^2) \partial^2 T^f_0}{H} \right) \frac{\partial \delta T^f_1}{\partial \xi},$$

or equivalently,

$$\frac{\partial \tilde{f}}{\partial \mu} + \frac{\partial \delta \tilde{f}}{H \partial \xi} = \left( \frac{\mathcal{L} + \delta^2 \tilde{t}^2} {H} \right) \frac{\partial^2 \tilde{f}}{\partial \xi^2} \right) \frac{\delta \tilde{f}}{H} \frac{\partial T^f_0}{\partial \mu} - \frac{\partial T^f_0}{H} \frac{\partial \delta \tilde{f}}{\partial \xi}.$$ This equation includes the second derivative with respect to the short length-scale of the leading order temperature at the current time and not just the second derivative of the initial condition for temperature. In an unbounded space domain, we obtain

$$\tilde{f} \left( \mu, \tilde{x} - \frac{\delta \tilde{t} \tilde{x}} {H} \right) = \int_{\eta = 0}^{\mu} \int_{y = -\infty}^{\infty} \frac{\partial^2 \tilde{f}}{\partial y^2} \left( y - \frac{\delta \tilde{t} \tilde{x}} {H} \right) \sqrt{\mathcal{L} + \delta^2 \tilde{t}^2} \exp \left( -\frac{\mathcal{L} (y - \tilde{x})^2}{2 \eta \mathcal{L}} \right) dy d\eta$$

This expression for $\tilde{f}$ describes the change to the leading-order temperature on the long time-scale, it is independent of the long length-scale. The second derivative with respect to the short length-scale is controlling this change.

The analysis in the burnt region is similar with $\mathcal{L}$ and $\mathcal{H}$ replaced by $\mathcal{K}$ and $1$, respectively.

### 4.2.4 Boundary layer at input

This subsection is concerned with the boundary layer in space adjacent to the input (we take the input to be $\tilde{x} = 0$) immediately after the flow direction switches. There are two time-scales to consider, in the first of which we scale $\tilde{t}$ in (11) and (13) by writing $\tilde{t} = \sigma \tilde{t}_1$ and $\tilde{x}$ by writing $\tilde{x} = \delta \tilde{Z}$ to obtain

$$\frac{\partial \dot{\tilde{T}}_s}{\partial \tilde{t}_1} + \frac{\partial \delta \dot{\tilde{T}}_s}{\partial \tilde{Z}} = \dot{\tilde{T}}_s - \dot{\tilde{T}}_f,$$

with boundary conditions

$$\dot{\tilde{T}}_f = 0 \quad \text{and} \quad \frac{\partial \dot{\tilde{T}}_s}{\partial \tilde{Z}} = 0 \quad \text{on} \quad \tilde{Z} = 0,$$

and a matching condition as $\tilde{Z} \to \infty$ and initial conditions $\dot{\tilde{T}}_f(\tilde{Z}, 0) = F(\tilde{Z})$ and $\dot{\tilde{T}}_s(\tilde{Z}, 0) = S(\tilde{Z})$. We have $\dot{\tilde{T}}_s = S(\tilde{Z}) + O(\sigma/\delta)$ and

$$\dot{\tilde{T}}_f = \exp \left( -\frac{\tilde{Z}} {\delta \tilde{t}} \right) \left( \frac{1}{\delta \tilde{t}} \int_0^{\tilde{Z}} S(y) \exp \left( \frac{y}{\delta \tilde{t}} \right) dy + g(\tilde{Z} - \delta \tilde{t}_1) \right) + O(\frac{\sigma}{\delta})$$

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where \( g(Z) = 0 \) for \( Z < 0 \) and

\[
g(Z) = F(Z) \exp \left( \frac{Z}{\lambda \varepsilon} \right) - \frac{1}{\lambda \varepsilon} \int_0^Z S(y) \exp \left( \frac{y}{\lambda \varepsilon} \right) dy
\]

for \( Z \geq 0 \). This first time-scale is very short (~ \( 10^{-3}s \)) and represents the rapid changes in the fluid temperature immediately after a switch. This time-scale is too short for the solid temperature to respond.

