An Indicator to Evaluate the Thermodynamic Maturity of Industrial Process Units in Industrial Ecology

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Summary

The article suggests a measure to evaluate the thermodynamic maturity of industrial systems at the level of single process units. The measure can be quantified with reasonable confidence on the basis of entropy production as defined by irreversible thermodynamics theory. It quantifies, for one process unit, the distance between its actual state of operation and its state with minimum entropy production or optimum exergy efficiency, when the two states are constrained with a fixed production capacity of the process unit. We suggest that the minimum entropy production state is a mature state, or that processes that operate at this state are mature. We propose to call the measure “the thermodynamic maturity indicator” ($\pi$), and we define it as the ratio between the minimum entropy production and the actual entropy production. We calculated $\pi$ on the basis of literature data for some examples of industrial process units in the chemical and process industry (i.e., heat exchanger, chemical reactor, distillation column, and paper drying machine). The proposed thermodynamic measure should be of interest for industrial ecology because it emerges from the entropy production rate, a dynamic function that can be optimized and used to understand the thermodynamic limit to improving the exergy efficiency of industrial processes. Although not a tool for replacing one process with another or comparing one technology to another, $\pi$ may be used to assess actual operation states of single process units in industrial ecology.
**Introduction**

Attempts have been made throughout scientific history to find universal principles that would determine the development of a system. A certain success was achieved in optics (the Fermat’s principle) and mechanics (the principle of least action). The minimum entropy production principle (or the Prigogine theorem) was introduced in 1931 and used to describe irreversible, dissipative processes (Onsager 1931a, b; Prigogine 1947, 1955, 1961). In the last 2 decades, energy efficiency problems in design and optimization of thermal and power systems (i.e., heat exchangers, power plants) have been solved via the entropy generation minimization method (Bejan 1996a, b; Bejan et al. 1996). Chemical and separation systems have also been studied (Tondeur and Kvaalen 1987; Tondeur 1990; Johannessen and Kjelstrup 2004; de Koeijer et al. 2004; Røsjorde and Kjelstrup 2005; Kjelstrup et al. 2006; Zvolinschi et al. 2006). The entropy concept was first proposed as a measure in industrial ecology by Lowenthal and Kastenberg (1998). Their perspective was intended to assign an entropy value to stages in a product’s life cycle, a value that could be seen as a cost, like a negative monetary cost or an externality of the product (Lowenthal and Kastenberg 1998). Other authors proposed entropy production as a thermodynamic measure for resource use (Gößling et al. 2001; von Gleich et al. 2007), waste generation (Baumgärtner and de Swaan Arons 2003), and the ultimate ecotoxicity of economic systems (Ayres and Martinás 1995). As a continuation of these efforts, this article introduces an additional measure to the entropy efficiency in an effort to improve the thermodynamic performance of industrial process units. We name this measure the *thermodynamic maturity indicator* ($\pi$). It is defined below as the ratio between minimum and actual total entropy production for a given production capacity in a given system boundary of one process unit. To calculate $\pi$ it is not necessary to define the environmental reference state as in the exergy efficiency calculations and exergy accounting (Ayres and Masini 2004). This may be seen as an advantage. More information about the process is needed to calculate the thermodynamic maturity indicator than to calculate the exergy efficiency, however.

Our emphasis is also on the second-law thermodynamic efficiency as given by the exergy efficiency and, more precisely, on a replacement of the maximum limit of 100%. This article introduces an additional measure to the exergy efficiency in an effort to improve the thermodynamic performance of industrial process units. We name this measure the *thermodynamic maturity indicator* ($\pi$). It is defined below as the ratio between minimum and actual total entropy production for a given production capacity in a given system boundary of one process unit. To calculate $\pi$ it is not necessary to define the environmental reference state as in the exergy efficiency calculations and exergy accounting (Ayres and Masini 2004). This may be seen as an advantage. More information about the process is needed to calculate the thermodynamic maturity indicator than to calculate the exergy efficiency, however.

To illustrate and assess the thermodynamic maturity indicator, we use process units such as heat exchangers, chemical reactors, distillation columns, and a paper-drying machine. Literature data are available on these units (de Koeijer et al. 2004; Johannessen and Kjelstrup 2004; Røsjorde et al. 2004; Zvolinschi et al. 2006). By a process unit we mean a device or piece of equipment that processes, assembles, applies, blends, or otherwise uses material inputs to produce or store an intermediate or a completed product. In our opinion, the performance of single process units should be of interest for industrial ecology because from this level emerges the resource exergy loss and corresponding emissions of all industrial activities.

