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Review

Efficiency in the process industry: Three thermodynamic tools for better resource use

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ABSTRACT

In a world where resources are limited and their use will necessarily have an impact, efficient handling of resources becomes essential. This review concerns three thermodynamic tools that can be systematically used to evaluate and improve resource use. The tools are related to the second law of thermodynamics, which sets a general framework for all conversion processes, including food processing.

We address the benefits of using exergy analysis to map the losses of energy quality in a process. This can be done at every scale, from a nation scale to a process unit, and the results of the analysis can be used at different levels of decision making processes, by policy makers, plant managers, scientists or engineers. Moreover, knowledge on coupling between transport processes can be used to drive processes using driving forces other than the conventional ones. This would allow us to recover some of the resource potential which is currently wasted (e.g. process waste heat). Finally, inspiration for efficient design can be found in nature; two examples of nature-inspired chemical engineering (NICE) design are reviewed and used to encourage a development in this direction.

1. Introduction

Urgent measures seem now necessary to mitigate the effects of climate changes and meet the targets set by the Paris agreement (Paris Agreement). At the same time, all society sectors are called to contribute to the United Nations' sustainable development goals (Nations, 2015). In this context, systematic tools are available within the framework of thermodynamics to help quantifying and improving resource use. This review focuses on three such systematic tools, which seem to have the unexploited potential to point at the inefficient use of resources. These tools are of a general type and may also benefit the process industry, where the food processing industry is an important part.

Thermodynamic tools are essential, since thermodynamics governs energy and mass conversion in all processes, natural as well as man-made ones. Every process, slow or fast, must obey energy, momentum and mass conservation principles. On the other hand, the rate at which a process takes place and the process efficiency are governed by the second law of thermodynamics. In a fast moving world, where a process cannot be infinitely slow, the second thermodynamic law is fundamental. The three tools that we advocate are all related to the second law.

Before we go into details, we need to establish some concepts and terminology (Section 2). After that, we proceed to present the first tool; exergy analysis (Kotas, 1980; Lior & Zhang, 2007). A large number of works on the topic exists in the literature, but we shall highlight a review (Magnanelli, Berglihn, & Kjelstrup, 2018), and a recent book that makes the connection to the underlying theory of non-equilibrium thermodynamics (Kjelstrup, Bedeaux, Johannessen, & Gross, 2017). This theory, the second tool, brings exergy analysis to a deeper level, by giving an alternative and more detailed expression for the second law. The theory allows us to describe and understand coupling between transport processes. The third and last tool is interdisciplinary; we propose to create optimal operating conditions and designs for processes, by combining a mathematical theory, optimal control theory (Johannessen & Kjelstrup, 2005), with knowledge of performance of natural systems under strain. This last tool can be called nature-inspired chemical engineering (NICE) (Coppens, 2012). It allows us to take different types of constraints into account (e.g. costs or minimum yield). In NICE, one can include structure as a variable to be optimized. This is a relatively new scientific line of thought.

The analysis in the present work is aimed at everybody, in particular at those working in the process industry. We want to show that a

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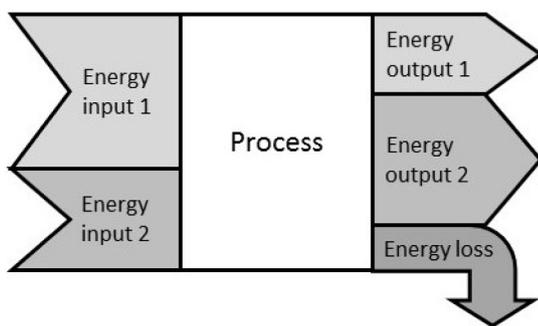


Fig. 1. Energy conservation in a process as illustrated by a Sankey diagram. The sum of the energy inputs to the process (arrows on the left-hand side) equals the sum of the energy outputs and of the energy losses (right-hand side).

large fraction of today's resource potential is lost, and that part of the loss can be harvested by working more systematically. Tools exist that can (1) map resource use today, (2) describe precisely how energy is converted from one form to another, and (3) create new efficient paths of operation based on 1 and 2. As of always, there is no quick fix. Deep knowledge and understanding are needed.