In the second time-scale we scale \( \tau \) by writing \( \tau = \delta t_2 \). We introduce expansions \( \dot{T}_s \sim T_0^s \) and \( \dot{T}_f \sim T_0^f \) to give the new leading-order balance

\[
A \varepsilon \frac{\partial T_0^f}{\partial Z} = T_0^s - T_0^f, \quad \mathcal{H} \frac{\partial T_0^s}{\partial Z} = \mathcal{L} \frac{\partial^2 T_0^s}{\partial Z^2} - (T_0^s - T_0^f),
\]

with boundary conditions \( T_0^f(0, t_2) = 0, \partial T_0^s/\partial Z(0, t_2) = 0 \) and \( T_0^s - T_0^f \to 0 \) as \( Z \to \infty \). Solution of these equations is algebraically complex (despite being separable) and we omit details. On this time-scale (~ \( 3s \)), both the temperature of the fluid and solid vary. After these two time-scales have elapsed, the solution in the region \( z < \lambda \varepsilon \delta/\mathcal{H} + O(\delta) \) is the trivial solution, that is \( \dot{T}_f = \dot{T}_s = 0 \).

### 4.2.5 Boundary layer at output

A boundary layer is required at the output in order to guarantee that the insulating boundary condition is satisfied. In (11) and (13) we scale \( \xi = \xi_2 + \delta Y \) (\( Y \leq 0 \)) to give (17)-(18) with \( X \) replaced by \( Y \) and the boundary conditions \( \dot{T}_s \to T_{\text{output}} + O(\delta) \) and \( \dot{T}_f \to T_{\text{output}} + O(\delta) \) as \( Y \to -\infty \) and \( \partial T_0^s/\partial Y = 0 \) at \( Y = 0 \). The solution is \( \dot{T}_s = T_{\text{output}} + O(\delta) \) and \( \dot{T}_f = T_{\text{output}} + O(\delta) \) throughout the boundary layer. This solution represents the flattening of the thermal wave profile in the neighbourhood of the output.

### 4.3 \( \varepsilon \ll 1, \delta \ll 1, \beta \gg 1 \) and \( T_{in} - 1 = O(1) \) and positive

The reaction region simplifies in this parameter regime and analytical solutions may be obtained. We adopt the scalings \( \xi = \xi_3 + \delta X \), \( \dot{C}_f \sim C_0^f \), \( \dot{T}_f \sim T_0^f \) and \( \dot{T}_s \sim T_0^s \), where \( \dot{C}_0 \) and \( \theta \) are exponentially small. We thus obtain

\[
A \frac{\partial C_0^f}{\partial X} = -C_0^f, \quad A \varepsilon \frac{\partial T_0^f}{\partial X} = T_0^s - T_0^f, \quad K \frac{\partial^2 T_0^s}{\partial X^2} - (T_0^s - T_0^f) + D(1 + F)C_0^f = 0, \tag{27}
\]

with boundary conditions

\[
on X = 0 \quad \frac{\partial T_0^s}{\partial X} = \lambda_+(T_0^s - T_{in}), \quad \mathcal{L} \lambda_+(T_0^s - T_{in}) = A \varepsilon (T_0^f - T_{in}), \quad C_0^f = 1, \tag{28}
\]

and the matching condition \( T_0^s - T_0^f \to 0 \) as \( X \to \infty \). The first equation in (27) has uncoupled and with the third boundary condition in (28) implies that \( C_0^f = \exp(-X/A) \). The remaining two equations in (27) represent a linear boundary value problem with solution

\[
T_0^s = \tilde{G}(1 - \varepsilon) \exp(-X/A) + \tilde{E} + \tilde{F} \exp(\lambda_- X), \quad T_0^f = \tilde{G} \exp(-X/A) + \tilde{E} + \tilde{F}(1 - K \lambda_-^2) \exp(\lambda_- X),
\]

where

\[
\begin{pmatrix}
\tilde{E} \\
\tilde{F}
\end{pmatrix} = \frac{1}{\bar{D}} \begin{pmatrix}
\bar{H} + K \lambda_-^2 - 1 & \lambda_- - \lambda_+ \\
1 - \bar{H} & \lambda_+
\end{pmatrix} \begin{pmatrix}
G(\varepsilon - 1)/A - \lambda_+ (\tilde{G}(1 - \varepsilon) - T_{in}) \\
\bar{G} - T_{in} - \bar{H}(\tilde{G}(1 - \varepsilon) - T_{in})
\end{pmatrix}, \quad \bar{G} = \frac{-A^2 D(1 + F)}{K(1 - \varepsilon) + \varepsilon A^2},
\]

