

# *Two established process technologies confirmed by entropy production minimization*

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## **ABSTRACT**

The method of entropy production minimization for finding energy efficient paths of operation of process equipment is first presented using an instructive example with optimal control theory. With reference to the earlier investigations, the researchers present some design rules that relate to the designs' entropy production. Minimum entropy production is not obtained in special cases, not generally, by equipartition of entropy production or of thermodynamic forces. The researchers show that two well established industrial technologies, namely the Haldor Topsøe steam reformer and the Linde technology for air separation understood in terms of the design rules. The entropy production minimization technique is thus able to predict well proven technology, technology that has developed over several decades. This gives an argument for early use of this technique in the designing phase of energy intensive processes.

## **Keywords**

Entropy production minimization, energy efficient design rules

## **1. Introduction**

Numerous energy efficiency studies that apply the method entropy production minimization or exergy analysis/ optimization, have been carried out in attempts to increase the energy efficiency of a given industrial process or of parts of process equipments, see e.g. [1-12, 15, 16, 17]. During periods of method developments, the systems to be solved have been highly idealized, however, and uncommon degrees of freedom have been assumed [9, 10, 12]. This may lead to a perception that such methods are not useful, and may also have delayed their possible industrial application.

In practice, process design is a result of several trade-offs and practical considerations. Besides product quality, product safety, and the control and operability of processes as central elements of a responsible development, the energy efficiency is recognized as a keyvariable to be

optimized in conceptual process design. Second law analyses have often been considered only at a late stage in the development, however. The purpose of this work is to introduce arguments in favor of using the method of entropy production minimization at an early stage in the design process. In doing so, the issue of the energy efficiency can be approached and optimized in a more systematic manner.

In the study of lost work or entropy production, it is important to realise that every process operates with some loss. Industrial processes which are far from the reversible limit may have large losses. When we speak of entropy production minimization, we speak of getting rid of excesses in the lost work in a controlled manner. To avoid losses completely, is unrealistic and not on the agenda. Control theory is an efficient tool to accomplish a goal of reducing losses to a mini-

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mum needed to accomplish the process goal, because it enables us to handle realistic boundary conditions as well as relevant restrictions on performance. We shall therefore formulate our optimisation problem within the context of optimal control theory [14]. This theory distinguishes between control variables; that is variables that the engineer can control from the outside, and system variables, which develop freely according to the natural laws. The researchers explain first how control theory can be applied, using an instructive example.

they go on to demonstrate how they have been able to generate the state-of-the-art performance of two industrial processes, processes that have evolved and been optimized by experience over long periods of time. The processes are the reformer technology of Haldor Topsø, and the Linde technology for cryogenic distillation. These processes shall be used to defend some systematic rules for energy efficient design, rules that can improve earlier rules of thumb for such design [15,16].

## 2. Optimal isothermal expansion

The process of isothermal gas expansion is sufficient to demonstrate how optimal control theory can be used to find a state of operation that has minimum entropy production [2] (see Johannessen and Kjelstrup [3,4] for more realistic cases).

Consider therefore a container filled with an ideal gas, as illustrated in Fig. 1. The container has a piston, so work can be extracted by expanding the gas. Heat is transferred to the gas from the surroundings in order to keep the temperature constant. The temperature of the surroundings and the system is  $T_0$  (reversible heat transfer). The researchers consider expansion of the gas from an initial pressure  $P_1$  to a final pressure  $P_2$ . The corresponding volumes are  $V_1$  and  $V_2$ , respectively.

Processes in nature as well as in industry proceed in a finite time. The researchers shall therefore fix the duration of the expansion,  $\theta$ . By doing this, The researchers also need details about the dynamics of the process. The researchers assume that the movement of the piston can be described by the following differential equation.

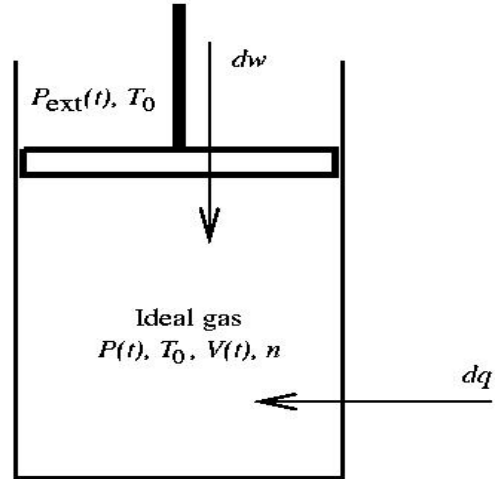


Fig. 1: A container with a piston filled with  $n$  mol of an ideal gas with pressure  $P(t)$ , temperature  $T_0$ , and volume  $V(t)$ . Heat  $dq$  is added to the gas and work,  $dw$ , is done on the gas in a small time interval,  $dt$ . The gas expands isothermally against an external pressure  $P_{\text{ext}}(t)$ . The temperature of the environment is  $T_0$ .

