A highway in state space for reactors with minimum entropy production

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Abstract

Thousands of numerical solutions of an optimal control problem for plug flow reactors were found to give, what we call a “highway in the reactors’ state space”. The problem was to find the heat transfer strategy which minimise the entropy production in reactors with fixed chemical conversion. The control variable was always the temperature of the heating/cooling medium along the reactor. The highway represents the most energy efficient way to travel far in state space. Such highways were studied for five reactor systems, endothermic and exothermic ones. Numerical analysis showed that the reactor highway is characterised by approximately constant thermodynamic driving forces/local entropy production for reasonable process intensities. Each solution represents a compromise between the entropy production of reactions, heat transfer and frictional flow (pressure drop). The solutions enter and leave the highway at different positions depending on how far from the highway their initial and final destinations are. Knowledge about the nature of the highway, e.g. when the reactor operates in a reaction mode or a heat transfer mode, may be important for energy efficient reactor design. The theoretical formulation of the optimisation problem is valid for plug flow as well as batch reactors. We showed that important results in literature like the Spirkl–Ries quantity, the theorems of equipartition of entropy production and equipartition of forces are contained in our general formulation. The numerical results showed that the analytical results are good approximations to the optimum also in problems where they do not apply in a strictly mathematical sense.

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1. Introduction

Entropy production minimisation (or entropy generation minimisation) is now established as a field in engineering. The reason for this is that the entropy production is related to the energy efficiency of a system or process (Bejan, 1996). We study entropy production minimisation with plug flow reactors as examples. The problem is to find distribution of the cooling or heating duty along a reactor which is compatible with minimum entropy production in the system. By applying the optimal cooling/heating strategy, the reactor operates in the state of minimum entropy production. This paper is devoted to the properties of this state.

Some works have already been published on entropy production minimisation in plug flow reactors, namely the sulphur dioxide oxidation reactor (Johannessen and Kjelstrup, 2004), the ammonia reactor (Nummedal et al., 2003), the propane dehydrogenator (Røsjorde et al., 2003), and the tubular steam reformer (Nummedal et al., 2004). These papers give interesting details about the state of minimum entropy production in the respective cases. A description of the general properties of this state has not been given, however. We shall give such a description in this paper, by generalising these earlier solutions. This will be done by adding both numerical and theoretical results. Special emphasis will be put on the situation where the number of state variables in the system exceeds the number of possibilities to control the system from the outside.

The numerical results reveal that the state of minimum entropy production in a chemical reactor has some general properties. We have extracted these properties from thousands of numerical solutions of the optimisation problem.
The properties shall be clarified, by contrasting the solution of the full reactor problem to problems where some of the driving forces are zero.

When the optimisation problem is formulated in the standard manner using optimal control theory, its Hamiltonian is constant throughout the reactor (Johannessen and Kjelstrup, 2004). In the theoretical section we show how results from the literature (Andresen and Gordon, 1994; Bedeaux et al., 1999; Diosi et al., 1996; Johannessen et al., 2002; Saur et al., 1996; Spirkl and Ries, 1995; Tondeur and Kvaalen, 1987) are contained in this condition. The Hamiltonian itself does not have any direct physical interpretation, but by adding assumptions in a stepwise manner, we obtain first the Spirkl–Ries quantity (Spirkl and Ries, 1995), next the theorem of equipartition of entropy production (EoEP) (Andresen and Gordon, 1994; Bedeaux et al., 1999; Diosi et al., 1996; Johannessen et al., 2002; Spirkl and Ries, 1995; Tondeur and Kvaalen, 1987) and finally the theorem of equipartition of forces (EoF) (Bedeaux et al., 1999; Saur et al., 1996). We have used plug flow reactors as examples in the numerical analysis, but theory predicts that the conclusions hold true, also when the length coordinate is exchanged with time as a variable.

The numerical results show that there is a path in the reactor’s state space which is especially crowded by solutions. The path exists for all process intensities, also in the domain where the flux–force relations are nonlinear. The solutions follow this path only in the central part of the reactor. The boundary conditions account for deviations from the path at the reactor inlet and outlet. A solution enters and leaves the path at different locations depending on where the initial and final points are in the reactor’s state space. A collection of solutions with different initial and final points (different boundary conditions) looks therefore like a highway with its connecting roads. We have adopted the highway picture and call it the “reactor highway”.

The reactor highway has a surprising property; the local entropy production and the thermodynamic driving forces are approximately constant, provided that the process intensity is not too high. This means that the EoEP and EoF theorems are good approximations to the highway, even though we find that they are not strictly valid in a mathematical sense: some of the underlying assumptions for these theorems are not fulfilled.

Inspection of the underlying properties of the solutions reveals that the reactor operates partly in what we have called a heat transfer mode, partly in what we have called a reaction mode, when the production of entropy is minimum. This may have some important consequences for energy efficient reactor design. We can find the optimal length of the reactor, and the proper partial length for each mode of operation. We shall see that we through this can give theoretical support to examples of engineering practises.

The famous work of Prigogine (1955) on the nature of states with minimum entropy production was not relevant for this work. Prigogine found that minimum entropy production was compatible with globally linear flux–force relations at stationary state, if Onsager’s reciprocal relations were obeyed. Our analysis does not necessarily concern stationary states. We deal equally well with ordinary differential equations describing evolution in time. The rather restricted situation, of having globally linear flux–force relations, is also not an issue here. More important, the problem to be solved is entirely different from Prigogine’s. While he was asking for the rate laws and their governing principle, we are taking the laws as granted, and we ask how to optimally control the state of a constrained system. Our problem formulation may also be relevant for natural systems, however, since these are often constrained.

The organisation of the paper is as follows. In Section 2 we give the governing equations for the example, a plug flow reactor. The formulation of the optimisation problem follows in Section 3. In Section 4 we give theoretical results for the state of minimum entropy production. Section 5 presents the five reactor cases that we have studied and the numerical method we have used. Section 6 presents and explains the numerical results. In Section 7 we discuss the results, and in the last section we give some conclusions. Some of the numerical results have been reported in a short communication (Johannessen and Kjelstrup, 2005).

2. The plug flow reactor

A sketch of a fixed bed tubular reactor is given in Fig. 1. A gas mixture of n components flows through a tube filled with catalyst. On the catalyst, m different reactions take place. Heat is exchanged with a fluid with temperature $T_a$ through the tube wall. In addition, the friction between the reaction mixture and the catalyst causes the pressure to drop from the inlet to the outlet of the reactor.

The plug flow model of the reactor has zero radial gradients inside the tube, and a temperature difference across the tube wall. The flow is plug-like, there is no back-mixing, and all transport in the flow direction is considered to be by convection. We also neglect gradients inside the catalyst pellets and gradients in the film around each pellet. With this reactor model, the state of the reacting stream can be characterised by the following state variables: The temperature, $T$, the total pressure, $P$, and the degrees of conversion in the $m$ reactions that take place in the reactor, $\xi_j$, where $j = 1, \ldots, m$.