\( \bar{H} = \mathcal{L} \lambda_+ / A \varepsilon, \quad \bar{D} = \lambda_-(K \lambda_+ \lambda_- + \bar{H} - 1) \) and \( \lambda_- = \left(-1 - \sqrt{1 + 4(\lambda \varepsilon)^2/K}\right)/2\lambda \varepsilon \). We note that \( \bar{D} \) is non-zero for typical parameter values which indicates that this solution is unique in this parameter régime,
that is there exists only one hot solution branch. This asymptotic solution is shown in Figure 3 across the
preheat and reaction regions. We note that the solid temperature increases rapidly to its maximum value
and then decreases very slightly to its final value, whilst the fluid temperature slowly rises to this same value
across both regions.

We note that the reaction region ceases to exist when 
\[ T_0^* \sim \frac{\ln(\delta) + \beta}{\beta - \gamma \ln(\delta)}. \]
This estimation predicts the reaction switches off at approximately 470K; the agreement with Figure 2 being reasonable. A
word of caution is required concerning this last result
as it presumes the somewhat
ad hoc scaling \[ \beta \sim \ln(1/\delta). \]

5 Numerical solution

We discretise the spatial variable in (9)-(14) leading to a system of ordinary differential equations. The
convection terms in (9) and (11) are represented by a first-order upwind discretisation. The diffusion terms
in equations (12)-(13) are approximated by the standard conservative central difference. The thermal diffusion
coefficient in (12)-(13) is sufficiently small to only become significant in a thin region of space. We chose
a uniform mesh across the entire domain (thin layers where the dependent variables have large derivatives
occur in several positions). The smallest relevant length-scale is \( O(\delta) \), the mesh spacing is selected to resolve
boundary layers on this length-scale. The parameter values in Table 2 indicate that a number of very
different time-scales are present and the stiff ordinary differential equation solver D02EJF was accordingly
selected from the NAG library. Numerical results have been obtained for a variety of meshes to ensure grid
independence.

The numerical solution exhibits two main time-scales. A short time-scale associated with the period of
flow direction reversal and a long time-scale related to the decay of the initial transient. The system of
equations (9)-(16) is sensitive to the choice of initial conditions. In Figure 4, we select three initial conditions
\[ T_{\text{initial}} = 430K, 450K \text{ and } 1000K. \]
The simulations predict two stable steady states: one at 300K and another
with maximum temperature of approximately 800K. We expect an unstable steady state to exist between
these two stable steady states, although this will not be observed in physical experiments. It is important
that the initial conditions are chosen sufficiently large to avoid extinction. Extinction is associated with the
reaction not being switched on (as predicted by Figure 2) or excessive
gas velocity (see below).

We now examine the numerical solution after the reactor has settled into periodic oscillation. The solid
temperature moves across the reactor as a thermal wave with a constant velocity (shown in Figure 5). The
effect of the chemical reaction at the inert/catalyst interface is evident in the sudden temperature rise which
takes place near \( x = 0.15m \) and a smaller temperature rise near \( x = 0.25m \) when \( t = 18200s \). The decrease in
the maximum temperature and increase in the temperature in the tail can be seen by comparing \( t = 18400s \)
and \( t = 18600s \). The reaction reduces the surface coverage (shown in Figure 6) and ammonia concentration
(shown in Figure 7) in the bulk gas phase very rapidly near \( x = 0.15m \) due to the high temperatures
at \( t = 18200s \). As the temperature decreases the reaction rate decreases until the ammonia is just being
adsorbed in the catalyst. Once the flow switches direction this stored ammonia either convects out of the
reactor or reacts, but the majority of this stored ammonia leaves without reacting. This ammonia output is
highly undesirable.

Reverse flow reactors are known to have complex dependence on process parameters. In Khinast and
Luss (1997), this dependence was illustrated for Damköhler number and adiabatic temperature rise as the
bifurcation parameters. We now consider the effect of the variation of gas velocity on the reactor operation.
The results of several numerical simulations are presented in the bifurcation diagram shown in Figure 8. It
is clear that extinction takes place above a critical value of velocity. This behaviour is due to thermal energy
loss outweighing thermal energy gain. If the velocity is chosen below this critical value then the choice of
initial condition becomes important in predicting whether extinction occurs. The bifurcation diagram does
not show the behaviour for small velocities, this is a singular limit.