2. The laws of energy conversion

The first law of thermodynamics concerns the conservation of energy. Energy conversion, and conservation in a process, is often illustrated by a Sankey diagram (Fig. 1). A typical industrial process uses work, heat and energy from material resources (reactants) and delivers useful products in the form of work, heat and material products. During the conversion process, some energy is usually dissipated to the surroundings in the form of heat. As an example, Fig. 1 shows a process that uses two energy inputs (left-hand side) to produce two energy outputs, while dissipating some energy to the environment (right-hand side). At stationary state, the sum of the energy streams entering and leaving the process must be the same. The quality of the energy streams is not an issue in this kind of analysis. The diagram pictures a sort of book-keeping of energy flows; all energy entering the process must exit it.

On the other hand, the second law makes a distinction between energy qualities. Different forms of energy are not necessarily equivalent (Kotas, 1980, 2013; Lior & Zhang, 2007). It is well known that work can be completely converted into heat, while the maximum work that a certain amount of heat can be converted to, is limited by the Carnot efficiency (Cengel & Boles). It is therefore, possible to carry out another type of energy accounting, where we quantify energy through the maximum amount of work that can be produced from it. The ability to produce work is called exergy (Kotas, 1980).

A Grassmann diagram is typically used to represent the exergy accounting in a process. Fig. 2 shows the Grassmann diagram for the same process depicted by the Sankey diagram in Fig. 1. When exergy flows are represented instead of energy flows, we first notice that the total exergy flow leaving the process is *always* smaller than that entering the process. This is because no process is reversible, and some friction will always take place: energy conversion from one form to another causes deterioration of energy quality. We can consider a water boiler as an explanatory example. A well insulated water boiler can produce hot water with nearly 100% energy efficiency (e.g. 1 kWh of electricity will be converted to 1 kWh of heat at 80 °C). However, while the energy input to the process is completely converted to a useful energy output with an energy efficiency close to 100%, its quality (i.e. its exergy) has been considerably reduced. Indeed, 1 kWh of electricity, whose exergy is 1 kWh, is converted to an exergy output of 0.17 kWh, when the ambient temperature is 20 °C (Kotas, 1980) (in practice, we all know

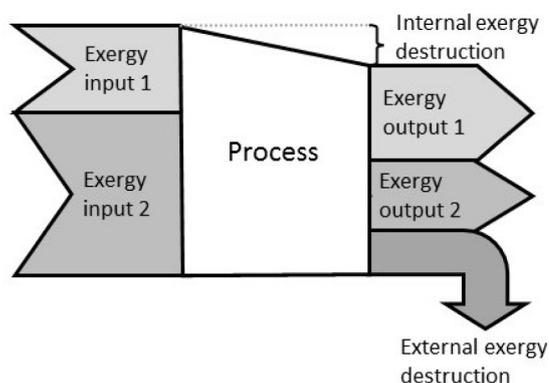


Fig. 2. Exergy balance in a process as illustrated by a Grassmann diagram. The sum of the exergy inputs to the process (arrows on the left-hand side) is larger than the sum of the exergy outputs and of the external energy destruction (right-hand side), due to friction and to loss of energy quality during the process (internal exergy destruction).

that usefulness of 1 kWh heat at 80 °C is rather limited when compared to a 1 kWh of electricity). The remaining part of the exergy input is destroyed during the energy conversion process. From this example, it is clear that a mere book-keeping of energy flows is not sufficient, when we want to look at resource use.

Exergy loss due to friction and conversion of energy to a lower-quality energy form is defined as internal exergy destruction ($\dot{E}_{d,int}$). The internal exergy destruction of a process is related to the entropy produced during the process, dS_{irr}/dt , by the Gouy–Stodola theorem (Gouy, 1889):

$$\dot{E}_{d,int} = T_0 \frac{dS_{irr}}{dt} \quad (1)$$

where T_0 is the temperature of the surrounding ambient.

Similarly to energy, exergy can also be lost by discharging some output streams into the environment (i.e. external exergy destruction, $\dot{E}_{d,ext}$).

By looking at if and how exergy is destroyed in a process, we can get an idea of if the process can be improved and of what measures could be taken to improve it. A recent work in the literature gives an overview of how different exergy-based parameters can be used to quantify process performances (Magnanelli et al., 2018).

3. Three thermodynamic tools

Tool 1: Exergy map to provide overview on losses

In Section 2, we have seen that the Grassmann diagram provides an overview of the resources used in a process in terms of their quality and their overall quality loss during the process. Such information is useful on several levels, from a process component level, to the plant level, to a full sector level. We provide some examples in the following subsections.