The state variables are governed by differential equations which are derived from the balance equations of the system. These are the mole balances, the energy balance and the momentum balance (Ergun’s equation), see for instance Fogler (1992). These balances give (Johannessen and Kjelstrup, 2004):

$$\frac{d\xi_j}{dz} = f \xi_j = \frac{Q P_B}{F A} r_j \quad j = 1, \ldots, m, \quad (1)$$
The symbols are defined in the symbol list.

The three independent phenomena that produce entropy in this reactor are the reactions, the heat transport through the reactor wall and the frictional flow (pressure drop). The local entropy production (on a unit length basis), as formulated by irreversible thermodynamics (de Groot and Mazur, 1984; Forland et al., 2001) is (Johannessen and Kjelstrup, 2004),

\[ \sigma = \Omega \rho_B \left[ \sum_j \left( r_j \left( -\Delta_t G_j \right) \right) \right] + \pi D J_q \frac{1}{T} + \Omega v \left( -\frac{1}{T} \frac{dP}{dz} \right), \] (4)

Each term in Eq. (4) contains a product of a flux and its conjugate force. The first term is a sum over all reactions; the flux is the reaction rate, \( r_j \), and the chemical force is \( -\Delta_t G_j / T \). The second term is due to heat transfer across the reactor wall; the flux is the sensible heat flux, \( J_q \), and the thermal force is \( A(1/T) = 1/T - 1/T_a \). The last term is due to frictional flow; the flux is the gas velocity, \( v \), and the force is \( (-1/T)(dP/dz) \). Each flux is a function of only one force, since the scalar and vectorial phenomena do not couple. The chemical reaction rate is a highly nonlinear function of its driving force.

The total entropy production is the integral of \( \sigma \) over the spatial coordinate \( z \)

\[ \left( \frac{dS}{dz} \right)_{irr} = \int_0^L \sigma \, d\zeta. \] (5)

The complete model contains flux–force relations (reaction rate expressions, heat transfer law and friction parameters). These relations were documented earlier for the five reactors that are studied here, see also Section 5.

3. Optimal control theory formulation of entropy production minimisation

We are concerned with optimisation problems, where one control variable (\( T_a \)) is used to optimise the behaviour of the system. This type of problem is standard in optimal control theory (Bryson and Ho, 1975; Johannessen and Kjelstrup, 2004).

The problem is to find the \( T_a \)-profile of the reactor which is compatible with minimum entropy production in the system. State variables are \( T, P \) and \( \zeta_j \) for \( j = 1, \ldots, m \) (\( m + 2 \) variables). With three types of dissipative phenomena in the reactor (cf. Eq. (4)), the outcome of the optimisation is diverse and difficult to interpret. General properties can be demonstrated by contrasting the solution of the full problem to simpler problems. We have solved:

1. The RQF-problem: the full problem, with all terms in Eq. (4).
2. The RQ-problem: reactions and heat transfer are considered, \( dP/dz = 0 \) in Eq. (4).
3. The R-problem: reactions are considered, \( dP/dz = 0 \) and \( A(1/T) = 0 \) in Eq. (4).

In each problem, we are seeking the state that produce as little entropy as possible, and the best trade-off between the phenomena involved.

3.1. The RQF-problem

In the optimal control theory formulation, the necessary conditions for minimum entropy production are derived from the Hamiltonian of the problem (Bryson and Ho, 1975):

\[ H = \sigma + \sum_j \left[ \lambda_{\zeta_j} f_{\zeta_j} \right] + \lambda_T f_T + \lambda_P f_P. \] (6)

The Hamiltonian contains the local entropy production and products of multiplier functions, \( \lambda \)'s, and the right hand sides of the balance equations (see Eqs. (1)–(3) for the definition of \( f_{\zeta_j}, f_T \) and \( f_P \)).

The Hamiltonian of our optimal control problem is autonomous. This means that it does not depend on \( z \) explicitly. It has only an indirect dependence on \( z \) through the state variables, the control variable (\( T_a \)) and the multiplier functions. The state of minimum entropy production has therefore a constant Hamiltonian along the \( z \)-coordinate. This is a general property of optimal control problems where the Hamiltonian is autonomous (see for instance Bryson and Ho, 1975).

The necessary conditions for a minimum are the following 2m + 4 differential equations

\[
\begin{align*}
\frac{d\zeta_j}{dz} &= \frac{\partial H}{\partial \lambda_{\zeta_j}}, \\
\frac{d\lambda_{\zeta_j}}{dz} &= -\frac{\partial H}{\partial \zeta_j}, \\
\frac{dT}{dz} &= \frac{\partial H}{\partial \lambda_T}, \\
\frac{d\lambda_T}{dz} &= -\frac{\partial H}{\partial T}, \\
\frac{dP}{dz} &= \frac{\partial H}{\partial \lambda_P}, \\
\frac{d\lambda_P}{dz} &= -\frac{\partial H}{\partial P},
\end{align*}
\] (7)

and the algebraic equation

\[ \frac{\partial H}{\partial T_a} = 0 \quad \text{for all } z \in [0, L]. \] (8)
where \( j = 1, \ldots, m \). The left column in Eq. (7) reduces to the balance equations, Eqs. (1)–(3).

We allow \( T_a \) to take any positive value. Experience has shown that zero and infinity are not optimal values of \( T_a \) for the present problem. The weak condition, Eq. (8), is therefore sufficient. Optimal control theory gives a stronger form of this condition, if required (Johannessen and Kjelstrup, 2004).

There are \( 2m + 4 \) boundary conditions to go with the \( 2m + 4 \) differential equations in Eq. (7). Four of these boundary conditions are connected to the inlet/outlet pressures and temperatures. We have studied both fixed and free temperatures/presures at the boundaries, meaning that \( 2^4 = 16 \) different combinations of boundary conditions have been tried. When a temperature or pressure is free at one end of the reactor, the transversality conditions of optimal control theory give that the corresponding multiplier function is zero at the position in question. If for instance the inlet temperature is free, the transversality condition gives \( \lambda_T = 0 \) at the inlet (Bryson and Ho, 1975).

The remaining boundary conditions are connected to the chemical conversion in the reactor. For reactors with one reaction, we used fixed inlet and outlet conversions (\( 2m \) boundary conditions). For reactors with more than one reaction, we fixed the inlet conversions and the outlet molar flow rate of one component (\( m + 1 \) boundary conditions). The remaining boundary conditions were found from the transversality conditions. The transversality conditions give the following conditions at the outlet: \( \lambda_{z_j} (L) = \gamma y_{j,i} = c \) for \( j = 1, \ldots, m \), where \( \gamma \) is an additional unknown which must be determined, and \( C \) is the component with fixed outlet molar flow rate. In total there are \( 2m + 1 \) unknowns (inlet/outlet conversions and \( \gamma \) ) and \( 2m + 1 \) conditions, connected to the chemical conversion in the multiple reaction cases.

The solution of the optimisation problem is found by solving Eq. (7) for the given set of boundary conditions. In addition, Eq. (8) must be fulfilled at every position. This is a nonlinear two-point boundary value problem, which has to be solved numerically.