We first give a theoretical background of exergy and irreversible thermodynamics. We then
define and illustrate the thermodynamic maturity indicator for the cases mentioned above. Finally, we address the meaning of the indicator.

**Theoretical Background**

**The Exergy Balance and Exergy Efficiency**

Research efforts in industrial ecology are related to accounting, analyzing, and optimizing the use of resources in industrial processes or systems. Wall (1977, 1988) has proposed a thermodynamic concept for accounting any type of resource stocks and flows in society and industry. Wall’s proposal was based on the measure called *l’énergie utilisable* by French academicians (Carnot, Navier, and Poncelet) in the 18th century, *availability* by American scientists, and exergy by researchers in Europe. The exergy balance was then proposed as a method to evaluate the use and transformation of resources in any engineering system. The following equation represents the exergy balance of a system:

$$E_{\text{in}} = E_{\text{out}} + E_{\text{loss}}$$

where $E_{\text{in}}$ is the input exergy of the resources of the system; $E_{\text{out}}$ is the output exergy of the products, by-products, and wastes; and $E_{\text{loss}}$ is the total exergy lost or dissipated as dictated by the second law of thermodynamics.

The method of exergy analysis was developed in response to the request to determine the maximum thermodynamic potential for work and for lost work or exergy loss in our engineering systems. This is generally measured with the exergy efficiency ($\varepsilon$), as given by

$$\varepsilon = \frac{E_{\text{out}}}{E_{\text{in}}} = \frac{E_{\text{in}} - E_{\text{loss}}}{E_{\text{in}}}$$

One can determine the value of the exergy loss ($E_{\text{loss}}$) without using the exergy balance, equation (1). This is possible if the corresponding total entropy production is known. The Gouy–Stodola’s theorem is here useful (Gouy 1889; Stodola 1898), because it expresses the relation between the total exergy loss and the total entropy production as

$$E_{\text{loss}} = T_0(dS/dt)_{\text{irr}}$$

where $E_{\text{loss}}$ is the total exergy loss in the system—the same quantity as in equation (1), $T_0$ is the standard value of the environmental temperature ($T_0 = 298$ K), and $(dS/dt)_{\text{irr}}$ is the total entropy production.

Using equation (3) in equations (1) and (2), one can have another formulation of the exergy balance and the exergy efficiency, respectively:

$$E_{\text{in}} = E_{\text{out}} + T_0(dS/dt)_{\text{irr}}$$

and

$$\varepsilon = \frac{E_{\text{in}} - T_0(dS/dt)_{\text{irr}}}{E_{\text{in}}} = 1 - \frac{T_0(dS/dt)_{\text{irr}}}{E_{\text{in}}}$$

Equation (4) tells us that the higher the rate of total entropy production is, the higher is the amount of input resource exergy required to sustain the same output exergy from the system. This was stated by Tolman and Fine in 1948. Their work supplemented the earlier work of Onsager (1931a, 1931b), and of Prigogine (1947, 1955, 1961) on the entropy production in stationary state systems.

As we can see from equation (5), knowledge of entropy production has the advantage that the exergy efficiency can be calculated without information about the outlets of a system (i.e., by-products, wastes); only information about the main product must be known. This may be seen as an advantage, as the information about chemical compositions of many industrial outlets is not easily available (this information is needed to compute the chemical exergy). The information about the entropy production of the system requires more local information about every process in that system, however. As we show, this information can be obtained from irreversible thermodynamics, a discipline of science that relates the thermodynamic forces and fluxes with the local entropy production, dating back to Onsager (1931).

**The Local and Total Entropy Production**

A process unit in its stationary operating state can be characterized by its total entropy production, $(dS/dt)_{\text{irr}}$. Any change of operating conditions determines a new state for the process and a new value for the total entropy production. The total entropy production can be calculated either as an entropy balance applied to the incoming ($J_{\text{in}}$) and outgoing ($J_{\text{out}}$) entropy flows throughout the cross area of the system (A) or through integration of the local entropy production.
production rate \((\sigma)\) over the volume \((V)\) of the system; see equation (6).

\[
\frac{dS}{dt}_{\text{irr}} = A (J_{s,\text{out}} - J_{\text{s, in}}) = \int_V \sigma dV > 0 \quad (6)
\]

The entropy balance, the first equality in equation (6), gives a black box description of the process unit, whereas the integral of the local entropy production, the latter equality in equation (6), gives more information. The local entropy production contains information on all transport phenomena that take place within a system boundary of a process unit. One can gain information on fluxes and forces along the unit in the actual state of operation and in the state of minimum entropy production. The disadvantage is that more information is needed on the process. We assume here that such information is available.