Exergy map for the society/sector scale

Policy makers may like to have information on a country scale, to gain overview on how the national resources are spent in each sector, or within a specific sector. An example of such an exergy map, made for Norway, is shown in Fig. 3 (Ertesvåg & Mielnik, 2000). Further examples regarding other countries or specific sectors can be found in the literature (e.g. Brockway, Barrett, Foxon, & Steinberger, 2014; Brockway, Steinberger, Barrett, & Foxon, 2015; Ertesvåg, 2001; Rosen, 1992; Schaeffer & Wirtshafter, 1992; Soundararajan, Ho, & Su, 2014). Fig. 3 shows that Norwegian resources come from waterfalls, oil and gas, mineral ores, forests, and agricultural products. These are being used to produce useful products and services such as paper, metals,

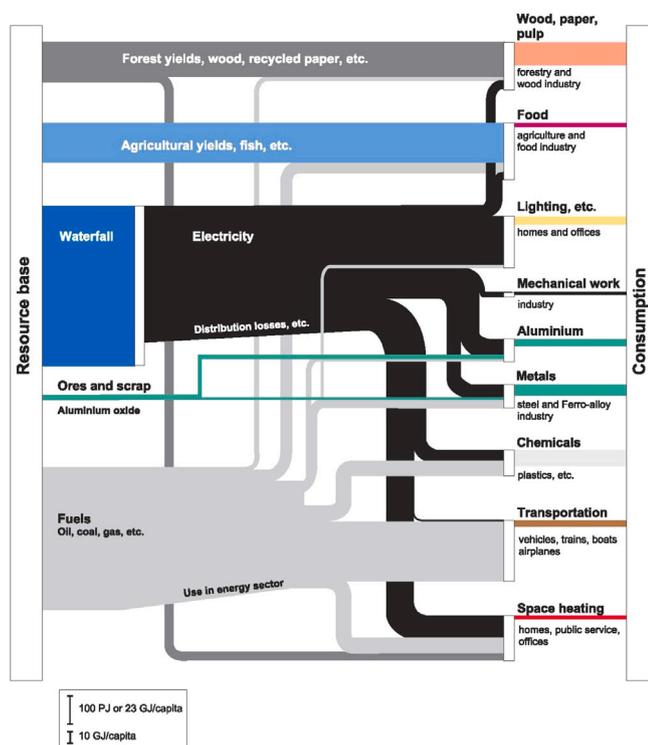


Fig. 3. A Grassmann diagram of the Norwegian economy mapping its exergy flows in 1995 (petroleum export is excluded).

Source: Image taken from Ertesvåg and Mielnik (2000).

chemicals, lighting, transport and space heating. The height of the white bar next to each product indicates the exergy of the resources necessary to produce that specific product. The exergy of the products is represented by the height of the colored lines on the right-hand side of the white bars. By comparing these two, one can get an immediate feeling of how efficiently resources are used in the production of each product. For instance, we can see that large losses are present in the two last sectors (transportation and space heating), as well as in the food sector, making them suitable targets to look at when trying to improve the resource use of the country.

If we look closer to the space heating sector, we see that high-quality energy forms such as electric power (from hydroelectric sources) and fossil fuels are transformed by electric space heaters into a low-quality energy form (i.e. heat at circa 20 °C). The use of heat pumps instead of electric heaters would reduce to one third the exergy destroyed in the process, and would require only one third of the electric power used by electric heaters.

Exergy map at the plant scale

A plant manager may, likewise, need to make decisions on where to focus the future efforts to improve the plant, based on the current state of operation. It might therefore be useful to look at where most of the resource potential is dissipated, as done by many works in the literature (Børset, Kolbeinsen, Tveit, & Kjelstrup, 2015; Cortés & Rivera, 2010; Genc, Genc, & Goksungur, 2017; Madloul, Saidur, Rahim, Islam, & Hossian, 2012; Zvolinschi, 2006). A good example of such an exergy mapping can be found in Ref. Voldsund, Ertesvåg, He, and Kjelstrup (2013), where exergy dissipation is mapped through all process steps of oil and gas processing on a North Sea oil platform. The analysis carried out in that work made it possible to identify the sub-processes responsible for the largest exergy dissipation, as well as to propose measures to decrease exergy destruction and increase resource use.