$$\begin{aligned}
 \frac{dV}{dt} &= -\frac{f}{P^2} (P_{\text{ext}} - P) \\
 \Leftrightarrow \frac{dP}{dt} &= \frac{f}{nRT_0} (P_{\text{ext}} - P)
 \end{aligned} \tag{1}$$

where  $V$  is the gas volume,  $f$  is a constant that describes the velocity of the piston in the container,  $P$  is the gas pressure,  $P_{\text{ext}}$  is the external pressure,  $n$  is the number of moles,  $R$  is the gas constant, and  $T_0$  is the temperature. Expansion produces the familiar work on the gas:

$$w = -\int_{V_1}^{V_2} P_{\text{ext}} dV \tag{2}$$

The ideal limit of this work is given by a reversible process, when the external pressure equals the pressure of the gas at all times, and the expansion proceeds infinitely slow. The ideal work is:

$$w_{\text{id}} = -\int_{V_1}^{V_2} P dV = nRT_0 \ln \frac{P_2}{P_1} \tag{3}$$

This work is called ideal since the extracted work ( $-w$ ) in any version of the expansion cannot be larger than  $-w_{\text{id}}$ . An irreversible version of the process has always lost work,  $w_{\text{lost}} = w - w_{\text{id}}$ , and the lost work is always positive. The name "lost work" reflects that this is potential work which

we are not able to extract because of irreversibilities. The ideal work is one yardstick, with which all other processes can be compared.

One class of irreversible expansions is  $K \geq 1$  step expansions where the external pressure is constant in each step. The value of the external pressure varies from step to step. The work of this class of processes is found from Eq. (2) and is:

$$w = -nRT_0 \sum_{i=1}^K P_{\text{ext},i} \left( \frac{1}{P_{2,i}} - \frac{1}{P_{1,i}} \right) \quad (4)$$

where  $P_{\text{ext},i}$ ,  $P_{1,i}$  and  $P_{2,i}$  are the external pressure, the initial pressure of the gas and the final pressure of the gas in step number  $i$ , respectively. Given the values of  $P_{\text{ext},i}$  and  $P_{1,i}$ , we can find  $P_{2,i}$  by integration of Eq. (1). The lost work is:

$$w_{\text{lost}} = -nRT_0 \left[ \sum_{i=1}^K P_{\text{ext},i} \left( \frac{1}{P_{2,i}} - \frac{1}{P_{1,i}} \right) + \ln \frac{P_2}{P_1} \right] \quad (5)$$

In texts on thermodynamics the work in an isothermal expansion is often illustrated in a  $PV$ -diagram. Examples of such diagrams are given in Fig. 2. The ideal work of the expansion, Eq. (3), is minus the area below the isotherm in these diagrams. The work in a  $K = 1$  step expansion, Eq. (4), is minus the area of the shaded rectangle in Fig. 2(a). The lost work of the same process, Eq. (5), is the area between the isotherm and the rectangle in the same figure. Figure 2(b) shows the expansion with 5 steps

## 2.2 Entropy production of a K-step expansion

During the expansion, the entropy of the gas and the surroundings changes, and the local entropy production is:

$$\sigma = \frac{dS^{\text{system}}}{dt} + \frac{dS^{\text{sur.}}}{dt} = \frac{1}{T_0} \frac{dq_{\text{rev}}}{dt} + \frac{1}{T_0} \left( -\frac{dq}{dt} \right) \quad (6)$$

Here,  $dq_{\text{rev}}/dt$  is the rate of heat transfer in a reversible expansion between the same initial and final states of the gas. The researchers have taken advantage of entropy being a state function in this calculation. Furthermore,  $-dq/dt$  is the rate at which heat is transferred (reversibly) to the surroundings in the irreversible expansion.

