Thermodynamics and the feasibility of sustainable technology
Use and abuse of the second law

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Abstract

As current technology lacks a significant level of sustainability, focus is more and more on alternative technologies such as fuel cells, biomass conversion, and photovoltaics. However, it is often unclear whether the large-scale application of these 'sustainable' technologies is feasible and indeed more sustainable than current technological solutions. Thermodynamics, essentially the science of the conversion of energy and matter, can greatly help to answer such fundamental questions, and especially the second law of thermodynamics can give powerful insights into the possibilities and limitations of technological concepts. Unfortunately, there is much confusion about what the second law truly tells us about the feasibility of sustainable technology. In this paper, we will discuss the main aspects of this issue, while also addressing some persistent misconceptions. We will make use of the principles of thermodynamic process analysis, as it is more and more recognized that this can play a significant role in the design and evaluation of future technological processes.

Introduction

Resource depletion, detrimental effects on the environment, and low thermodynamic efficiencies make it difficult to sustain the current ways of producing useful forms of energy and matter. Much of the academic work is directed at developing alternative technologies, but the practical implementation of these technologies still is a major obstacle. Often the expectations of higher efficiency or less environmental impact cannot be met in practical situations, and the feasibility of large-scale applications becomes doubtful. In some cases this also leads to fundamental arguments against the feasibility of sustainable technology in general, and typically these arguments involve some interpretation of the second law of thermodynamics.

Thermodynamics is essentially the science of the conversion of energy and matter, and, when properly performed, thermodynamic analysis can unambiguously reveal the possibilities and constraints of technological concepts (Szargut et al., 1988; Rosen, 2002). Unfortunately, the principles of the second law are not always fully understood or they are applied in an unsound manner, and this has led to various, often-persistent misconceptions regarding the feasibility of sustainable technology. The concept of sustainability can have a very broad meaning, involving many different disciplines, but in this paper the focus is on the basic thermodynamic requirements of sustaining technological material and energy conversions. Within this framework the feasibility of sustainable processes is addressed.

The paper first reviews some basic thermodynamics of processes in general, and describes how the concept of exergy can facilitate thermodynamic evaluations. The rest of the paper deals with four main issues regarding sustainable technology. The first issue is that of material degradation and the possibilities to recycle and regenerate wastes. The second issue is the usefulness and applicability of solar energy, which leads to the third issue of environment impact. The fourth and final issue is that of efficiencies and thermodynamic losses.

Thermodynamics of processes

The thermodynamics of processes is essentially based on two laws. The first law of thermodynamics states that the quantity of energy is always conserved: energy cannot be destroyed or created, but only converted from one form into another. Hence, for all steady-state processes this means that the total amount of outgoing energy always equals the total amount of ingoing energy.

The second law of thermodynamics provides additional limitations to energy and material conversion. For historic reasons, the second law is closely related to the concept of entropy (S) and to the postulate that processes must always obey:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \geq 0 \qquad (1)$$

which states that the total entropy of a system and its surroundings can never be reduced, and is in fact always increased in real processes. It was Boltzmann who showed that entropy is a thermodynamic measure of probability given as:

$$S = k_B \cdot \ln \Omega \qquad (2)$$

where k_B is the Boltzmann constant and Ω is the number of different ways a system can arrange itself in a given state. In this way, entropy is often associated with disorder, and eqn (1) then states that while it is possible to create order locally (i.e. within the system), the universe as a whole (i.e. the system plus its surroundings) always moves to a more disordered state.

Although the latter interpretation makes the second law somewhat more accessible, entropy remains a highly elusive concept to most people. This is unfortunate because it stands in the way of properly understanding and effectively communicating the second-law principles that underlie all (technological) energy and material conversions. Moreover, the most comprehensive form of thermodynamic analysis is not based on entropy, but on exergy (Rosen, 1999).

Exergy: a useful concept

The primary aim of thermodynamic evaluations is to clearly and unambiguously reveal the thermodynamic consequences of material and energy conversion, and this is why a new thermodynamic concept was developed called exergy. Although exergy is more formally defined by Szargut (1988), the basic goal is to express to what extent matter or energy is thermodynamically out of equilibrium with the natural living environment on earth (usually at or near the earth’s surface).

Exergy may seem highly conceptual, but it also has great practical meaning for technological processes: exergy tells us how much work (e.g. shaft work or electrical work) is *minimally* required to produce useful energy and materials (e.g. heat, light, fuels, metals, plastics, medicines etc.) from energy and matter that for all practical purposes is thermodynamically stable at the natural conditions on earth, which includes thermal energy at ambient temperature, water, air, and soil minerals. Also, when applying useful energy and materials in processes, exergy tells us how much work can be *maximally* performed when these are brought (back) to their thermodynamically stable states in the natural environment.