3.2. The RQ-problem

The equations for the RQ-problem were obtained from the RQF-problem, by taking away all terms and equations related to the pressure drop. This means that Eq. (3), the third line in Eq. (7), and the terms related to the pressure drop in Eqs. (4) and (6) were taken out. Boundary conditions (described in Section 3.1) related to the pressure were thus irrelevant.

3.3. The R-problem

The equations for the R-problem were obtained from the RQF-problem, keeping only terms and equations related to the reactions. This means that Eqs. (2), (3) and (8), the second and the third line in Eq. (7) and all terms not related to the reactions in Eqs. (4) and (6), were taken out.

In this problem we can consider \( T \) as the control variable. Since there is no resistance towards heat transfer, \( T = T_a \). We therefore replace Eq. (8) with

\[
\frac{\partial H}{\partial T} = 0 \quad \text{for all } z \in [0, L].
\]  

That \( T = T_a \), corresponds to an infinitely large heat transfer coefficient in the expression for the heat flux \( (J_q = U(T_a - T) \) and \( J_q = U T^2 A (1/T) \) ). The R-solution is therefore the same as the solution of the RQ-problem with \( U = \infty \).

Minimum entropy production is obtained in the R-problem with inlet and outlet temperatures that are different from the specified values. The temperature jumps infinitely fast at the inlet and outlet of the reactor in order to meet the fixed temperatures there. This is physically possible only when \( U = \infty \).

4. The state of minimum entropy production

4.1. Matrix formulation of the RQF-problem

We give here a more general form of the above optimisation problems. As a first step, we give a matrix formulation of the RQF-problem for a specific case, a reactor with one reaction.

There are \( N = 2 + m = 3 \) state variables and \( M = 1 \) control variable in the RQF-problem, when one reaction takes place (i.e., \( m = 1 \)). We organise these variables in the state vector, \( \mathbf{y} = [z_1, T, P]^T \), and the control vector, \( \mathbf{u} = [T_a] \). This state vector is governed by Eqs. (1)–(3). For \( m = 1 \), we obtain

\[
\frac{d\mathbf{y}}{dz} = \begin{bmatrix}
\frac{dz_1}{dz} \\
\frac{dT}{dz} \\
\frac{dP}{dz}
\end{bmatrix} = \begin{bmatrix}
0 & 0 & 0 \\
-\frac{\Delta H_1}{\sum_i F_i C_{p,i}} & 0 & 0 \\
0 & 0 & 0
\end{bmatrix} + \begin{bmatrix}
\frac{z_1}{T} & \frac{z_1}{P} & \frac{z_1}{T^2 A (1/T)}
\end{bmatrix} \mathbf{A}(y).
\]  

Furthermore, the local entropy production, Eq. (4), is

\[
\sigma = \begin{bmatrix}
-\Delta G_i \\
\Delta H_1 - T_f \frac{\rho}{\rho}
\end{bmatrix} \begin{bmatrix}
\frac{z_1}{T} & \frac{z_1}{P} & \frac{z_1}{T^2 A (1/T)}
\end{bmatrix} \mathbf{J}(y, u, x(y, u)).
\]  

In Eqs. (10) and (11) \( \mathbf{A}(y) \) is a matrix with proportionality factors where \( f \) is the parenthesis on the left hand side of Eq. (3). The diagonal matrix \( \Gamma \) contains geometric factors. Furthermore, \( \mathbf{J}(y, u, x(y, u)) \) and \( \mathbf{x}(y, u) \) are vectors with the fluxes and the forces, respectively. We have indicated
that \( \Gamma \) is a constant matrix, \( A \) depends on the state vector, and \( J \) and \( x \) depend on both the state vector and the control vector. We have also indicated that the fluxes and forces are related.

In this matrix formulation, the Hamiltonian in Eq. (6) is

\[
H(y, u, \lambda) = x(y, u)^T J(y, u, x(y, u)) + \lambda^T A(y) J(y, u, x(y, u)),
\]

(12)

where \( \lambda = [\lambda_1, \lambda_2, \lambda_3]^T \) is a vector with multiplier functions. The Hamiltonian is autonomous, as before, and is thus constant along the \( z \)-coordinate (Bryson and Ho, 1975). The necessary conditions for minimum entropy production, Eqs. (7) and (8), can now be written as

\[
\frac{dy}{dz} = \left( \frac{\partial H}{\partial \lambda} \right)^T,
\]

(13)

\[
\frac{d\lambda}{dz} = -\left( \frac{\partial H}{\partial y} \right)^T
\]

and

\[
\frac{\partial H}{\partial u} = 0.
\]

(14)

Here, we use that the derivatives of \( H \) (\( \frac{\partial H}{\partial \lambda} \), \( \frac{\partial H}{\partial y} \) and \( \frac{\partial H}{\partial u} \)) are row vectors. This is the convention in Bryson and Ho (1975).

4.2. The general problem

The set of Eqs. (10)–(14) is a general formulation, valid for cases beyond the particular reactor problem that was presented. The vectors and matrices particular for the problem in question, were given to illustrate the general expressions.

The general formulation describes evolution in one dimension, in time or space. We have chosen to use the spatial coordinate \( z \) here. This means that the system is stationary. All equations and results in this section hold, however, equally well if we switch from space to time as variable. We are thus not restricted to stationary systems.

Many models of engineering systems fit into this form. Among stationary systems some examples, in addition to the plug flow reactor, are heat exchangers, packed columns used for distillation, absorption or extraction, and membrane processes. The batch counterparts of these systems are examples of time-dependent systems.

We focus from now on the necessary conditions for the optimum, Eqs. (13) and (14), and the fact that the Hamiltonian is constant. We still assume that the weak form in Eq. (14) is sufficient, see discussion below Eq. (8). The necessary conditions in Eqs. (13) and (14) and the fact that the Hamiltonian is constant are therefore mathematically robust. The details of the state of minimum entropy production are not obvious, though. We shall see below, how physical insight into the solution can be gained by introducing assumptions in a stepwise manner.

4.2.1. The Spirkl–Ries quantity

We start by making the assumption of enough control variables:

(1) There are enough control variables to control all the forces independently and without any constraints on their values. This means that there are at least \( N \) control variables (\( M \geq N \)).