Since the expansion is isothermal, the internal energy of the ideal gas,  $U$ , is constant and  $dq = -dw$ . Using this and Eqs. (1) and (2), we can write the local entropy production as:

$$\sigma = \frac{(P_{\text{ext}} - P)}{T_0} \left( -\frac{dV}{dt} \right) = \frac{1}{T_0} \frac{f}{P^2} (P_{\text{ext}} - P)^2 \quad (7)$$

The total entropy production of the expansion is the integral of the local entropy production over the process duration.

We return to the  $K \geq 1$  step expansions. The total entropy production becomes:

$$\begin{aligned} \frac{dS_{\text{irr}}}{dt} &= \sum_{i=1}^K \int_{t_{1,i}}^{t_{2,i}} \frac{1}{T_0} (P_{\text{ext}} - P) \left( -\frac{dV}{dt} \right) dt \\ &= -nR \left[ \sum_{i=1}^K P_{\text{ext},i} \left( \frac{1}{P_{2,i}} - \frac{1}{P_{1,i}} \right) + \ln \frac{P_2}{P_1} \right] \end{aligned} \quad (8)$$

By comparing this result with the lost work, Eq. (5), we see that  $w_{\text{lost}} = T_0 dS_{\text{irr}}/dt$ . This is Gouy-Stodola's theorem [1]. In the proof of this theorem, we use that all heat is discarded or extracted from a reservoir at the reference temperature  $T_0$ . In this example The researchers assumed that the system and the surroundings were at  $T_0$ . In the case that the system has temperature  $T$ , we can add to the system the performance of a Carnot machine, to discard (or extract) the heat to a reservoir at  $T_0$ .

## 2.3 Entropy production minimization

The researchers intended to minimize the entropy production of the above expansion. Since we fix the initial and final states of the gas, the ideal work is also fixed (cf. Eq. (3)). This means that maximizing the work output ( $-w$ ) and maximizing the second law efficiency are equivalent optimization problems. There is no sense to maximize the work output or minimize the entropy production of this process without fixing the ideal work: Given that the process duration is fixed, maximum work would give an infinite pressure ratio  $P_2/P_1$ , and minimum entropy production would give  $P_2/P_1 = 1$  (no expansion at all).

If we had no restriction on the duration of the expansion, the minimum entropy production would be a trivial zero, and the maximum work

output would be  $-w_{id}$ . Since we have a fixed process duration,  $\theta$ , the entropy production is not zero and the maximum work output is lower than  $-w_{id}$ .

For a  $K = 1$  step expansion, there is only one external pressure which takes the pressure of the gas from  $P_1$  at time 0 to  $P_2$  at time  $\theta$ . The work and the lost work of this process is illustrated in Fig. 2(a). For  $K > 1$ , there are infinitely many feasible choices of external pressures. This freedom can be used to minimize the entropy production (maximize the work output) of the expansion approximates the dashed line in the figures better and better as  $K$  increases. The dashed line, characterized by infinitely many steps and a continuously changing external pressure, is a limit for the performance of the process, given that the process duration is fixed. It is thus another limiting process, or yardstick for a process of finite duration. This limiting process is not as general as the reversible one; it depends on the piston/container used and the dynamics of the system (Eq. (1)). But in this manner it becomes a practical yardstick.

We say that the system is in the state of minimum entropy production when the expansion proceeds along the dashed line that is given in both sub-figures of Fig. 2. We show below that this expansion has constant local entropy production throughout. This is one example of the theorem of equipartition of entropy production (EoEP); a result describing the characteristics of the state of minimum entropy production [9, 11, 13, 15, 16].

## 2.4 The state of minimum entropy production

The state of minimum entropy production for the expansion, the dashed lines in Fig. 2 is of interest. This state is the solution of the following optimization problem: Minimize the total entropy production

$$\frac{dS_{irr}}{dt} = \int_0^\theta \sigma dt = \int_0^\theta \frac{f}{T_0 P^2} (P_{ext} - P)^2 dt \quad (9)$$

subject to the governing equation for the pressure of the gas, Eq. (1). Again, the process duration,  $\theta$ , and the initial and final pressures of the gas,  $P_1$  and  $P_2$ , are fixed. We search is done for

the optimal variation of the external pressure, the control variable, throughout the process.

The optimization problem can be solved using several mathematical tools, i.e. optimal control theory, calculus of variations and dynamic programming. The researchers have chosen to use optimal control theory [14], because this method handles real restrictions on the control variables very well. In optimal control theory, the variables of the system are divided into state variables and control variables. The state variables are the variables which are governed by differential equations. The pressure of the gas (or alternatively its volume) is thus a state variable in the present example since it is governed by Eq. (1). The control variables are the practical handles on the system, or the means with which we control it. In the present example, the external pressure is the control variable. We full control over the pressure, and allow that it can take any positive value.