The total entropy production can be independently calculated, via either the exergy balance in combination with the Gouy–Stodola theorem (equations [1] and [2]), or the entropy balance (equation [6]), and/or the integral of the local entropy production (equation [6]). The answer must be the same and be a positive value. Each of these methods for calculating the total entropy production has its own advantages and range of applicability. For example, it is possible to check for the consistency of the mathematical models that are used to model and simulate processes of a single process unit. This is done by checking whether the local entropy production is positive in all points of that unit.

Irreversible thermodynamics (Onsager 1931a, b; de Groot and Mazur 1962; Førland et al. 2001) defines the function of the local entropy production by equation (7),

\[
\sigma = \sum_i J_i X_i \quad (7)
\]

Here, \(J_i\) is the local flux of any entity \(i\) considered to model the process, and \(X_i\) is the conjugate thermodynamic driving force. Each flux \((J_i)\) is a local linear combination of all thermodynamic driving forces by means of the phenomenological coefficients \((L_{ij})\):

\[
J_i = \sum_{i,j} L_{ij} X_j \quad (8)
\]

For example, for a system with two fluxes and two thermodynamic driving forces, the following relations can be written to characterize the process:

\[
J_1 = L_{11} X_1 + L_{12} X_2 \\
J_2 = L_{21} X_1 + L_{22} X_2
\]

Onsager’s (1931a, 1931b) reciprocal relation, \(L_{ij} = L_{ji}\), gives a relationship between the phenomenological coefficients. Defining the total entropy production from the local entropy production rather than from the entropy balance gives us more information about the local dissipation of exergy. Therefore, it gives more insight into how exergy loss or entropy production develops within the boundary of the system. The calculation of the total entropy production from the integral of local entropy production is often difficult, however, because of our limited knowledge of the phenomenological coefficients, \(L_{ij}\).

To give an example of the local entropy production, we give the expression for a plug flow reactor (Nummedal et al. 2005). Normally in a reactor, there are three phenomena that produce entropy: the reactions that take place, the heat transfer between the reaction mixture and the cooling/heating agent, and the pressure drop due to the material flows throughout the reactor. The local entropy production per unit area of the reactor \((\sigma\) in \(\text{W/K/m}\)), becomes (Nummedal et al. 2005)

\[
\sigma = A \rho \left[ \sum_j \left( -\frac{\Delta G_j}{T} \right) \right] + \pi DJ_q \Delta \left( \frac{1}{T} \right) \\
+ A \nu \left( -\frac{1}{T} \frac{dP}{dz} \right) \quad (10)
\]

where \(A\) is the cross-sectional area of the reactor \((\text{in m}^2)\), \(\rho\) is the catalyst density \((\text{in kg catalyst/m}^3\text{ reactor})\), \(D\) is the reactor diameter \((\text{in m})\), \(\Delta G_j\) is the Gibbs energy of reaction \(j\) \((\text{in J/mol})\), and \(T\) is the temperature of the volume element \((\text{in K})\).

Equation (10) was used to study the total and local entropy production in a tubular steam reformer (Nummedal et al. 2005). It contains products of fluxes and their conjugate thermodynamic forces. The first term is due to all reactions in the reactor; the flux is the reaction rate of reaction \(j\), \(r_j\), and the chemical force is \(-\Delta G_j/T\). The second term is due to heat transfer; the flux
is the measurable heat flux, $J_q$, and the thermal force is $\Delta(1/T)$ across the reactor walls. The last term is due to the pressure drop; the flux is the fluid velocity, $v$, and the thermodynamic force is $-(1/T)(dP/dz)$, where $P$ is the total pressure of reaction mixture and $z$ is the length of the reactor tubes.