This assumption makes it possible to use \( x \) as the control instead of \( u \). We can then eliminate \( u \) from the problem and obtain a simpler Hamiltonian

\[
H(y, x, \lambda) = x^T \Gamma J(y, x) + \lambda^T A(y) J(y, x).
\]

(15)

The forces appear now explicitly in \( H \), and implicitly in the flux relations. The necessary conditions, equivalent to Eq. (14), become

\[
\frac{\partial H}{\partial x} = (\Gamma J(y, x))^T + x^T \frac{\partial (\Gamma J(y, x))}{\partial x} + \lambda^T A(y) \frac{\partial (\Gamma J(y, x))}{\partial x} = 0.
\]

(16)

By solving this equation for \( \lambda^T A \) and introducing the result in Eq. (15), we obtain

\[
H = - (\Gamma J(y, x))^T \left( \frac{\partial (\Gamma J(y, x))}{\partial x} \right)^{-1} (\Gamma J(y, x)).
\]

(17)

The combination of geometric factors and fluxes, and their derivative, on the right hand side of Eq. (17), is constant along the \( z \)-coordinate. This was called the Spirkl–Ries quantity by de Vos and Desoete (2000) because these authors were the first who proved the result (Spirkl and Ries, 1995). The Spirkl–Ries quantity is valid for any flux–force relation, given that the number of control variables is at least as high as the number of state variables. It has no simple meaning, unless the flux–force relations are linear. It then reduces to the theorems discussed below.

In the reactor problems discussed in Sections 3 and 4.1, there is only one control variable, \( T_a \). There are more than one driving force in all the reactor problems, except the R-problem with one reaction (\( m = 1 \)). Assumption (1) holds therefore only for this simplest of the reactor problems, meaning that the Hamiltonian reduces to the Spirkl–Ries quantity only for this case.

4.2.2. The theorem of equipartition of entropy production

To the result above, we can now add the assumption that is standard in irreversible thermodynamics (de Groot and Mazur, 1984; Førland et al., 2001)

(2) The flux–force relations are linear, that is \( J(y, x) = L(y)x \).

Here, \( L(y) \) is the matrix with conductivities. With this assumption we obtain \( \partial (\Gamma J(y, x))/\partial x = \Gamma L(y) \) and a
reduction of Eq. (17) to $H = -\sigma$. In other words: the local entropy production is constant along the $z$-coordinate when assumptions (1) and (2) are valid. This is the theorem of equipartition of entropy production (Eq. EP) which has been reported by many authors (Andreassen and Gordon, 1994; Bedeaux et al., 1999; Diosi et al., 1996; Johannessen et al., 2002; Spirkl and Ries, 1995; Tondeur and Kvaalen, 1987).

4.2.3. The theorem of equipartition of forces

Another result in literature is the theorem of equipartition of forces, EoF (Bedeaux et al., 1999; Saur et al., 1996). In order to obtain EoF, we first make the assumption of constant conductivities

(3) The conductivity matrix, $L$, does not depend on $y$ and is therefore constant.

Assumption (3) reduces EoEP to EoF immediately for a system with one force. In the general case ($N > 1$), the fact that $\sigma = x^T \Gamma L x$ is constant, makes a combination of the forces, but not necessarily each force, constant. In order to derive EoF when $N > 1$, we first rearrange Eq. (16) using assumption (2) and obtain

$$x^T = -\frac{1}{2} \lambda_{\text{EoF}}^T \Lambda. \quad (18)$$

This equation shows that all forces are constant if $\lambda_{\text{EoF}}^T \Lambda$ is constant. It is possible that $\lambda_{\text{EoF}}^T$ and $\Lambda$ vary in such a way that the product is constant, but in general both $\lambda_{\text{EoF}}^T$ and $\Lambda$ must be constant. In order for $\lambda_{\text{EoF}}^T \Lambda$ to be constant, the Hamiltonian cannot depend on $y$ (see the right part of Eq. (13)). We therefore need to make a fourth assumption in order to prove EoF for the general case ($N > 1$):

(4) The matrix $\Lambda$ does not depend on $y$ and is therefore constant.

When assumptions (1)–(4) hold, the constant Hamiltonian reduce to EoF. The derivation of EoEP required only assumptions (1) and (2). EoEP is therefore generally a better approximation to the constant Hamiltonian. The numerical results presented in Section 6.1 confirm this.

Some comments to the original proof of EoF can be given (Saur et al., 1996). The original proof considered the minimisation of the total entropy production

$$\left(\frac{dS}{dr}\right)_{\text{irr}} = \int_0^L x^T \Gamma L (y, z) x \, dz \quad (19)$$

subject to constraints on the total duty of the process:

$$I = \int_0^L \Gamma L (y, z) x \, dz = \text{constant.} \quad (20)$$

The problem was solved by formulating the functional

$$F = \int_0^L \left[ x^T L (y, z) x + \lambda_{\text{EoF}}^T \Gamma L (y, z) x \right] dz, \quad (21)$$

where $\lambda_{\text{EoF}}$ is a constant vector with Lagrange multipliers. EoF was obtained by setting the functional derivative of $F$ with respect to $x$ equal to zero, i.e., $\delta F/\delta x = 0$.

The original proof of EoF does not take the balance equations of the system into account. This means that the original proof considers systems with parallel and unconnected transfer paths. The optimisation problem is therefore different from the one in this paper. Only assumptions (1) and (2) were needed to derive EoF in the original proof (Saur et al., 1996).

The optimisation problem we study here coincides with the optimisation problem in the original proof of EoF when assumptions (1)–(4) hold. This can be seen by writing the Hamiltonian, when all these assumptions hold, as

$$H = x^T \Gamma L x + \lambda_{\text{EoF}}^T \Gamma L x, \quad (22)$$

where $\Gamma$, $L$ and $\lambda_{\text{EoF}}^T \Lambda$ are constant. We see that the integrand in Eq. (21) is the same as the Hamiltonian in Eq. (22) when $L$ is constant. This means that $\delta F/\delta x = 0$ is equivalent to $\delta H/\delta x = 0$, where $F$ and $H$ are given in Eqs. (21) and (22), respectively.

Bedeaux et al. (1999) showed that EoF is valid when the conductivity matrix, $L$, depends on $z$. We study systems with a constant Hamiltonian, meaning that we do not have any explicit $z$ dependence in $L$ or in other quantities. However, Eq. (18) and the discussion below are still valid when assumption (3) is changed to

(3*) The conductivity matrix does only depend on $z$, that is $L = L(z)$.

This means that EoF is also valid when assumptions (1), (2), (3*) and (4) hold. The Hamiltonian, the Spirkl–Ries quantity and the local entropy production are not constant in this case, though.

5. Calculations

The five reactor systems given in Table 1 were studied. The systems are the sulphur dioxide oxidation reactor (Johannessen and Kjelstrup, 2004), the ammonia reactor (Nummedal et al., 2003), the methanol synthesis reactor (Kjelstrup et al., 2000), the propane dehydrogenator (Rosjorde et al., 2003), and the tubular steam reformer (Nummedal et al., 2004).

Thermodynamic data, transport properties and reaction kinetics data for these systems were all reported in detail earlier. They were all taken from well established sources, and we refer to these earlier publications for this factual input. The same data were used here, if not otherwise indicated. For each reactor, a reference was first established in order to define the primary constraint on the entropy production minimisation; the amount of chemical produced.

The first three reactor systems are exothermic reactors and the two last are endothermic reactors. There are three
casess with one reaction \((m = 1)\), one case with two reactions \((m = 2)\), and one case with three reactions \((m = 3)\). Through these choices, a great variety of results was generated for systems with up to five state variables. This was needed to separate case specific and general properties. For each reactor we solved all optimisation problems (RQF, RQ and R), varying parameters like the reactor length, \(L\), the overall heat transfer coefficient, \(U\), and the inlet molar flow rates.