There is a The first step is to construct the Hamiltonian of the optimal control problem. In our example, the Hamiltonian is:

$$H = \frac{f}{T_0 P^2} (P_{ext} - P)^2 + \lambda \frac{f}{nRT_0} (P_{ext} - P) \quad (10)$$

The first part of  $H$  is the local entropy production. The second part has terms which are products of multiplier functions ( $\lambda$ 's) and the right hand sides of the governing equations. In this problem, there is only one governing equation. A general result in optimal control theory is that the Hamiltonian is constant along the coordinate of the system, time in this case, when it is autonomous [14]. This is a property which one often can take advantage of. The Hamiltonian is autonomous when it does not depend explicitly on the coordinate of the system (here time), but only implicitly through the state variables (here pressure), the control variables (here external pressure), and the multiplier function This is the case for the optimization problems studied in this paper. Necessary conditions for minimum entropy production are derived from the Hamiltonian and consist of differential and algebraic equations. There are two differential equations for each state variable, and one algebraic equation for each control variable. In the present problem the differential equations are:

$$\frac{dP}{dt} = \frac{\partial H}{\partial \lambda} = \frac{f}{nRT_0} (P_{\text{ext}} - P) \quad (11)$$

$$\frac{d\lambda}{dt} = -\frac{\partial H}{\partial P} = \frac{2f}{T_0 P^2} (P_{\text{ext}} - P) \frac{P_{\text{ext}}}{P} + \lambda \frac{f}{nRT_0} \quad (12)$$

ur case, the optimal external pressure is always positive. The algebraic equation is therefore:

$$\frac{\partial H}{\partial P_{\text{ext}}} = \frac{2f}{T_0 P^2} (P_{\text{ext}} - P) + \lambda \frac{f}{nRT_0} = 0 \quad (13)$$

Optimal control theory gives a stronger form of the algebraic equation when the value of the external pressure is more constrained. The first differential equation is the governing equation for the pressure, and is thus not "new". The second differential equation is new and describes the time variation of the multiplier function.

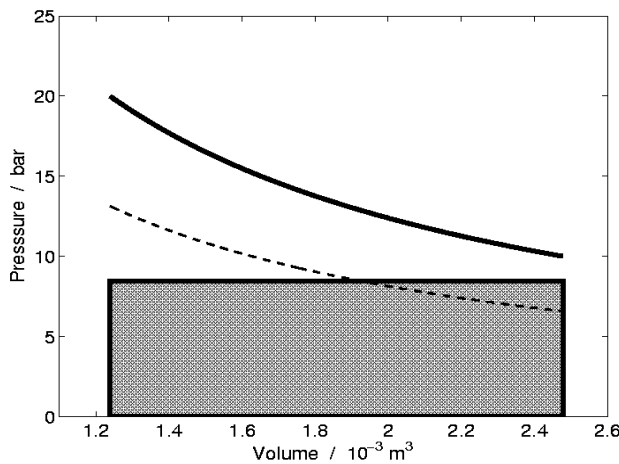
The present problem can be solved analytically. The researchers have used that the Hamil-

tonian is constant in time, solve Eq. (13) for  $\lambda$ , introduce the result in the Hamiltonian, and obtained:

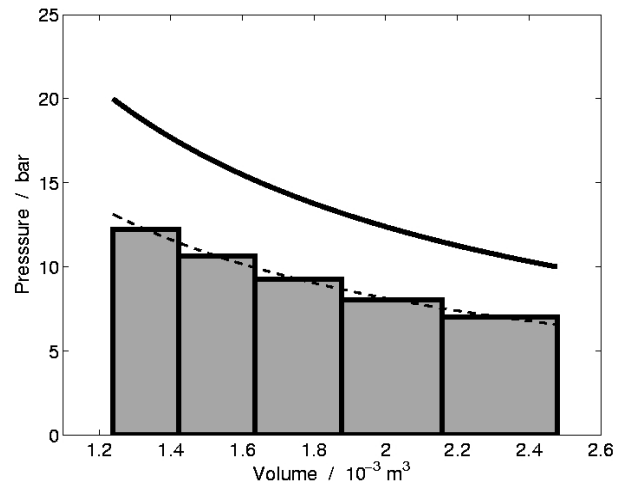
$$H = \frac{f}{T_0 P^2} (P_{\text{ext}} - P)^2 - \frac{2f}{T_0 P^2} (P_{\text{ext}} - P)^2 = -\sigma \quad (14)$$

The Hamiltonian reduces to the local entropy production,  $\sigma$ , meaning that the state of minimum entropy production is characterized by constant local entropy production. This is an example of the theorem of equipartition of entropy production (EoEP) which has been demonstrated by many authors [9-13].