On the other hand, such an exergy mapping can also be used to decide what alternative to choose, when several options are being considered. Ref. Zvolinschi, Kjelstrup, Bolland, and Kooi (2007) presents an example where a natural gas and a hydrogen fired power plant are compared through mapping of the respective exergy losses throughout the process. In this case, three different exergy-based indicators were used. In their work, Zvolinschi et al. showed how a technical analysis such as exergy analysis can be translated to an aggregated level where it becomes comprehensible and, therefore, useful to decision makers (Zvolinschi et al., 2007).

Mapping the entropy production of a process unit

As we have seen in the previous examples, exergy maps are convenient constructions for the overall scale, for instance, to point at the component of a process where the improving potential is the largest. However, when it comes to finding ways to improve that component, a more detailed analysis of the process is necessary, and local knowledge on the causes of the internal exergy destruction becomes fundamental.

Eq. (1) shows that internal exergy destruction is directly related to the entropy production in a process. It is therefore useful to look at where and how entropy is locally produced within the unit (i.e. entropy production density, σ).

Adiabatic distillation is a widely spread process that requires large amounts of energy (King, 2013). In adiabatic distillation columns, heat is added/withdrawn only at the bottom and top of the column. Therefore, the distillation process takes place without any exchange of heat along the column itself.

On the other hand, in diabatic columns, heat can be added and removed from the column in each tray (Rivero, 2001). Knowledge on the local entropy production of a process and how this relates to transport phenomena within the system, allows us to use the entropy production as the objective function to be minimized in an optimization process. As an example, Røsjorde and Kjelstrup (Røsjorde & Kjelstrup, 2005) found that entropy production can be reduced by 6% with respect to the adiabatic case, by optimally controlling the heat exchanged along a diabatic column with 90 trays. Moreover, the diabatic column produced up to 30% less entropy than the adiabatic one for larger numbers of trays and larger heat exchange surfaces (Røsjorde & Kjelstrup, 2005). An updated review of studies on minimum entropy production in distillation columns can be found in Ref. Kingston, Wilhelmsen, and Kjelstrup (2020).

The distillation column is, however, only an example, and many other optimization works can be found in the literature where entropy production has been minimized in other kinds of process units (Johannessen & Kjelstrup, 2004; Johannessen, Nummedal, & Kjelstrup, 2002; Magnanelli, Johannessen, & Kjelstrup, 2017; Nummedal, Røsjorde, Johannessen, & Kjelstrup, 2005; Wilhelmsen, Johannessen, & Kjelstrup, 2010; Zhang, Chen, Xia, Wang, & Sun, 2018; Zvolinschi, Johannessen, & Kjelstrup, 2006).

Remarks

The examples in the previous paragraphs show that exergy analysis can provide a solid base for decision making. It can not only point at where effort should be focused for a more efficient use of resources, but it can also help comparing alternatives and finding ways to improve a process. This makes it a powerful tool to use in the development of a sustainable process industry. It supports the slogan proposed in a European popular science publication, "Think exergy - not energy" (Brockway et al., 2016).

Tool 2: Nonequilibrium thermodynamics

The entropy production has a precise definition in the theory of nonequilibrium thermodynamics (NET), see e.g. Kjelstrup et al. (2017). The total entropy production of a process is obtained by integrating

the entropy production density (also called local entropy production), σ , over the whole system. All transport phenomena and transformations taking place in a process generate entropy. The local entropy production has, therefore, contributions from all process flows and rates, J_i , and their unique driving forces, X_i :

$$\sigma = \sum_i J_i X_i \geq 0 \quad (2)$$

Nonequilibrium thermodynamics provides not only a definition for the local entropy production, but it also gives an accurate description of the coupling between transport processes (Kjelstrup et al., 2017). Even though this is very often neglected, all transport processes are in principle coupled. This means, for example, that a temperature difference between two sides of a room will not only give rise to a heat flux from the hot side to the cold side, but it will also promote an often neglected mass flux. While this effect might be small at times, the knowledge on coupling between transport processes allows us to use driving forces other than the conventional ones to drive transport processes.