In the single reaction cases we fixed the inlet and outlet conversions, and in the multiple reaction cases we fixed the inlet conversions and the outlet molar flow rate of one component. We chose to fix the outlet molar flow rate of methanol/hydrogen in the methanol synthesis reactor/tubular steam reformer. Furthermore, we studied all 16 combinations, except the ones where the temperature and the pressure are free at both boundaries, are contained in the results presented in the next section. The exceptions gave the trivial solution of zero entropy production, because the pressure approached infinity.

We used the same method as reported in Johannessen and Kjelstrup (2004): the two-point boundary value problem obtained from optimal control theory was solved by collocation with the Matlab® 6 function bvp4c. The collocation method needs a reasonably good initial guess of the solution in order to converge. We found good initial guesses using the method described by Nummedal et al. (2003). This method is based on a discretisation of the optimisation problem and the solution by sequential quadratic programming using the Matlab® 6 function fmincon.

6. Results

We present corresponding values of \(T(z)\) and \(\xi(z)\) of selected cases, in order to demonstrate general properties of the states of minimum entropy production in chemical reactors. The plots shall be called “state diagrams for minimum entropy production” or simply state diagrams from now on. They refer to dynamic states, and must be distinguished from phase diagrams for systems in equilibrium. We do not present the corresponding \(T_i^*\) and \(P\)-profiles.

While all reactors have been studied in the same detail, we present state diagrams mainly for the sulphur dioxide oxidation reactor, see Figs. 2, 6, 8 and 9. For this particular exothermic reactor, the reference reactor had the inlet conversion 0 and the outlet conversion 0.8547 (Johannessen and Kjelstrup, 2004). These values give the end points on the abscissa in diagrams in Figs. 2 and 6–9. State diagrams for the propane dehydrogenator and for the steam reformer are presented in Figs. 4 and 5, respectively.

We present first the characteristic properties of the R-problem, for all reactors (Figs. 2–5), before we give the more complicated solutions of the RQ-problem (Figs. 6–8). We then present the essence of the full problem (the RQF-problem, Fig. 9).

6.1. The R-solution

We shall see in this section that the R-solutions for all reactors given in Table 1, are characterised by approximately constant local entropy production and forces (EoEP and EoF), except when the process intensity is very high. By process intensity we mean the average chemical conversion per meter, \(\Delta \xi / L\) where \(\Delta \xi = \xi_{\text{out}} - \xi_{\text{in}}\).

The state diagram for SO\(_2\) oxidation in the small frame in Fig. 2 shows the effect of varying process intensity. The dashed lines are R-solutions for four values of the reactor length \(L\), the lowest dashed line being the shorter of the lengths. The upper solid line in the figure is the equilibrium line. Along this line, \(\Delta G\) and the reaction rate are both zero. The lower solid line in the figure is the maximum reaction rate line. For each value of the conversion, the temperature
given by this line corresponds to maximum reaction rate. There is a unique relation between the process intensity and the distance between the R-solution and the equilibrium line. The higher the process intensity, the further the solution is from the equilibrium line. For long reactors the solution is almost parallel with the equilibrium line. The equilibrium line is itself a solution for an infinitely long reactor. For short reactors the solution approaches the maximum reaction rate line. The maximum reaction rate line is also a solution. The reactor length has then its lowest possible value. For the SO₂ oxidation case with the above mentioned inlet and outlet conversions, this minimum length is 1.42 m.

Infinitely efficient heat transfer is implicit in the R-problem; the overall heat transfer coefficient, \( U \), is infinitely large (see Section 3.3). The R-solutions have thus temperature jumps at the reactor inlet and at the reactor outlet in order to fulfil the boundary conditions for the temperature. These discontinuous profiles, obtained with zero resistance to heat transfer, become continuous in the RQ-problem (see below). We have not included the jumps in Fig. 2.

The large frame in Fig. 2 and Fig. 3 present a central property of the R-problem. The upper and lower thick solid lines in the large frame in Fig. 2 are again the equilibrium line and the maximum reaction rate line, respectively. Between these two lines, R-solutions are given for two reactor lengths (thick dashed lines). In addition, selected lines corresponding to constant local entropy production (thin solid EoEP lines) and constant driving force (thin dashed EoF lines) are given. The solution for reactor with \( L = 6.0 \text{ m} \), follows the EoEP and EoF lines closely. The process intensity is reasonable for this \( L \). In other words, EoEP and EoF are good approximations to this solution of the R-problem. The EoEP and EoF approximations become better, the longer the reactor is. In the limit of an infinitely long reactor, they are equal to the R-solution, since then both the local entropy production and the driving force are zero. In the other limit, for reactor lengths close to the minimum possible value, the agreement between EoEP, EoF and the optimal solution is poor. An example of this is the R-solution for the shortest reactor in the large frame in Fig. 2 (\( L = 1.6 \text{ m} \)). This solution does not behave like the EoEP and EoF lines in this part of the state space.

Fig. 3 shows the total entropy production of the R-solution (solid line), the EoEP-solution (dashed line) and the EoF-solution (dash–dotted) as a function of the reactor length. Three vertical solid lines are also added. These lines are drawn at the lowest possible reactor lengths where a solution exist for the R-problem (1.42 m), for EoF (1.77 m) and for EoEP (3.33 m). These lowest limits follow in each case from the maximum reaction rate line. The figure shows that the total entropy production of the EoEP solution is very close to the value of the R-solution for reactor lengths (or process intensities) in the range where both exist. The EoF solution approximates the optimal solution slightly worse in this range, but it exists for lower reactor lengths than the EoEP solution. In summary, the large frame in Fig. 2 and Fig. 3 show that EoEP and, to a slightly lesser degree, EoF are good approximations to the R-solution for reasonable process intensities.

A second set of R-solutions exists, but is not presented. These solutions all lie below the maximum reaction rate line. They have higher entropy production than the set above the maximum reaction rate line, and are therefore not interesting.

The results for the ammonia synthesis case are qualitatively the same as for the sulphur dioxide case. In both these cases there is a single exothermic reaction.

The differences between the exothermic and endothermic reactors are best seen by comparing the large frame in Fig. 2 and Fig. 4. These figures refer to the SO₂ oxidation.
reactor and the propane dehydrogenator, respectively. We see that the equilibrium line starts high and decreases for SO₂ oxidation while it starts low and increases for propane dehydrogenation. There is no maximum reaction rate line in the latter case, since a maximum reaction rate line is only possible for exothermic reactions.