The constant local entropy production can be used to work out all details of the optimal solution analytically. The solution explains which pressure variation (control variable) to use, once the time span of the process and the apparatus constants are established.



(a) 1 step



(b) 5 steps

Fig. 2: External pressure vs. Volume in a one and five step process. The grey areas are the work in each step. The lost work is the area between the rectangle(s) and the isotherm (the solid line). The dashed line corresponds to the state of minimum entropy production. ( $n = 1$  mol,  $T = 298$  K,  $P_1 = 20$  bar,  $P_2 = 10$  bar,  $f = 500$  m<sup>3</sup> Pa / s,  $\theta = 10$ s)

### 3. Rules for second law energy efficient design

As we have seen above that the optimal expansion process occurs with constant local entropy production. According to the researchers experience [2-7] this simple result can not be expected in more complicated cases, especially not when the

number of control variables are smaller than the number of thermodynamic forces [4]. An actual optimization of the process unit in question is therefore unavoidable. For instance, the optimal behaviour of a chemical reactor is very different in

its first and second part (see below), and we need the optimization to establish the ratio of the lengths of these parts,  $L_1/L_2$

Equipartition of entropy production or of thermodynamic forces have both been suggested as design rules for energy efficient operation [13,15,16]. Even if we find that parts of the optimal paths in realistic systems have this property, The researchers do not recommend EoF or EoEP as a priori design rules. We have seen for instance, that the opposite of energy efficient behaviour can be obtained by applying EoF to the whole length  $L$  of a chemical reactor. The equipartition results offer insight, however. Given enough degrees of freedom to approach a local internal equilibration [2, 4], the system will seek a path of operation characterised by EoEP, with EoF as a good approximation. The surprising feature is that this occurs also in spite of flux-force relations being highly non-linear [4]. Realistic systems are often restricted severely, however. This limiting behaviour is then not obtainable.

On the basis of this broader experience, some that has emerged over the last years, i.e. [3-9,11,18], we shall therefore attempt to formulate revised guidelines for energy efficient design of chemical reactors (Rules 2a-c) and distillation columns (Rule 3) to replace the above-mentioned equipartition rules. For completeness The researchers include also the case of the simple heat exchange process, (no phase changes in the system), which is well established in engineering (Rule 1)

**Rule 1)** The most energy efficient heat exchange process is well approximated by a counter-current heat exchanger, because the entropy production for heat exchange has a rather flat minimum [11].

**Rule 2a)** A tubular chemical reactor of length  $L$ , operating in an energy efficient way has an inlet section, of length  $L_1$ , that is close to adiabatic. The heat of the reaction (positive or negative) moves the reacting mixture temperature towards chemical equilibrium in this section. The researchers say that the reactor operates in a reaction mode in  $L_1$  [4].

**Rule 2b)** A tubular chemical reactor of length  $L$ , operating in an energy efficient way has a central section,  $L_2$ , characterised by a fine balance be-

tween heat transfer and reaction rate(s), so that the temperature of the reacting mixture,  $T$ , is (approximately) at constant distance from the temperature,  $T_{eq}$ , at which the mixture is in equilibrium. The researchers include that the reactor operates in a heat transfer mode in  $L_2$  [4].

**Rule 2c)** A tubular chemical reactor operating in an energy efficient way has a total length  $L \geq L_1 + L_2$ , that gives the best trade-off between low entropy production of heat transfer and reactions (long reactors are favourable) and low entropy production due to pressure drop (short reactors are favourable) [4].

**Rule 2d).** In the case of efficient heat transfer (high heat transfer coefficients), the design should consist of an adiabatic pre-reactor followed by a tubular reaction section for heat exchange.

**Rule 2e).** In the case of small heat transfer coefficients, the design should contain one or more adiabatic reactor stages with interstage heating/cooling in dedicated heat exchangers.

**Rule 3)** An energy efficient distillation column allows for heat exchange along the column, facilitated by a *distribution* of the available heat exchanger area. The heat may be exchanged through means of heating/cooling media, or by direct interaction with other columns matching the required heating/cooling duty.