**Equipartition as a Feature of the State of Minimum Entropy Production**

Work over the last 20 years on process units with a prescribed production has shown that the one important feature of the state of minimum entropy production is its *equipartition* (Tondeur and Kvaalen 1987; Tondeur 1990; Andresen and Gordon 1992; S sauar et al. 1996; Sauar et al. 1997; Bedeaux et al. 1999; Kjelstrup et al. 1999; Kjelstrup et al. 2000; Nummedal and Kjelstrup 2001; Sauar et al. 2001; Johannessen et al. 2002; de Koeijer et al. 2004; Johannessen and Kjelstrup 2004; Johannessen and Kjelstrup 2005; Zvolinschi et al. 2006). Tondeur and Kvaalen (1987) proposed that the total entropy produced in a contracting or separating device (e.g., heat exchanger, distillation column) is minimal when the local rate of local entropy production is uniformly distributed (equipartitioned) along the state space and/or time variables. This theorem was called *equipartition of entropy production* (EoEP), and it was demonstrated for globally linear flux–force relations obeying Onsager’s reciprocal relations (Tondeur and Kvaalen 1987). In a further study of applications of the EoEP theorem, Tondeur (1990, 185) argued that “minimal dissipation for a specified duty corresponds to equipartition of flux, driving force and entropy production along the time and space variables of the process.” This statement was linked to the flow configuration in heat exchangers, sorption and distillation columns, and other separation devices. Using some assumptions, Tondeur also made a link between equipartition of entropy production and economic optimization. The optimal size distribution in an economic sense is that in which the cost of energy quality degradation in any element is equal to the amortized proportional investment cost in that element. In more popular terms, EoEP means that “the heat transfer area should be concentrated in that region of the heat exchanger where heat transfer (regardless of direction) is most intense” (Bejan 1982, 149). Other authors have found related theorems in different ways and for different conditions (Andresen and Gordon 1992).

The work by Sauar and colleagues (1996) gave the theorem of *equipartition of forces* (EoF), which states that a production system in the state of minimum entropy production can be characterized by constant thermodynamic driving forces. The theorem was proven via irreversible thermodynamics for stationary processes where all transfer paths were parallel. No conservation equations were considered in the proof. The EoF theorem was proposed as a design criterion for heat exchangers (Nummedal and Kjelstrup 2001), chemical reactors (Sauar et al. 1997; Bedeaux et al. 1999; Kjelstrup et al. 1999; Kjelstrup et al. 2000), and distillation columns (Sauar et al. 2001). Vulnerability of the EoF theorem appeared when difficulties were met in obtaining the minimum entropy production rate in a reactor system (Kjelstrup et al. 2000) and in obeying conservation equations in a diabatic distillation (Sauar et al. 1997).

A more convincing formulation of the optimization problem, to find minimum entropy production for a process unit with constant production, was given by Johannessen and Kjelstrup (2005) using optimal control theory (Bryson and Ho 1975). This theory emphasizes the number of control variables that can be used to change the system, versus the number of state variables in the system itself. Conservation equations and other constraints can be properly taken into account. Johannessen and Kjelstrup (2005) revealed the nature of the state of minimum entropy production when there are fewer control variables than state variables in the system. Taking the plug flow reactor as an example, they found that the operating path with minimum entropy production followed a highway in state space, to a larger or smaller degree, depending on the systems’ boundary conditions. The following chemical reactors were investigated: sulfur dioxide oxidation, ammonia synthesis, steam reforming, methanol synthesis, and propane dehydrogenation. The results obtained were concluded as a hypothesis,
which stated that the “EoEP, but also EoF, is a good approximation to the state of minimum entropy production in the parts of an optimally controlled system that have sufficient freedom” (Johannessen and Kjelstrup 2005, 3358).

Knowledge of the nature of the state of minimum entropy production is thus accumulating, and industrial ecology might take advantage of this. It seems that a thermodynamically efficient system should possess certain characteristics; it should follow a highway in state space for energy-efficient operation, operate with equipartition of entropy production, or have relatively constant driving forces. Technological systems that incorporate processes operating at minimum entropy production states can be called mature. In keeping with Tondeur (1990), this may also, under favorable conditions, lead to economic advantages.

Therefore, we propose as a measure for thermodynamic maturity the state in which the process operates with minimum entropy production, with the aim of producing the product $J$. This state of minimum entropy production has the realistic highest exergy efficiency that is possible to obtain for this particular production (of $J$). The indicator has as its limit value unity (or 100%), as it can be well achieved for a finite production.

### Defining the Thermodynamic Maturity Indicator

So far, exergy efficiency has been used in industrial ecology as an indicator to evaluate the thermodynamic performance of industrial processes and systems. Through the exergy efficiency concept, many industrial processes have been improved. The upper limit of the exergy efficiency of any process in steady-state operation of one (or 100%) is unrealistic to compare with, however, as it is an unphysical limit attainable only by reversible processes, which has zero entropy production. In our opinion, it may be useful to use another limit to show how far a process in a certain state of operation is from the thermodynamically ideal state, namely the state of minimum entropy production.