This becomes particularly interesting when we look at the abundance of waste heat everywhere in the process industry. In the European Union, the industry sector generates each year circa 300 TWh of thermal energy which is wasted (Papapetrou, Kosmadakis, Cipollina, La Commare, & Micale, 2018). Waste heat has typically too low quality (i.e. too low temperature) to find application within the process itself, and it is therefore discharged into the surroundings. By turning to nonequilibrium thermodynamics, we might be able to recover some of this wasted potential (e.g. Børset, Wilhelmsen, Kjelstrup, & Burheim, 2017; Keulen et al., 2017; Kristiansen, Barragán, & Kjelstrup, 2019; Magnanelli, Wilhelmsen, Johannessen, & Kjelstrup, 2016). We present some examples in the following paragraphs.

Water purification by thermal osmosis

Selective membranes are often used to purify water. Let us consider a water permeable membrane separating clean water and contaminated water (e.g. sea water). If temperature and total pressure at the two sides are the same, the pure water pressure on the contaminated side will be lower than that on the clean side (due to the presence of contaminants). This will cause pure water to flow from the clean side to the contaminated one, which is opposite of the effect we want to achieve. The most exploited solution nowadays is to use electricity to pressurize the contaminated water, so that its water pressure becomes larger than that on the clean side. The so established partial pressure gradient generates a flux of pure water from the contaminated to the clean side. This is the reverse osmosis principle. While the desired effect is achieved, a large amount of electricity is necessary.

Due to coupling between transport phenomena, we can also use a temperature difference to drive the flow of pure water in the desired direction. This can be achieved by using a special type of membrane that water can get across to only in the form of vapor (i.e. hydrophobic membrane). Fig. 4 shows a schematic representation of the concept. By heating up the contaminated water side, we can create a temperature gradient that will make pure water evaporate at the membrane surface on the contaminated water side (while absorbing heat), get across the membrane in the form of vapor, and condense again at the clean water side (releasing heat) (Keulen et al., 2017). In addition, due to the flow of mass from one side to the other, pressure will build up on the clean water side. The pressurized clean water can, therefore, also be used to drive a turbine and produce electricity.

Gas separation membranes

Membrane technology is a valid alternative when it comes to removal of carbon dioxide (CO₂) from natural gas (Baker & Lokhandwala, 2008). High pressure natural gas (containing mainly methane and

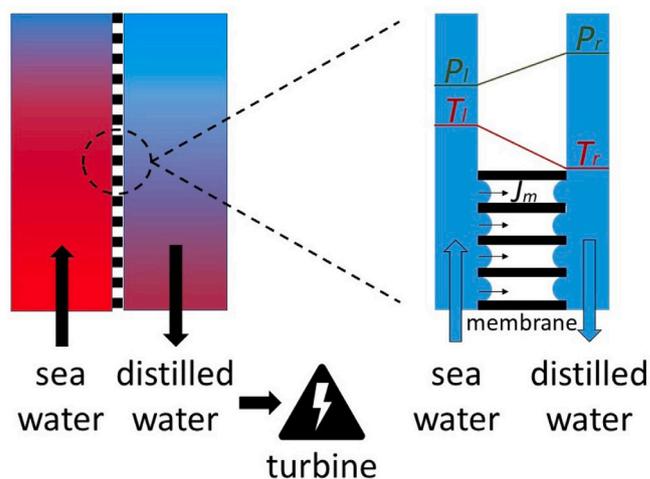


Fig. 4. The PoreWatt Concept: pure water is driven across a hydrophobic membrane by a temperature difference (Keulen et al., 2017).

Source: Figure courtesy of M. Rauter.

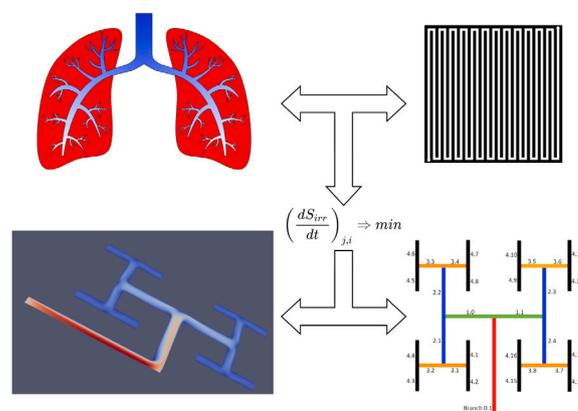


Fig. 5. A flow field for the fuel cell inspired by the human lung.