Experimental observations with reverse flow reactors have indicated that the wave speed appears to increase at smaller input ammonia concentrations. This observation would seem to contradict the analysis in the inert and burnt regions. Numerical experiments were undertaken with an input ammonia concentration of $4 \times 10^{-3}$ mol to simulate this effect. The results are shown in Figures 9 and 10 which should be compared with Figures 5 and 7. A simple calculation with the distance travelled by the maximum temperature between the times $t = 18400s$ and $t = 18600s$ shows that the wave speed is indeed the same and the expressions for the wave speed are again confirmed. However, the maximum at $t = 18400s$ has moved further across the bed in Figure 9 than Figure 5 and the maximum temperature in the reaction region is achieved further away from the inert/catalyst interface at $t = 18200s$ in Figure 9. In Figure 10 the reaction region is larger than in Figure 7; this larger reaction zone being due to the slower reaction rate. The apparent increase in wave speed using lower input concentrations of ammonia is explained by the position of the maximum temperature in the reaction region at lower temperatures.

We now propose a new switching strategy to minimise the ammonia output from the reactor following a switch. The basic idea is to switch when the temperature drops so far that the reaction stops. Our criteria will be that over the preheat and reaction regions the temperature must rise by $C_a(\Delta H_{\text{react}} + |\Delta H_{\text{ads}}|) / \rho_f c_f$ ($\sim 70K$). The preheat region will be assumed to start at the inert/catalyst interface minus $10s_d$ ($\sim 1cm$) and the reaction region to end at the interface plus $10s_d$ ($\sim 1cm$) where $s_d = \phi_0/\beta_0a_v$. These temperatures may easily be measured in a reactor by placing thermocouples in the positions indicated. Here we perform numerical experiments to simulate the effect of this new switching strategy. However, the maximum temperature may become too high with the new strategy. These high temperatures may be avoided by, for example, operating with lower input ammonia concentration. We chose an input ammonia concentration of $3 \times 10^{-3}$ mol in this case. The fluid and solid temperatures calculated with this strategy are shown in Figure 11 just as the reaction stops and a switch is about to take place. The corresponding ammonia concentrations adsorbed in the catalyst part (shown in Figure 12) are significantly less than in Figures 6 and 7 at $t = 18600s$. The ammonia output has been significantly reduced.

6 Summary and Conclusions

A time-dependent mathematical model for a reverse flow reactor has been introduced with parameter values based on the oxidation of ammonia on the Pt/Al$_2$O$_3$ catalyst. The solution reacts on several very different time-scales. The non-dimensionalisation has revealed the reaction time-scale $1/r_{\text{H,react}}$ ($\sim 0.1s$), the desorption time-scale $1/r_{\text{H,des}}$ ($\sim 10^{-5}s$), the time-scale for variations in the ammonia concentration of the bulk gas phase $\phi/\beta_0a_v$ ($\sim 2 \times 10^{-3}s$) and the time-scale for variations in the ammonia concentration of the catalyst pore phase $(1 - \phi)C_a/r_{\text{H,react}}$ ($\sim 4 \times 10^{-4}s$).

The reactor may attain one of two stable steady states. The hot solution branch is the only one of practical interest and a representative value of the temperature rise is given by the larger of the two positive real roots of

$$\frac{a_0a_v\Delta H}{|H_{\text{react}}|k_{\text{react}}} = \exp\left(\frac{-E_{\text{react}}}{R(T_a + \Delta H)}\right).$$

We note that the temperature rise ($\Delta H$) increases as the reaction rate ($k_{\text{react}}$) decreases provided that $a_0a_vR(T_a + \Delta H)^2/|H_{\text{react}}|k_{\text{react}}E_{\text{react}} < \exp(-E_{\text{react}}/R(T_a + \Delta H))$. This suggests a mechanism for the larger maximum temperature observed in the case of a less active catalyst.