On the basis of this background, we propose a measure that indicates how far a process is operating from its state of minimum entropy production. We name this measure the thermodynamic maturity indicator ($\pi$). The $\pi$ is defined as the ratio of the minimum entropy production to the actual entropy production in a process, which takes place in the same system boundary and with the same operating conditions, as

$$\pi = \frac{(dS/dt)_{\text{min}}}{(dS/dt)_{\text{actual}}} \quad (11)$$

The indicator uses the result of the following constrained optimization:

$$\text{Find } (dS/dt)_{\text{min}} \text{ for a given } J \quad (12)$$

where $(dS/dt)_{\text{min}}$ is the minimum total entropy production. A given sizable production capacity $J$ must occur in a finite time for the industrial process to be of practical interest.

The minimum total entropy production for the constrained production capacity of the process unit is thus a finite and realistic reference for the actual value. This proposal for a new indicator therefore introduces a new and more realistic limit than is attained by the maximum exergy efficiency.

The indicator shows how far a particular process is from its thermodynamic maturity level. We suggest here that a process with a given production capacity is mature if it is operated with minimum entropy production. This state of operation has the lowest possible rate of resource exergy dissipation, and therefore it contributes to a longer preservation of natural resource reservoirs (e.g., the nonrenewable fossil fuels).

When $\pi$ is low, it means that the process is wasting resource exergy unnecessarily. Such a conclusion cannot be reached on the basis of information on exergy efficiency ($\epsilon$) alone. A low $\pi$ means that there is a real potential for thermodynamic improvement. The indicator approaches unity when the process is operated in the state of minimum entropy production. The process is then mature, and nothing can be done to improve this particular process. Different patterns of operation for a process with the same production capacity rate can be evaluated and compared by their thermodynamic maturity indicator ($\pi$), as well as by their exergy efficiency ($\epsilon$). By changing the number of system variables or system boundaries, we change the unit, and a new reference must be established and optimized.
A mathematical relation can be obtained between the exergy efficiency, equation (5), and the thermodynamic maturity indicator, equation (11), if the amount of the input exergy of resources is kept constant in the two states of the actual and minimum entropy production rate ($E_{\text{in}}^{\text{actual}} = E_{\text{in}}^{\text{optim}} = E_{\text{in}}^{\text{min}}$). Using equation (11) and the relations of the exergy efficiency written for the actual state and the optimum state of operation in a system, namely

$$
\varepsilon_{\text{actual}} = 1 - \frac{T_0 (dS/dt)^{\text{actual}}_{\text{irr}}}{E_{\text{in}}^{\text{actual}}}
$$

(13)

and

$$
\varepsilon_{\text{optim}} = 1 - \frac{T_0 (dS/dt)^{\text{min}}_{\text{irr}}}{E_{\text{in}}^{\text{optim}}}
$$

(14)

one can find the following correlation between the thermodynamic maturity indicator and the exergy efficiency

$$
\pi = \frac{1 - \varepsilon_{\text{optim}}}{1 - \varepsilon_{\text{actual}}}
$$

(15)

which is equivalent to

$$
\varepsilon_{\text{optim}} = 1 - \pi (1 - \varepsilon_{\text{actual}})
$$

(16)

From equation (15), the limit of 1 for $\pi$ can be obtained when the $\varepsilon_{\text{actual}}$ equals $\varepsilon_{\text{optim}}$. In the case that $\pi$ is unity, the actual path of operation for the process unit is the path with minimum total entropy production. Because the value of $\varepsilon_{\text{optim}}$ cannot be unity for any real process, the lower limit of $\pi$ differs from zero. Note that $\varepsilon_{\text{optim}}$ is not the same as the maximum exergy efficiency, which is unity (or 100%).

## Calculations

We calculate below $\pi$ for several process units, where data can be found in the literature. These are the processes of heat exchange in two heat exchangers, catalytic oxidation of sulfur dioxide ($\text{SO}_2$) in two reactors, two-component separation in an adiabatic distillation column, and a paper-drying process in a steam-heated multicylinder machine. The data for the calculations were obtained from Nummedal and Kjelstrup (2001), de Koeijer and colleagues (2004), Johannessen and Kjelstrup (2004), and Zvolinschi and colleagues (2006), respectively.