Source: Courtesy of M. Sauermoser (Sauermoser, Kizilova, Pollet, & Kjelstrup, 2020).

CO₂) is fed on one side of the membrane, while the other side is kept at low pressure. Due to the difference in driving forces and the different membrane permeability to the gas species in the natural gas, the gas components permeate through the membrane at different rates, creating a selective effect and the desired separation. Similarly to the reverse osmosis case, the driving force exploited by the process is a difference in total pressure. Also in this case, one could use a thermal driving force as an additional driving force for mass transport. Indeed, the gas components (e.g. CO₂) release heat as they are absorbed into the membrane material on the high pressure side, while they absorb heat when they are released on the low pressure side. Therefore, the coupling between heat and mass transport allows us to use waste heat or a temperature difference between the high pressure side (cold side) and the low pressure side (hot side) to enhance mass transport. With a temperature difference of only 20 °C, it is theoretically possible to enhance permeation and selectivity by 14% and 8% respectively (Magnanelli, Wilhelmsen, Johannessen et al., 2016). This is very attractive when large amount of waste heat are typically available in gas processing facilities.

Remarks

Detailed knowledge on the system's transport properties may enable us to use part of the resources, which are usually lost, for useful

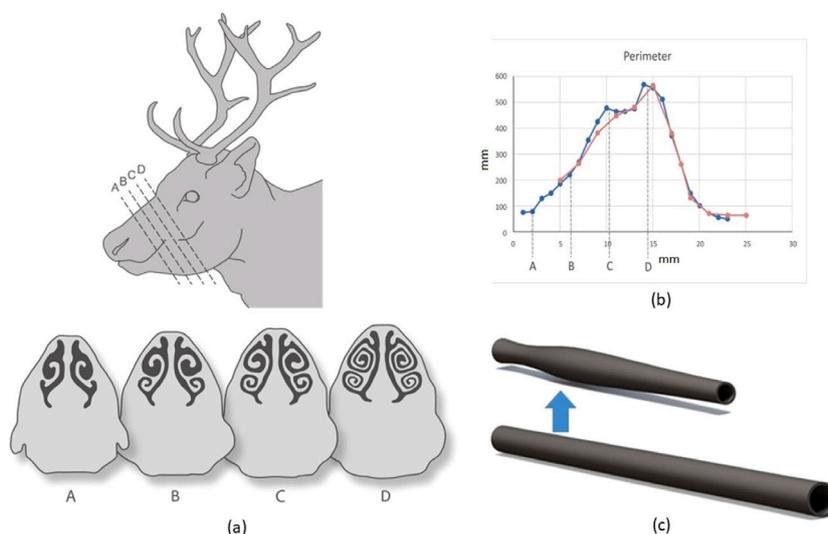


Fig. 6. Taking inspiration from biological flow systems like the reindeer nose (a), a chemical reactor has been optimized to minimize energy dissipation in the process (c). Fig. (b) shows the cross sectional perimeter of the right side of the nose (red line) and left side of the nose (blue line). The optimal reactor (top), which reduces dissipation by 16%, has a perimeter profile that resembles that of the reindeer nose (b).

Table 1
Three thermodynamic tools to improve resource use and their key contents.

Tool	Name	Purpose
1	Exergy map	Obtain overview of exergy losses and entropy production (Kotas, 2013)
2	NET	NonEquilibrium Thermodynamics to exploit coupling between transport phenomena (Kjelstrup et al., 2017)
3	NICE	Nature-Inspired Chemical Engineering design (Coppens, 2012) using optimal control theory (Johannessen & Kjelstrup, 2005)

purposes. This makes nonequilibrium thermodynamics a useful tool to harvest the unexploited potential of resources, and reduce the external exergy loss of processes (Fig. 2).

Tool 3: Learning from natural systems to improve process design

Many studies on entropy production minimization in process units under constraints have documented the interesting property that systems with lower dissipation (i.e. lower entropy production) have more uniform local entropy production (Johannessen & Kjelstrup, 2004, 2005; Johannessen et al., 2002) than other systems. The same trend has been observed in natural systems. The human lung, for instance, has a fractal-like structure that produces the same entropy across each generation of branches (Gheorghiu, Kjelstrup, Pfeifer, & Coppens, 2005). Similar observations have been made for leaves on plants (Kizilova, 2004). These findings may indicate a path to take for energy efficient design. We could possibly learn from efficient and functional biological systems that have developed over time under constrained resources and severe environmental conditions. Simply mimic nature is not enough, since natural and man-made systems operate in different context and might have different goals (Coppens, 2012). Understanding of the mechanisms and purpose of the natural system is therefore necessary, to transpose natural principles to man-made processes. Mathematical tools such as optimal control theory might be also useful.