The reactor may be split into regions, namely a preheat region, a reaction region, an inert region, a burnt region, a boundary layer at input and output and an adsorbed ammonia region.
The preheat region. This region is in the inert part adjacent to the interface between inert and catalyst parts of the reactor (depending on temperature and direction of flow). The typical thickness of this region is of the order of $s_d = \phi u / \beta_0 a_u (\sim 10^{-3} m)$. The major rise in temperature takes place in this region due to the thermal conduction from the reaction region.

The reaction region. This region is in the catalyst part adjacent to the preheat region. The typical thickness of this region is of the order of $s_d$. The main chemical reaction takes place in this region. The leading-order expression for the overall temperature rise across the preheat and reaction regions is given by

$$T_d = \frac{C_a (|H_{\text{react}}| + |H_{\text{ads}}|)}{\varphi \rho \varepsilon \sigma} (\sim 70 K),$$

providing the input temperature to the preheat region is sufficiently high to avoid extinction.

The inert/burnt region. The inert region is the inert part except for the preheat region and boundary layer at input and output. The burnt region is the catalyst part where no ammonia is present. The leading-order expression for the thermal wave speed in the inert region and burnt region are given by

$$\frac{\varphi \rho \varepsilon \sigma u}{(1 - \varphi) \varepsilon_i \rho c_i} (\sim 5 \times 10^{-4} \text{ms}^{-1}), \quad \frac{\varphi \rho \varepsilon \sigma u}{(1 - \varphi) \varepsilon_c \rho c_c} (\sim 5 \times 10^{-4} \text{ms}^{-1}),$$

respectively. The thermal wave not only traverses the bed, but also decreases where the wave profile is concave and increases where it is convex. This diffusive effect takes place by a combination of thermal conduction and convection. This is an unusual situation where convective terms produce a diffusive effect. The fluid temperature is slightly larger than the solid temperature on the descending slope of the wave and slightly smaller on the ascending slope.

The boundary layer at input. This is a region adjacent to the input with typical thickness of the order of $s_d$. The fluid temperature changes very rapidly ($\sim 10^{-3} s$) in this region immediately after the gas flow direction switches. This is followed by a longer time-scale ($\sim 3 s$) on which both the solid and fluid temperatures vary.

The boundary layer at output. This is a region adjacent to the output with typical thickness of the order of $s_d$. The temperatures are constant at leading order in this region.

The adsorbed ammonia region. This region corresponds to the part of the catalyst bed where adsorbed ammonia remains after a switch in the gas flow direction. This adsorbed ammonia is highly undesirable. Numerical simulations are obtained. Numerical results are used to compare with the analytical formulas; the agreement being good. These results are also used to examine the response to different gas velocities and initial conditions. Extinction may take place if the gas velocity is too high or the initial condition too low.

Finally, a new switching strategy is proposed to minimise the ammonia exiting the reactor after a switch in the gas flow direction. The switch must take place just as the reaction ceases, that is when the temperature rise across the preheat and reaction regions drops below $T_d$. Numerical experiments indicate that this strategy does indeed minimise the adsorbed ammonia.

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References


Figure 1: A schematic of the regions in the reactor, namely the preheat region (p), the reaction region (r), the inert region, the burnt region, the adsorbed ammonia region (a), the boundary layer at input (i) and output (o).
Figure 2: Numerical solution for the output temperature from the reaction region as a function of temperature input to the preheat region for the data given in Table 1.

Figure 3: First term in the asymptotic expansion of the solid and fluid temperature in the preheat and reaction regions for the data given in Table 1. The boundary between inert and catalyst parts is at 0.15m.
Figure 4: Numerical solution for the solid temperature at the midpoint of the catalyst as a function of time with three (constant) initial conditions (i) 1000K, (ii) 450K and (iii) 430K. The data is given in Table 1.

Figure 5: Numerical solution for the solid temperature as a function of distance at the times (i) 18200s, (ii) 18400s and (iii) 18600s, the flow direction is reversed every 600s. The data is given in Table 1.
Figure 6: Numerical solution for the surface coverage as a function of distance at the times (i) 18200s, (ii) 18400s and (iii) 18600s. The data is given in Table 1.

Figure 7: Numerical solution for the ammonia concentration in the bulk gas phase as a function of distance at the times (i) 18200s, (ii) 18400s and (iii) 18600s. The data is given in Table 1.
Figure 8: A bifurcation diagram of the reverse flow reactor equations with the maximum temperature at the midpoint of the catalyst as a function of gas velocity. The stable solutions are denoted by a continuous curve and the unstable by a dashed curve. The lines with arrows indicate the transient path of solutions.