The results of the calculations are given in table 1. The table lists the actual entropy production rate, $(dS/dt)^{\text{actual}}_{\text{irr}}$, and the minimum entropy production rate, $(dS/dt)^{\text{min}}_{\text{irr}}$, for the selected processes, as well as their thermodynamic maturity indicators.

The heat exchange processes were calculated because they are simplest to understand. The results are given in the two first lines of the table. Both exchangers were geometrically identical and exchanged the same heat (60 kW). The following conditions were also the same: the heat transfer coefficient (340 W/m$^2$/K), the mass flow of hot and cold streams (1 and 0.28 kg/s, respectively), and the inlet and outlet temperatures of the hot stream (400 and 370 K, respectively). The thermodynamic maturity indicators ($\pi$) were 0.8 and 0.98 in the cocurrent and countercurrent heat exchangers, respectively. The first case had a low maturity indicator, indicating that an improvement potential exists. In the second case, the EoF theorem was approximately fulfilled at the outset, and the thermodynamic maturity indicator was high, almost unity. We conclude that there is not much to do to improve the counter-current heat exchanger from the way it is operated now. The heat exchange process in a countercurrent heat exchanger is a mature process, as is already well known by engineers.

The thermodynamic maturity indicators for two chemical reactors for $\text{SO}_2$ oxidation are shown in the third and fourth lines of table 1. One process is well established in industry, having been used since the 1950s, whereas the other is newer. De Koeijer and colleagues (2004) calculated the total entropy production for the first reactor from the entropy balance over the system that comprised a four-bed reactor and five intermediate heat exchangers (figure 1). The system was an industrial-scale reactor, and the total entropy production was minimized by constraints on the inlet and outlet parameters of the reaction mixture, with exception of the outlet reaction mixture pressure. A savings of 16.7% in the total entropy production was reported (de Koeijer et al. 2004); the reduction of total entropy production was from 4.7 kW/K in the reference system to 4.1 kW/K in the second-law optimal one, for a total heat transfer area of 4,000 m$^2$ and an input molar flow rate of 480 mol/s. This
Table 1 The actual and minimum entropy production and the thermodynamic maturity indicator ($\pi$) of some processes/process units.

<table>
<thead>
<tr>
<th>Process \ process unit</th>
<th>$(dS/dt)_{\text{actual}}$</th>
<th>$(dS/dt)_{\text{min}}$</th>
<th>$\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat exchange in:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-current HE</td>
<td>0.48</td>
<td>0.38</td>
<td>0.80</td>
</tr>
<tr>
<td>Counter-current HE</td>
<td>0.48</td>
<td>0.47</td>
<td>0.98</td>
</tr>
<tr>
<td>SO$_2$ oxidation in:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Four-bed reactor$^c$</td>
<td>122.4</td>
<td>106.7</td>
<td>0.87</td>
</tr>
<tr>
<td>Tubular reactor$^d$</td>
<td>60.3</td>
<td>53.8</td>
<td>0.89</td>
</tr>
<tr>
<td>Separation in:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adiabatic DC$^e$</td>
<td>8.1</td>
<td>7.7</td>
<td>0.95</td>
</tr>
<tr>
<td>HIDiC$^f$</td>
<td>37.5</td>
<td>24.6</td>
<td>0.65</td>
</tr>
<tr>
<td>Paper drying in:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional PM$^g$</td>
<td>2400</td>
<td>2300</td>
<td>0.96</td>
</tr>
</tbody>
</table>

$^a$FU is functional unit; and $=\text{actual and minimum entropy production, respectively (in J/K per FU$^a$).}$

$^b$FU is kJ heat duty in heat exchanger (HE) (Nummedal and Kjelstrup 2001).

$^c$FU is one mole of SO$_2$ produced in reactor (de Koeijer et al. 2004).

$^d$FU is one mole of SO$_2$ produced in reactor (Johannessen and Kjelstrup 2004).

$^e$FU is one mole of a propylene-propane mixture (50:50 vol.%) separated in distillation column (DC) (Røsjorde and Kjelstrup 2005).

$^f$FU is one mole of benzene-toluene mixture (50:50 vol%), separated in heat-integrated distillation column (HIDiC) (Røsjorde et al. 2004).

$^g$FU is one kg of dry paper produced in paper machine (Zvolinschi et al. 2006).

A savings was possible without a change in the reactor design, or the total area available for heat exchange. The thermodynamic maturity indicator was 0.87 for the reactor, a relatively low number, considering that the reactor has been in use since the 1950s. The absolute value of the minimum entropy production of this reactor was high, however (4.7 kW/K).