We investigated the effect of multiple reactions by studying the methanol synthesis (two reactions) and the steam reforming of methane (three reactions). Fig. 5 shows one R-solution for the reformer (dashed line). The equilibrium lines for all three reactions are included (solid lines). The figure does not present the whole solution since the conversions of the second and third reaction are not included in the state diagram. The R-solution line in Fig. 5 is almost parallel with the two lower equilibrium lines. These represent the two reactions that produce most of the hydrogen, which is the component we fixed the production of. The results are therefore analogous to results for single reactions in long reactors, where the R-solution follows the single equilibrium line. The effect of changing the reactor length is similar for the steam reformer and the single reaction cases. The results for the methanol synthesis case have the same kind of behaviour as the steam reformer.

In summary, we have found that all R-solutions lie some distance below/above the equilibrium line for the exothermic/endothermic reactions. Exothermic reactions have a minimum reactor length, while endothermic reactions have not. All properties of the state diagrams for the single reaction case, hold equally well for exothermic and endothermic reactions. The differences between the single reaction cases and the multiple reaction cases are not significant. The important general feature of all R-solutions is that they approach EoEP and EoF lines in the state diagram, better and better as the process intensity decreases. But, already for reasonable intensities, EoEP and EoF are good approximations to the R-solution. EoEP is a slightly better approximation than EoF when both solutions exist.

6.2. The RQ-solution

Given that the results for SO₂ oxidation are qualitatively the same as for other reactors, we shall now use this case to illustrate the general nature of the RQ-solutions.

Fig. 6 shows the R-solution (black solid line) and RQ-solutions for fifty combinations of ten inlet temperatures and five outlet temperatures (grey solid lines). Only 10 grey lines can be distinguished in the figure. The equilibrium line (upper dashed line) and the maximum reaction rate line (lower dashed line) are shown as before. The figure reveals an interesting property: The central parts of the RQ-solutions fall more or less on the same line. This line extends from the inlet on the left hand side to the outlet on the right hand side, and it coincides with the R-solution. Solutions enter and leave this line at different positions depending on where their initial and final destinations are. The collection of solutions in Fig. 6 looks like a highway with its connecting roads. We have adopted the highway picture and call the band, which all solutions enter a “reaction highway”. The reaction highway is a path in state space which is especially crowded by solutions, just like a real highway is crowded by cars. Moreover, the solution does not enter the highway if its initial and final points are close in state space. (The exception is if both points are on or near the reaction highway.) The reaction highway is primarily used in order to travel “far” in state space. This is another analogy with the real highway. We shall not specify the details of what “far” and what “short” mean since this is case dependent. The aim is to give a qualitative description of the results.
A real highway makes it possible to get from one place to another very quickly; using the highway is time efficient because we are able to drive at high speed. This property of a real highway is not directly transferable to the reaction highway. The reaction highway is energy efficient, not time efficient.

The nature of the highway is further presented in Fig. 7. The figure shows the local entropy production as a function of the conversion for one RQ-solution (solid line). The part of the solution with approximately constant local entropy production is on the highway. The contributions from the reaction (dashed line) and the heat transfer term (dash–dot line) are also included. The entropy production is not constant in the beginning and in the end of the reactor since the reactor has to accommodate certain boundary conditions. These parts of the solution are off the highway. The figure shows that there is a shift of operation mode as the RQ-solution enters the highway. Up to this point the entropy production due to the reaction is much larger than the heat transfer term. The reactor operates with low heat transfer duty in this region. Once on the highway, the heat transfer term dominates the entropy production. It is the heat transfer that drives the solution along the highway, and we can say that the reactor is in a heat transfer mode of operation. There is a fine balance between the heat produced by the reaction and the rate of heat transfer. This fine balance prevents the reaction from reaching equilibrium and is therefore essential for the chemical production on the highway.

The relative lengths of the reaction mode and the heat transfer mode of the reactor depend on the inlet and outlet temperatures (see Fig. 6). By letting these be free during the optimisation we find the optimal inlet and outlet temperature and the optimal length of each mode. Fig. 8 shows four RQ-solutions with free inlet and outlet temperatures (dashed lines). Each line corresponds to a value of the heat transfer coefficient, \( U \). The lowest line corresponds to the lowest value of \( U \). The R-solution, which corresponds to \( U = \infty \), is also included (solid line). We see that the heat transfer mode becomes shorter and shorter as \( U \) decreases. Below a certain value of \( U \) there is no heat transfer mode (not shown). The optimal inlet temperature is then very low and the reactor is almost adiabatic. For large values of \( U \), the RQ-solution approaches the R-solution, as it should do.

Finally, comments should be given to the width of the highway. The highway has a finite width. In the R-problem there is a unique relation between \( \Delta \xi \), \( L \), and the distance between the solution line and the equilibrium line. This is not the case in the RQ-problem, because the inlet and outlet temperatures affect the solution. Depending on the inlet and outlet temperatures, slightly different amounts of chemicals are produced off the highway. The lengths in meters of the inlet and outlet sections vary also. This means that the process intensity on the highway is not the same for all the RQ-solutions. The highway is therefore not a single line, but has a finite width. The highway in Fig. 6 is an example of a narrow highway which corresponds approximately to the R-solution for one process intensity. Other highways are wider due to a distribution of process intensities. The nature of the reaction highway is the same, regardless of the width, though.

The RQ-solutions for the four other reactor cases are qualitatively the same as the results we have presented for the \( \text{SO}_2 \) oxidation case. They all have highways with properties as presented here. The differences that exist among the cases are natural extensions of the differences already discussed for the R-problem. For instance, the highway lies above the equilibrium line for the endothermic reactions, while it lies below the equilibrium line for exothermic reactions.
6.3. The RQF-solution

The RQF-solutions for all reactors confirm that a highway exists in state space also here (not shown). Again we shall take examples from the SO\textsubscript{2} oxidation reactor. The effects of the pressure drop on the solutions are of interest.

The effect of pressure drop on the optimal solution depends on the set of constraints we put on the system. If we fix the inlet pressure, the outlet pressure and the reactor length, the RQF-solution and the RQ-solution can be very different. If we let at least one of these parameters be free, the solutions are similar. An example from the SO\textsubscript{2} oxidation case is shown in Fig. 9. The figure shows one RQ-solution (solid line) and two RQF-solutions. All solutions have free inlet and outlet temperatures and the same inlet and outlet conversions. The lower RQF-solution (dash–dot line) has fixed values of inlet pressure, outlet pressure and reactor length. We see that it follows the highway only for a short while, before it goes down to lower temperatures close to the outlet. The reason is that the pressure drop increases as the temperature increases. The solution leaves the highway and goes to lower temperatures in order to arrive at the specified final pressure. The upper RQF-solution (dashed line) has fixed inlet pressure and reactor length, but the outlet pressure is free. There is a difference in optimal inlet temperature between this solution and the RQ-solution, but the solutions are qualitatively the same.

Since the pressure drop increases as the temperature increases, RQF-solutions have generally lower temperatures than the corresponding RQ-solutions. The RQF-solutions therefore follow a highway in state space which is shifted downwards compared to the highway of the corresponding RQ-problem. The highway of the RQF-problem is also slightly wider than the highway of the corresponding RQ-problem. The reason is that the pressure is not included in the state diagrams. A three-dimensional state diagram can be made, but it does not show anything more than the present one.