In this context, a special issue has been recently published gathering some of the works that focus on processes inspired by nature (Coppens, Xuereb, & Gerbaud, 2020).

We choose to illustrate the idea of NICE (nature inspired chemical engineering (Coppens, 2012)) through two examples.

The human lung and the fuel cell flow field

The design of the fuel cell flow field can be inspired by the structure of the human lung (Kjelstrup, Coppens, Pharoah, & Pfeifer, 2010; Sauer-moser et al., 2020). The lung flow field supplies the alveolar structure

with oxygen in a fractal-like flow field (Fig. 5). It can be shown that this conforms with optimal packing of channels in a confined volume (Murray's law (Sherman, 1981)). Due to its fractal, self-similar structure, this flow-field results in a uniform reactant distributions at the electrodes (Trogadas et al., 2018). The translation of this structure to a fuel cell allows us to reduce/avoid the concentration overpotential which is typically used to improve performance of such systems. This can lower material costs, volume and the overall entropy production significantly (by some 10%).

The reindeer nose and the chemical reactor

The reindeer nose has a very interesting and complex internal geometry (Fig. 6a). It has been shown that such a complex structure allows for a more efficient heat and mass exchange than a straight structure would do (Magnanelli, Wilhelmssen, Acquarone, Folkow, & Kjelstrup, 2016). On the other hand, chemical reactors are used for many applications, and many have studied them to find ways to improve their efficiency, optimizing different process parameters.

It is possible to draw an analogy between the evolution of the reindeer nose and the optimization studies on chemical reactors. Indeed, in both cases, the scope is to design a system that reduces dissipation and improves the efficiency of the system. While geometry is a key factor to achieve the goal in the reindeer nose case, reactor optimization studies have so far focused on other factors, such as cooling medium temperature and catalyst distribution.

Using the reindeer nose as inspiration, the geometry of a tubular chemical reactor can be optimized, to obtain the perimeter profile which minimized dissipation while maintaining the outputs constant (Magnanelli, Byremo Solberg, & Kjelstrup, 2019) (Fig. 6c). The resulting geometry has a 16% smaller entropy production than the reference reactor. Moreover, the optimal perimeter profile has some analogies to the one of the reindeer nose, with smaller perimeter at the inlet and outlet of the system, and larger perimeter in the central part (comparison of Fig. 6b and Fig. 6c).

Remarks

These examples indicate that the NICE line of working may be useful for the development of more energy efficient future designs.

4. Conclusions

In this perspective, we have presented three thermodynamic tools to systematically assess resource use and to determine ways to improve it. They all have origin in the second law of thermodynamics, which governs rate and efficiencies of all processes. Nature is also used for inspiration by one of these tools. Indeed, natural systems have developed under resource constraints over many years. It is therefore not unlikely that we can learn from them and use this knowledge in process design.

The three presented tools are summarized as follows (see also Table 1):

- Tool 1** — Mapping of exergy losses (entropy production): at every scale, the analysis of energy quality losses is a power tool to (1) determine areas that require improvement, (2) compare alternative processes, and (3) identify ways to improve a process.
- Tool 2** — Nonequilibrium thermodynamic description of coupled transport phenomena: the understanding of coupling between transport phenomena might help us to exploit driving forces other than the conventional ones to drive processes. This tool can allow us to harvest part of the unexploited potential of resources (e.g. waste heat).
- Tool 3** — Natural systems as inspiration for engineering design: the efficient features of natural systems can serve as inspiration to guide the choice of meaningful parameters to optimize when minimizing losses (i.e. entropy production) in a system; we call this Nature-Inspired Chemical Engineering design. This is NICE!

These are all quantitative, systematic tools, and have of course their limitations. With regard to the food industry, they do not directly address important issues as taste, health, safety. To some extent, however, optimal control theory can handle factual constraints, such as limiting operating conditions or product quality. Moreover, they are thermodynamic tools. Different tools can be found in other disciplines such as economics or engineering.

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