Johannessen and Kjelstrup (2004) studied the minimum entropy production for the sulfur dioxide oxidation in a plug flow reactor model (figure 2). The results for this reactor are given in the fourth line of table 1. Johannessen and Kjelstrup (2005) found that the second-law optimal tubular reactor was characterized by a reaction mode and a heat transfer mode. Only some parts of the reactor had a constant local entropy production. This may explain its low thermodynamic maturity indicator, 0.89. The number depends on the state of operation. This is illustrated in figure 3, which shows the state of minimum entropy production in terms of the temperature of reaction mixture and of cooling agent in two cases. The two actual systems are labeled reference in the figure. For the first case, a savings of 10.4% in the total entropy production was obtained, whereas in the latter case a savings of 24.7% was obtained (with a corresponding reduction of the length of the reactor from 6.1 m to 5.2 m). The first case is listed in table 1. The temperature of cooling agent in the shell side of
the reactor tubes was the control variable in the minimization. A hot spot, typical to an exothermic reactor, is observed at the inlet. One can see from the figure that a change in the premise for the optimization—for instance, a change in the number of variables—gives different results for the minimum entropy production and thus for the $\pi$ values.

The thermodynamic maturity indicator ($\pi = 0.89$) of the tubular reactor was only slightly higher than that of the four-bed reactor ($\pi = 0.87$). From the indicators alone, it is thus not clear that one reactor is significantly better than the other. This becomes clear when we consider the total entropy production, however. It is much smaller for the tubular reactor than for the fixed-bed reactor, both of which have the same functional unit. This shows that the thermodynamic maturity indicator alone should not be used to compare different processes or technologies. The first reactor is clearly less good than the second, with respect to the utilization rate of exergy resources, and this is seen from the absolute numbers, not from $\pi$.

For an adiabatic distillation column separating a propylene–propane mixture, Røsjorde and colleagues (2004) found a total entropy production of 8.1 J/K per 1 mol propylene–propane mixture. The optimal system, a diabatic column, gave a total entropy production of 7.7 J/K/mol. A value of 0.95 was calculated for the thermodynamic maturity indicator (see line 5 in table 1). This particular separation of a propylene–propane mixture by means of adiabatic distillation is thus close to being mature, because it has a high number of stages (see below). Industrial-scale distillation columns are mostly adiabatic columns, and they are often exergy costly. The adiabatic column has only two heat exchangers: the reboiler and the condenser. The second-law optimal column, conversely, allows for heat exchange on all trays (Fonyo 1974). It has been approximately adopted in the diabatic column (de Koeijer et al. 2002), in the heat-pump-assisted distillation (Null 1976), and in the heat-integrated distillation column (de Koeijer et al. 2002; Røsjorde et al. 2004), with large amounts of exergy saved.

The distillation column separating propylene–propane had a high value of the thermodynamic maturity indicator ($\pi = 0.95$), whereas the process separating benzene–toluene had a low value ($\pi = 0.65$; see table 1). Both mixtures were ideal, but the number of stages involved in the operation differed. The column with the lowest number of stages had the lowest indicator, as expected. Figure 4 shows that a large number of stages brought the operating line closer to the equilibrium line and to a smaller total entropy production.

The standard way to characterize a distillation column is by means of a McCabe–Thiele diagram (Linnhoff and Smith 1979). Figure 4 shows the
McCabe–Thiele diagrams for adiabatic and diabatic distillation columns for a binary mixture. The operating lines in the adiabatic columns are straight because the vapor and liquid flows are constant from tray to tray. The heat exchangers integrated on each tray of the diabatic distillation columns enable the operating lines to be curved and turn to approach the equilibrium line of operation. As a consequence, the total entropy production decreases, and the local entropy production along the column becomes more constant.

Finally, the thermodynamic maturity indicator was calculated for a paper-drying machine (see the bottom line in table 1). The total entropy production was calculated and minimized for a constant production of paper in a conventional paper-drying machine (Zvolinschi et al. 2006). A savings of 3% (from 15.5 to 15 W/K) in the total entropy production was reported for a fixed-inlet air composition (0.026 kg H₂O/kg dry-air). The value of the thermodynamic maturity indicator in the table refers to this case. The high value (0.96) shows that there is not much potential to improve the process by changing inlet steam temperatures in steam-heated cylinders while keeping the same inlet air composition.