The reactor length has now a pronounced effect on the entropy production of the optimal solution. The entropy productions of the R-solutions and the RQ-solutions decrease monotonically as the reactor length increases. The reason is that the amount of catalyst and the heat transfer area increase as the reactor length increases. The processes are therefore slowed down, and produce less entropy. As a result, there is no optimal reactor length for these problems. The entropy production of the pressure drop (or frictional flow) is in good approximation proportional to \(-\ln(P_{\text{out}}/P_{\text{in}})\). Since the total pressure drop over the reactor generally increases as the reactor length increases, there is an optimal reactor length for the RQF-problem. At the optimal reactor length, the differential effects of the reactions, the heat transfer and the pressure drop balance each other. For smaller reactor lengths, an increase in reactor length reduces the entropy production of the reactions and the heat transfer more than the entropy production of the pressure drop increases. The opposite is true for reactor lengths larger than the optimal value.

An exception to this behaviour is found when both \(P_{\text{in}}\) and \(P_{\text{out}}\) are fixed, meaning that the entropy production of the pressure drop is essentially independent of the reactor length. There is an optimal reactor length in this case too. The reason is that excessive heat transfer is needed to have a fixed chemical production and a fixed total pressure drop, when the reactor length is large. The entropy production of heat transfer has therefore a minimum close to the optimal reactor length, which dominates the whole behaviour (see Fig. 6 in Johannessen and Kjelstrup, 2004).

7. Discussion

7.1. The highway in state space

The purpose of this paper was to reveal the nature of the state of minimum entropy production when there are less control variables than there are state variables in the system. Taking the plug flow reactor as an example, we have found a highway in state space for the reactor systems with minimum entropy production. The extent to which the system uses the highway, depends on the boundary conditions we impose. The highway exists for any process intensity, and already at reasonable process intensities, interesting properties appear; the thermodynamic forces and the local entropy production are approximately constant. At reasonable process intensities, the flux–force relations are nonlinear.

We adopted the highway picture because the collection of RQ-solutions in Fig. 6 looks like a highway with its connecting roads. The analogy does also fit with the density of solutions (cars) on the highway, and the fact that highways are primarily used to travel far. The reaction highway is an
energy efficient path in state space while a real highway is a time efficient path. Time efficiency, or high speed, corresponds to a different optimisation problem: maximum chemical conversion. This problem has been studied by many authors (see for instance Aris, 1961; Månnsson and Andresen, 1986; Schönhage and Andresen, 1996). Large parts of the solutions of this optimisation problem lie on the maximum reaction rate line. Only the inlet and outlet sections are off the maximum reaction rate line if this is required by the boundary conditions. The maximum reaction rate line is therefore the time efficient highway in state space. One might also say that the maximum reaction rate line is the fast lane on the highway. The highway for the minimum entropy production problem corresponds then to the other lane—the lane for those who want to arrive in reasonable time with minimum use of fuel.

The fact that a highway in state space exists, is not trivial. The constraint on the process intensity means that a certain mean reaction rate must be obeyed. This fixes more or less the region in state space where the solutions must be: A solution with low process intensity must have large parts close to the equilibrium line, while a solution with high process intensity cannot stay close to the equilibrium line everywhere. This constraint does not specify the nature of the solution, though. There are many ways to obtain the given process intensity. The solution may for instance oscillate to and from the equilibrium line in a series of equilibration and quenching stages. The fact that the highway is preferred instead of other solutions, suggests that each dissipative phenomenon has an optimal behaviour. This behaviour can be analysed analytically when there are enough control variables available, see Section 4.2. The fact that this behaviour is important also when there are too few control variables, like in the RQ- and RQF-problem, cannot be proved rigorously. To cover this situation we propose a hypothesis for energy efficient behaviour in the next section.

7.2. A hypothesis for the state of minimum entropy production in an optimally controlled system

We study the state of minimum entropy production when there are less control variables than there are state variables. The effects of having too few control variables have not been discussed thoroughly in literature. Most studies in the literature concern systems with enough control variables (see for instance Andresen and Gordon, 1992; Diosi et al., 1996; Sauar et al., 1996; Spirkl and Ries, 1995; Tondeur and Kvaalen, 1987; Tsirlin et al., 1998). Such systems have analytical solutions (see Section 4.2) and are therefore easier to handle, but this number of control variables is seldom relevant in industry. We are therefore concerned with cases where the number of control variables are limited. Still, the problems with enough control variables are important limiting cases for the understanding of the more realistic problems.

It is interesting that the highway can be characterised by almost constant entropy production and forces. These properties have been proved when there are enough control variables and the flux–force relations are linear, see Section 4.2. Our experience is that they are more general than that: The system adjusts to some kind of optimal behaviour, if it is given enough freedom to do so, also when the flux is a nonlinear function of the force as in most cases in this paper. It is clear, that there is enough freedom to adjust in the central part of the reactors we have studied.

We have earlier proposed the following hypothesis for energy efficient behaviour of an optimal controlled system (Johannessen and Kjelstrup, 2004): “The state of minimum entropy production is characterised by subsection(s) where the thermodynamic forces and the local entropy production are relatively constant compared to the rest of the system. These subsections grow, as more variables are added and restrictions are lifted.” The present results allow us to give a more precise formulation of the hypothesis:

*EoEP, but also EoF are good approximations to the state of minimum entropy production in the parts of an optimally controlled system that have sufficient freedom.*

The first change is that we no longer use logical *and* between EoEP and EoF. We have shown theoretically that the EoEP solution is better, and we have also given numerical support for this. The difference is surprisingly small, however, see Fig. 3 and Johannessen et al. (2002).

The present formulation of the hypothesis is more correct in the way that the role of the control variables are now incorporated. The previous formulation on subsections which grow is not always correct, for instance when we go from certain fixed boundary temperatures to free boundary temperatures. We have therefore replaced this part of the previous version, by the more general formulation where “sufficient freedom” is important. A system with enough control variables has sufficient freedom in the whole system, provided that it is not too far from equilibrium. Nonlinearities in the flux–force relations may restrict the freedom far from equilibrium, however, because the possibility for the system to relax becomes limited. A system with too few control variables has generally not enough freedom in the whole system. Boundary conditions as well as the compromise that must take place between the dissipative phenomena, will restrict the solution. The central part of the system is relatively more free from these restrictions. Freedom is thus not only related to the number of control variables, but also to the number and type of constraints on the system. The sufficient freedom is then necessarily system specific.

The theorems of EoEP and EoF have often been criticised because they do not hold in a strictly mathematical sense when the flux–force relations are nonlinear (Sieniutycz, 2003; Xu, 1997). The effects of nonlinearities are well known in the literature (Andresen and Gordon, 1992; de Vos and Desoete, 2000; Diosi et al., 1996; Latifi, 1992; Spirkl and Ries, 1995). They are also visible in the R-solution
since nonlinearities make the nature of the R-solution vary as the process intensity change, see Figs. 2 and 4. This argument cannot be used to disprove the hypothesis for two reasons: firstly, the hypothesis says that EoEP and EoF are good approximations to the optimal solution. Small nonlinear effects in the flux–force relations can therefore be tolerated; secondly, states with large nonlinearities (for instance at high process intensity) do not have sufficient freedom because the process duration, in time or space, is too restricted.