The examples that follow support the main ideas of the new Rules 2a-e and 3.

#### 4. Reformer technology

Steam reforming of methane in a tubular steam reformer is used in the production of synthesis gas for ammonia synthesis, methanol synthesis, hydrogen production, etc. Heat must be added to the process because the main reactions are endothermic. The energy efficiency of the tubular steam reformer has been, and still is, subject to improvements [18-21].

Figures 3 and 4 show results of entropy production minimization for a reformer, using methods documented earlier [2-7]. The researchers used a Haldor Topsø-like tubular steam reformer to define the start of the optimization, or the reference for the calculations. They kept the inlet composition, the production of hydrogen and the

inlet temperature fixed in the optimization. The outlet temperature and the inlet and outlet pressures were allowed to vary. This means that the ideal work is only approximately fixed. Figure 3 shows the temperature profiles of the reference (black lines) and optimal (grey lines) reformers. We see that the temperatures of the reaction mixture (solid lines) are almost identical in the two cases. The temperatures on the outer tube wall (dashed lines) differ only significantly close to the outlet. We find that the total entropy production of the optimal reformer is only 2% lower than in the reference reformer. The gain is even smaller when we also fix the temperature out and/or pressure in/out. This means that the reference reformer, which one may consider as state-of-the-art technology, has near-optimal second law energy efficiency.

The local entropy production of the optimal reformer vs. position is shown in Fig. 4 (solid line). The contributions from heat transfer

(dashed line), reactions (dash-dotted line) and pressure drop (dotted line) are also given. The figure shows some general properties of the state of minimum entropy production in reactors [4]. The contribution from the reactions dominates in approximately the first 5% of the reactor. This part has the length  $L_1$  explained above. The reactor is here in the reaction mode. Secondly, we find that the heat transfer term dominates the local entropy production in the central part of the reactor, the part called  $L_2$  above. The reactor is here in the heat transfer mode, with a fine balance between the rate of heat transfer and the heat consumed by the reactions. We also see the local entropy production is constant in a large part of the system. This is the part, which is on the reactor's highway in state space, a general property of the state of minimum entropy production in reactors [4]. A reaction mode and a heat transfer mode is a general property for the state of minimum entropy production in chemical reactors [4] and was the background for our proposal of Rules 2a and b. The reaction mode might well occupy a larger part of the total length than shown here [3, 4]. In practice there is often a pre-reformer upstream of the tubular reformer. The pre-reformer is adiabatic and operates thus in a

reaction mode. Rules 2 d)-e) may be seen as a generalization of these observations. Depending on the heat conducting properties of the reactor wall, we are in one of two regimes, as illustrated schematically in Fig.5. When the heat transfer along the tubular reactor is less of a problem, one prewarming step seems sufficient. The chemical reaction can well be carried out in an adiabatic step. The system optimization can then concentrate on finding optimal boundary conditions of the two first units, and optimal heat transfer in the tubular reactor. If the heat transfer is limiting, however, it will pay to do dedicated heat transfer in stages intermediate to reactor stages, as illustrated in Fig.5, scheme 2.

The agreement between the reference reformer and the second law optimal reformer is very good, much better than for all other reactors we have studied [2-7]. One may speculate that this is, using words from biology, a result of evolution over many generations of reformers. As energy resources have become more and more restricted, energy intensive units like the reformer are more susceptible to changes in their design and operation than other units.

The results presented here *do not* mean that there is no way to increase the energy efficiency further! In an earlier paper, we found that the entropy production can be reduced with more than 60% if we allow the inlet temperature and inlet composition to vary in the optimization [6]. In the optimum, the temperature was higher and the steam to carbon ratio was lower than in the reference used for Figs. 4 and 5. Changes in the inlet temperature and steam to carbon ration have already contributed to the improved energy efficiency of the tubular steam reformer from Haldor Topsø the last 20 years [20, 21].