If we allow the inlet air moisture content to increase fivefold, the total entropy production can be drastically reduced, by as much as 35% (from 15.5 to 10 kW/K). Clearly, a second-law optimal paper-drying machine should preferentially be operated with inlet air conditions as close as possible to the saturation point of the drying air at every location near the paper surface. This may not be feasible in practice, however.

From table 1, we see that the absolute value of total entropy production per kilogram paper produced was several orders of magnitude larger than that found in the other processes. Thus, a very small technical improvement in the paper-drying machine may have an important impact on the depletion rate of exergy resources. The thermodynamic maturity indicator for the given inlet condition was high (π = 0.96), but a small improvement may still give a large exergy savings. If the inlet air composition is allowed to change, even larger improvements can be achieved. Again, we see that the absolute value of the total entropy production is important, not only π.

Discussion

The examples above have shown the strengths and the limitations of the thermodynamic maturity indicator, as it is defined in this article. The indicator is able to assess in a realistic way the operation of a given process unit. For instance, a direct indication was given of how to operate a heat exchanger: countercurrent, not cocurrent. The first operates closer to equipartition of entropy production and with a higher value of π. The indicator is a realistic measure, because it compares the actual process to an ideal version of itself (its state of minimum entropy production), not to an unrealistic state, as that of the reversible state of operation. An engineer as well as a layman may thus know the thermodynamic
improvement potential of a particular process unit, by knowing the thermodynamic maturity indicator.

The rate of dissipation of exergy resources is also a form of environmental damage. Diminishing the resource dissipation rate by operating at the state of minimum entropy production may reduce the environmental damage of that operation. As a consequence, the (exergy) emissions per unit of time, if not in total, can be reduced. We thus advocate a slower use of resources, with a rate of consumption that is real. The reversible limit for production cannot be used in this manner.

We cannot conclude from the thermodynamic maturity indicator, however, that we should prefer one process to an alternative one or one technology to an alternative one. For instance, almost the same thermodynamic maturity indicator was obtained for the two chemical reactors in table 1. We saw that information about the absolute values of the losses was necessary to know which reactor to prefer from an exergy efficiency point of view. A high value for the thermodynamic maturity indicator also does not necessarily indicate that improving the process is meaningless. The case of paper machine drying showed that. This process is very exergy intensive, so even a small improvement may make a large reduction in exergy loss and thus large savings in exergy resources.

In spite of its limitations, the indicator has some interesting properties. Researchers such as Ayres and colleagues (1998), Kuemmel and colleagues (1997), and von Spakovski and colleagues (1991) have suggested that a system can best be related to its environment by means of the exergy function. The exergy measures directly the departure of the state of a system from that of the environment. The departure is zero only when the system is in equilibrium with its environment. Such an equilibrium is, however, never available in a real process. A state of minimum entropy production is, as we have already discussed, obtainable and directly connected to the actual operating state of the process. The thermodynamic maturity indicator has a reference state that is independent of the environment. There is no need to define an environmental state with this reference, and an absolute comparison can be made on the process unit’s thermodynamic performance between different localities. Together with the exergy efficiency, the thermodynamic maturity indicator can be used by industry to set thermodynamic criteria for second-law optimal operations of industrial processes. It can also be used to defend chosen designs for the same process task in the public sector. The next step is to apply the thermodynamic maturity indicator for connected/integrated process units (see, e.g., the study by Røsjorde and his colleagues [2007] to minimize the entropy production of 21 connected process units). The application of $\pi$ also may be extended to higher levels of integrated and complex industrial processes through the functional unit employed in a life cycle assessment framework. More work is needed to bring it to an aggregated level.

**Conclusions**

We have proposed using a thermodynamic maturity indicator to evaluate the performance of process units. The indicator brings knowledge from irreversible thermodynamics and the state of minimum entropy production to a level of interest for industrial ecology. It introduces the state of (constrained) minimum entropy production in assessing single process units. This state is realizable. The indicator is a pure thermodynamic indicator, which does not depend on the environment. It indicates a way in which we should proceed in setting up industrial processes, possibly by paying more attention to equipartition theorems for process units. The $\pi$ may give an argument for industrial ecology to implement into industrial practice (operation and design) the state of minimum entropy production as a possible way to reduce the exergy loss in energy-intensive systems. It is only one of several indicators for evaluating optimal operation and/or design, however.

The thermodynamic maturity indicator cannot be used to argue, on thermodynamic grounds, that one process should be replaced by another. For this, we need to compare the total entropy production of the competing technologies, among other things.
Acknowledgements

We would like to thank the Research Council of Norway for funding this research.

References


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