The hypothesis is supported by the derivations in Section 4.2 when there are enough control variables. These derivations can be found in different forms in the literature (Andresen and Gordon, 1994; Bedeaux et al., 1999; Diosi et al., 1996; Sauar et al., 1996; Spirkl and Ries, 1995; Tondeur and Kvaalen, 1987). When there are too few control variables, we only have numerical support for the hypothesis. The numerical results in this work and earlier works on entropy production minimisation in reactors (Johannessen and Kjelstrup, 2004; Kjelstrup et al., 2000; Nummedal et al., 2003, 2004; Rosjorde et al., 2003) are examples.

The literature on the state of minimum entropy production in systems with too few control variables is limited, but there are some exceptions that give numerical support for the hypothesis. de Vos and Desoete (2000) studied an electric circuit with one control and two state variables. They showed that no quantity was equipartitioned in the state of minimum entropy production for this system. Their numerical results, especially Fig. 4 in de Vos and Desoete (2000), show that there are parts of the process where the thermodynamic driving forces are approximately constant. (They do not give the entropy production.) This is in agreement with the kind of behaviour we have found for problems with too few control variables.

7.3. Practical consequences

We saw in Section 6 that the optimal reactor is characterised by what we called a reaction mode and a heat transfer mode. This result is our most important one, when it comes to taking the results from theory to practise. We can draw three conclusions on reactor design from the results: (1) The inlet section should be (close to) adiabatic, because the heat of the reactions moves the reacting mixture towards chemical equilibrium. (2) The central part of the reactor should operate in the heat transfer mode, to provide a fine balance between heat transfer and reaction rate(s), and the heat transfer driven reaction. (3) A total reactor length should be chosen to have the best trade off between low entropy production of heat transfer and reactions (long reactors are favourable) and low entropy production of frictional flow or pressure drop (short reactors are favourable). These conclusions differ from rules of thumb proposed by some authors on the basis of EoF or EoEP alone (Leites et al., 2003; Sauar et al., 1996; Tondeur and Kvaalen, 1987).

Examples of engineering practises for energy efficient design, which coincide with the outcome of these calculations, can be found. We may mention steam reforming as an example. In state-of-the-art tubular steam reformers, the reacting mixture is heated from the outside by burners along the direction of flow (see e.g. Rostrup-Nielsen et al., 1993). The temperature of the reacting mixture follows the equilibrium lines of the reactions in the same way as on the highway. An adiabatic prereformer is often placed upstream of the tubular reformer. The two reactor vessels approximate the heat transfer mode and the reaction mode, respectively. In this manner we may say that our findings give theoretical support to engineering practises.

8. Conclusion

Through a numerical study of the states of minimum entropy production in plug flow reactors we have found that these states share a common path. We called the path a highway in state space due to its similarity to a real highway. The solutions enter and leave the highway at different positions depending on how far from the highway their initial and final destinations are. The highway is a path in the reactor’s state space which is especially crowded by solutions, and it is an energy efficient way to travel far in state space. The EoEP and EoF theorems are good approximations to the parts of the solutions that are on the highway for reasonable process intensities, EoEP slightly better than EoF.

Each optimal solution is a compromise between the entropy production of reactions, heat transfer and pressure drop (frictional flow). The control variable is the temperature of the cooling/heating medium. On the highway, the state of the reacting mixture is driven along the equilibrium line(s) for the reaction(s) by the heat transfer, i.e., the reactor operates in a heat transfer mode. These findings offer theoretical support for existing engineering practises, like state-of-the-art tubular steam reformers. Some conclusions related to reactor design have been formulated on these grounds.

On the basis of the theoretical form of the equations, we conclude that systems that develop in time rather than in space as here, have the same behaviour in state space. The optimal reactor has a constant Hamiltonian. The Hamiltonian can be reduced to results in the literature which have a physical interpretation. The two most important results are the EoEP and EoF theorems, obtained with two and four additional assumptions, respectively.

By comparing the numerical results with the analytical results, we have found that the EoEP and EoF theorems are more powerful than what can be proved analytically. The most critical assumption that must be fulfilled for EoEP and EoF to be valid exactly, is that all forces in the system can be controlled independently. To describe the situation in the absence of this number of control variables, we have formulated a hypothesis for the state of minimum entropy
The results from this study and the literature give support to the hypothesis. Sufficient freedom is given, according to EoEP, and also EoF. This hypothesis postulates that a system will seek to arrange itself, when production in an optimally controlled system. This hypothesis is supported by the work of de Vos, de Groot, and Bejan.

### Notation

- \( A \): proportionality factors
- \( C_{P,i} \): heat capacity of component \( i \), J/K mol
- \( D \): reactor diameter, m
- \( D_p \): catalyst pellet diameter, m
- \( \text{EoEP} \): Equipartition of Entropy Production
- \( \text{EoF} \): Equipartition of Forces
- \( f_p \): right hand side of Eq. (3), Pa/m
- \( f_T \): right hand side of Eq. (2), K/m
- \( f_{\xi} \): right hand side of Eq. (1), 1/m
- \( F_i \): molar flow rate of component \( i \), mol/s
- \( F_A \): molar flow rate of the reference component, mol/s
- \( \Delta G_j \): Gibbs energy of reaction \( j \), J/mol
- \( -\Delta G_j / T \): chemical force of reaction \( j \), J/K mol
- \( H \): Hamiltonian of the optimal control problem, J/K m s
- \( \Delta H_j \): heat of reaction \( j \), J/mol
- \( J_q \): sensible heat flux, J/m\(^2\) s
- \( J \): fluxes
- \( L \): reactor length, m
- \( L \): conductivities
- \( P \): pressure, Pa
- \( r_j \): rate of reaction \( j \), mol A/kg cat s
- \( R \): gas constant, J/K mol
- \( (dS/dt)_{irr} \): total entropy production rate, J/K s
- \( T \): temperature of reaction mixture, K
- \( T_u \): temperature of utility, K
- \( \Delta(1/T) \): thermal force across the reactor wall, 1/K
- \( U \): overall heat transfer coefficient, J/K m\(^2\) s
- \( u \): control variables
- \( v \): gas velocity, m/s
- \( x \): thermodynamic drivingforces
- \( x_i \): mole fraction of component \( i \)
- \( y \): state variables
- \( z \): position in the reactor, m
- \( \nu_{j,i} \): stoichiometric coefficient of component \( i \) in reaction \( j \)
- \( z_j \): conversion of reaction \( j \)
- \( \rho \): gas density, kg/m\(^3\)
- \( \rho_B \): apparent catalyst density, kg/m\(^3\)
- \( \sigma \): local entropy production rate, J/K m s
- \( \Omega \): cross sectional area, m\(^2\)

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### References