Figure 9: Numerical solution for the solid temperature as a function of distance at the times (i) 18200s, (ii) 18400s and (iii) 18600s. The data is given in Table 1 except that the input ammonia concentration is reduced to $4 \times 10^{-3}$ mol fraction.
Figure 10: Numerical solution for the ammonia concentration in the bulk gas phase as a function of distance at the times (i) 18200s, (ii) 18400s and (iii) 18600s. The data is given in Table 1 except that the input ammonia concentration is reduced to $4 \times 10^{-3}$ mol fraction.

Figure 11: Numerical solution for the solid and fluid temperature as a function of distance immediately before a switch with the new switching strategy. The data is given in Table 1 except that the input ammonia concentration is reduced to $3 \times 10^{-3}$ mol fraction.
Figure 12: Numerical solution for the ammonia concentration in the bulk gas phase, the ammonia concentration in the catalyst pore gas phase and the surface coverage as a function of distance immediately before a switch with the new switching strategy. The data is given in Table 1 except that the input ammonia concentration is reduced to $3 \times 10^{-3} \text{mol fraction}$. 
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<td>( T_{initial} )</td>
<td>initial temperature of solid</td>
<td>600 K</td>
</tr>
<tr>
<td>( \tau )</td>
<td>period of switching</td>
<td>600 s</td>
</tr>
</tbody>
</table>

Table 1: Physical data for the oxidation of ammonia
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Typical Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$\phi/\tau \beta_0 a_v$</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>$A\delta$</td>
<td>$\phi u/L \beta_0 a_v$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>$(1 - \phi) C_a/\tau_{\text{react}}$</td>
<td>$7 \times 10^{-7}$</td>
</tr>
<tr>
<td>$D$</td>
<td>$\beta_0 a_v C_a/\tau_{\text{react}}$</td>
<td>0.2</td>
</tr>
<tr>
<td>$B/\epsilon$</td>
<td>$r_{\text{ads}}/\tau_{\text{react}}$</td>
<td>$5 \times 10^{9}$</td>
</tr>
<tr>
<td>$1/\epsilon$</td>
<td>$r_{\text{des}}/\tau_{\text{react}}$</td>
<td>$1 \times 10^{4}$</td>
</tr>
<tr>
<td>$E\sigma$</td>
<td>$\phi \psi_c/\tau a_o a_v$</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\lambda \delta$</td>
<td>$\phi \psi_c u/\tau a_o a_v$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>$(1 - \phi) \rho C_c/\tau a_o a_v$</td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$K_d^2$</td>
<td>$\lambda_c(1 - \phi)/L^2 a_o a_v$</td>
<td>$2 \times 10^{-4}$</td>
</tr>
<tr>
<td>$F$</td>
<td>$</td>
<td>H_{\text{ads}}</td>
</tr>
<tr>
<td>$\mathcal{N}_\delta$</td>
<td>$(1 - \phi) \rho C_i/\tau a_o a_v$</td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$L_\delta^2$</td>
<td>$\lambda_i(1 - \phi)/L^2 a_o a_v$</td>
<td>$2 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$L_i/\tau_{\text{react}}$</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\beta_{\text{ads}}$</td>
<td>$E_{\text{ads}} \Delta H/RT_a^2(1 + \gamma)$</td>
<td>0.9</td>
</tr>
<tr>
<td>$\beta_{\text{des}}$</td>
<td>$E_{\text{des}} \Delta H/RT_a^2(1 + \gamma)$</td>
<td>6</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$E_{\text{react}} \Delta H/RT_a^2(1 + \gamma)$</td>
<td>15</td>
</tr>
<tr>
<td>$\bar{T}_{\text{initial}}$</td>
<td>$(T_{\text{initial}} - T_a)/\Delta H$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\bar{z}_1$</td>
<td>$z_1/L$</td>
<td>1.5</td>
</tr>
<tr>
<td>$\bar{z}_2$</td>
<td>$z_2/L$</td>
<td>2.5</td>
</tr>
<tr>
<td>$\bar{z}_3$</td>
<td>$z_3/L$</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2: Dimensionless parameters for the oxidation of ammonia