Nevertheless, better reformer designs may still be possible, by taking advantage of the systematic procedure described above. A systematic procedure takes normally less time than trial and error. By studying the contributions to the entropy production in the gas heated reformer Wilhelmssen and coworkers [18] suggested that rules **2d-e)** may provide a rapid path to an energy efficient design. These rules have not been listed by others [16]

## 5. Cryogenic distillation

Heat integrated distillation columns (HIDiCs) are distillation columns where heat is exchanged between different parts of the columns, with one part possibly at an elevated pressure. The part closest to the condenser (the rectifier) operates typically at a higher pressure than the part closest to the reboiler (the stripper). The pressure change is required for appropriate heat transfer. The need for heat (cooling) in the reboiler (condenser) can be drastically reduced or avoided [8,22,23] in such arrangements, compared to the common, adiabatic tray distillation column (our reference system). One particular arrangement for heat integration is to divide the column in two and allow each tray in one section to exchange heat with a tray in the other section (see Fig.5a). The performance of the HIDiC is determined by the number and size of the trays that are matched. Figure 5b illustrates a match involving only two trays in each section.

By varying the number of contact points, the state of minimum entropy production of the HIDiC as investigated in a column separating benzene and toluene [8]. The total area available for heat exchange was fixed in the optimization, while the area distribution and the pressure ratio were varied. This is an optimal control problem for a discrete system. The optimizations were carried out in Matlab using sequential quadratic programming and the function `fmincon` [24].

The results showed that the column with the least entropy production was the one in Fig.5b, where only one pair of trays exchanges heat. The relevant trays were next to the condenser and next to the reboiler. The need for addition of heat at high temperature(s) was drastically reduced, compared to the adiabatic reference that produced the same product, but mechanical power was needed in terms of compressor work to raise the pressure in column S (not shown). The net saving in high quality energy was still substantial [8]. These results give the basis for our design Rule 3 Results supporting Rule 3 have also been found by others [8, 23-26].

The resemblance of Fig. 4 to the well-established Linde double-column for air separation is striking. This separation process operates at temperatures far below 0°C, and is known as

highly power consuming. A considerable effort has been devoted to its development, starting already near the end of the 19<sup>th</sup> century. In 1905, Carl von Linde then introduced his double column concept with one column operating at atmospheric conditions, and the other at higher pressures [19]. The distillate from one column was used as feed for the other, where the highest purity was obtained. The Linde concept was further developed over the years to come, and is now one

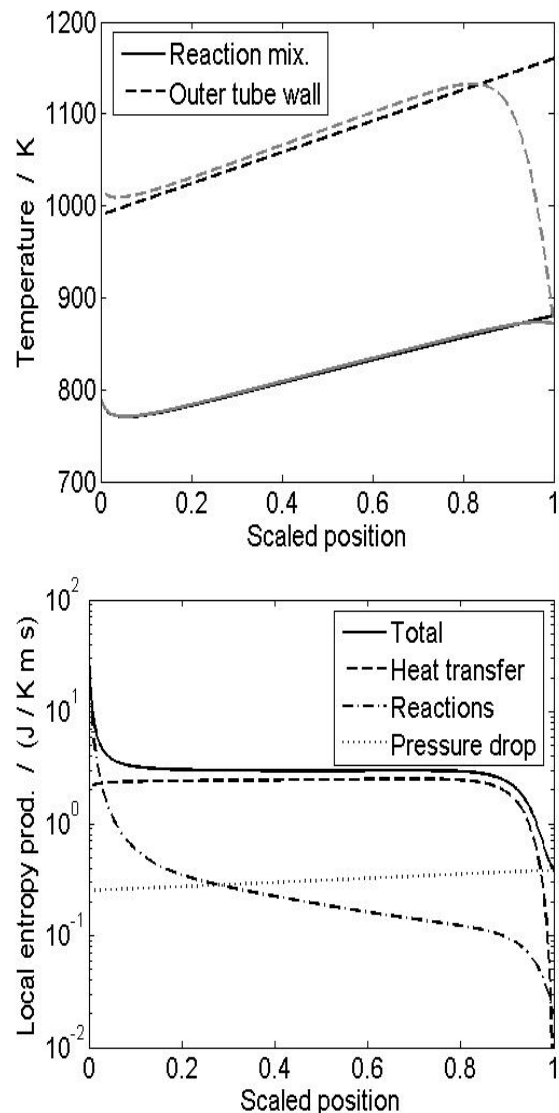


Fig. 3: Temperature profiles for the reference (black lines) and optimal (grey lines) reformer.



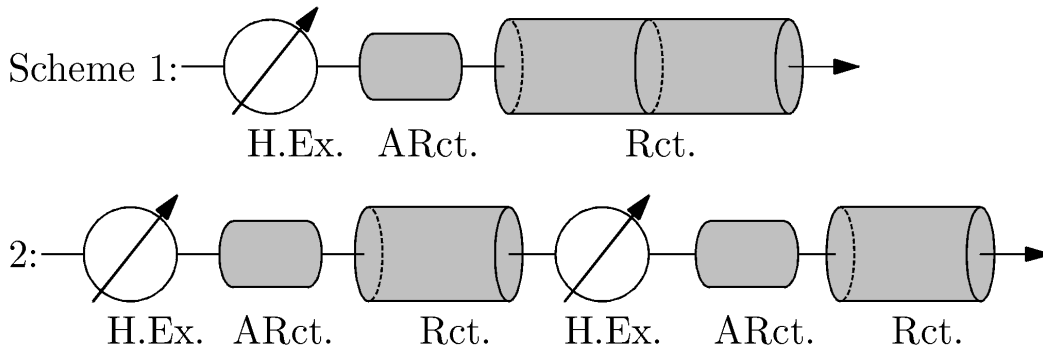


Fig. 4: Proposed design of chemical reactors with high (scheme 1) or low heat transfer coefficients (scheme 2) [18]

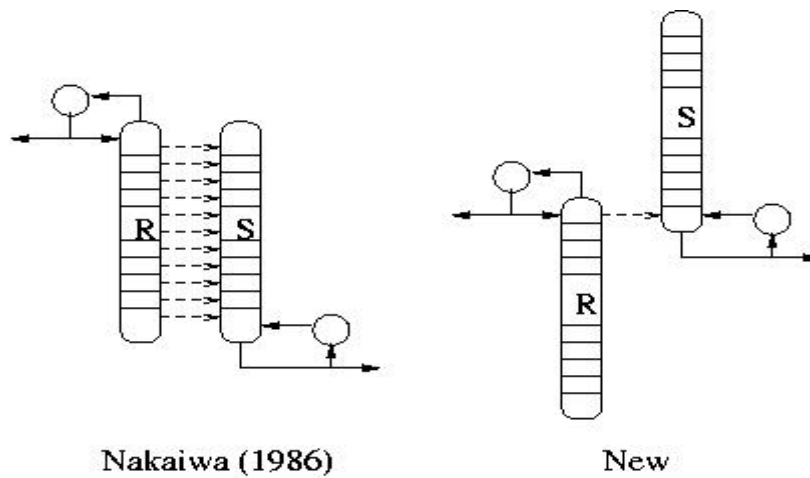


Fig. 5: Schematics of a simple HIDiC (left) and a column with shifted sections resembling the Linde double-column (right). Both columns S are operated at elevated pressure.

### Concluding remarks

The researchers have demonstrated in detail for a simple example how the well established optimal control theory can be used to find the state of minimum entropy production of process equipments. they have presented some new rules for energy efficient design emerging from recent research, and have shown that the results predict existing structures of two energy demanding industrial technologies, namely the reformer of Haldor Topsøe AS and the Linde cryogenic distillation arrangement. The concepts of these technologies are old and have been refined over several decades to reach present days level of operation. The researchers have seen that this level of operation is as near that of minimum entropy production as it

probably is possible to come given practical boundary conditions. The ability of the method of entropy production minimization to predict these well-known technologies, gives an argument for using the method at an early state in the design process, along with other optimization tools. Energy intensive processes major target candidates for such use. From knowledge of the practical limits of the restricted industrial operations, one can make feasible approximations, find improved performances, and hopefully develop the design rules 2-3 further. The minimum lost work requirement for a process, may serve the industrial as well as the public sector in several ways. The industry can use this yardstick to defend their power needs and

their mode of operation. The public sector may use the yardstick to demand good practice from the industry. The researchers believe that the method of minimization of entropy production has a large, untapped potential in the development of chemical process equipment for energy intensive tasks

### Nomenclature

$F$	Friction constant
$H$	Hamiltonian
$K$	Number of steps in process
$N$	Number of moles [mol]
$P$	Gas pressure [bar]
$P_1, P_2$	Initial/final gas pressure [bar]
$P_{\text{ext}}$	External pressure [bar]
$Q$	Heat [J]
$R$	Gas constant [J / K mol]
$S$	Entropy [J / K]
$dS_{\text{irr}}/dt$	Total entropy production [J / K]
$T_0$	Gas/surroundings temperature [K]
$T$	Time [s]
$U$	Internal energy [J]
$V$	Volume [m <sup>3</sup> ]
$W$	Work [J]
$w_{\text{id}}$	Ideal work [J]
$w_{\text{lost}}$	Lost work [J]

### Greek letters

$\lambda$	Multiplier function
$\theta$	Process duration [s]

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