Exergy values can greatly facilitate the thermodynamic evaluation of processes and process concepts because of some inherent advantages. First of all, exergy rigorously includes the principles of both the first and the second law of thermodynamics. Secondly, second-law inefficiencies are not expressed in terms of entropy generation, but as a loss of the potential of energy or matter to perform work, which is intuitive and thereby easy to communicate. Finally, exergy is by definition relative to the natural environment, and this is not just useful for addressing issues of sustainability: energy and matter can only dissipate to the levels found in the natural environment, so that this reference state forms a fundamental thermodynamic constraint to all processes operating on the planet. In the following sections the concept of exergy will be used to address some issues regarding the basic feasibility of sustainable technology.

Closing material cycles

The fundamental solution to the current depletion of useful materials, is to recycle or regenerate the waste materials, so that processes can operate within closed material cycles. It is frequently thought that the main problem of closing material cycles is the minimum (second-law) energy requirement of converting waste compounds (low-exergy) into useful products (high-exergy). However, it is important to realize that the real problem lies elswhere.

Consider an ideal technological material cycle that has no material losses and is thermodynamically completely efficient. In this cycle, the materials alternate between a state of high exergy (i.e. the useful-product state) and a state of low exergy (i.e. the waste-compound state), and the difference between the exergy of both states directly shows that a minimum amount of work is required to converting the ‘waste’ materials to ‘product’ materials. However, in the ideal material cycle this work or exergy is not lost but becomes part of the exergy of the products, so that the same amount of exergy is obtained again during the degradation stage. Hence, the ideal cycle requires no net input of exergy, even though exergy is required for regenerating the wastes.

The real problem is that there can never be ideal material cycles: both the regeneration of the wastes and the degradation of the products involve real processes, which unavoidable show thermodynamic losses. For the non-ideal material cycle this means that more than the ideal work is required for the regeneration (i.e. more exergy input) and that less than the ideal work can be obtained during the degeradation (i.e. less exergy ouput), creating a net thermodynamic loss for operating the cycle. Hence, the thermodynamic costs of operating material cycles are not the minimum second-law requirements of converting wastes into products, but the thermodynamic losses sustained in the regeneration and degradation processes.

Practically, these losses may be considerable: current regeneration processes are typically quite inefficient (see later) and for certain types of products its is difficult to imagine how exergy can be obtained during the degradation stage. In addition, some material can dissipate to such a high degree that recovering it from the environment is not feasible. Nevertheless, materials can in principle be regenerated and reused, and the only fundamental requirement is that work must be done to cover the thermodynamic losses of the processes involved.

Georgescu-Roegen’s fourth law

Georgescu-Roegen (1971, 1979) formulated what he referred to as the ‘fourth law’ of thermodynamics. This law basically states that matter becomes dissipated and permanently unavailable for human use, and that ultimately this will lead to a run down of the economy. This statement raised much criticism and Ayres (1999) thoroughly describes the fundamental flaw in GR’s reasoning. Nevertheless, the reasoning is not entirely wrong, and in fact it has considerable empirical truth.

So let us consider the reasoning in terms of exergy. GR realized that, like energy, all materials spontaneously dissipate and become highly dispersed in the natural environment. Upgrading these materials e.g. by recycling would not be able to fundamentally change this, because the upgrading processes would require the input of exergy (see figure 1), while according to GR this exergy can only be obtained by degrading or dissipating other, still available materials such as fossil fuels or other valuable resources. Moreover, the material degradation that provides the exergy would always exceed the material upgrading that requires the exergy, because even the most efficient production and recycling processes cannot entirely escape thermodynamic (second-law) losses. In this way, GR concluded that all human activities, including even recycling, deplete a limited amount of useful materials on the planet, so that ultimately all materials will become permanently unavailable for human use.

Fortunately, this reasoning does not hold per se. It is true that production and recycling processes require the input of exergy, but obtaining this exergy does not necessarily require the degradation of *materials*. Indeed, it follows directly from the second law that exergy can also be derived from the degradation of high-quality forms of *energy* (e.g. solar energy). In this way, GR’s law of ongoing material dissipation does not hold generally and in fact it follows from second-law principles applied to material conversion. Nevertheless, the law roughly applies to present-day economies, where most exergy is indeed obtained by material degradation, i.e. the combustion of fossil fuels.

Solar energy: exergy from the sun

Solar energy is often considered the most promising sustainable energy source, and in principle it can be used to drive all sorts of technological processes. Apart from the commonly mentioned advantages (i.e. plentiful, long-lasting, reliable, and continually renewed), the main features that make solar energy so suitable are its high quality (second-law) and the fact that its availability does not require material conversions on the planet. Note that without such an ‘immaterial’ source of useful energy, all processes on earth could only proceed by material degradation, which brings us back to the scenario as described by Georgescu-Roegen (see above).

But why is solar energy thermodynamically so useful on earth? Incoming solar energy is short-wavelength radiation (mostly visible and ultraviolet light) and a representative of thermal energy at about 5800K, i.e. roughly the temperature at the surface of the sun. At the much lower temperature of the earth this solar radiation is strongly out of equilibrium with the natural environment and therefore capable of doing considerable work in (technological) processes. Each 100 Joules of solar energy contains more than 90 Joules of exergy, which means that solar energy could theoretically be converted to electricity, or any other form of work, at an efficiency exceeding 90%.

However, the advantages of utilizing the enormous supply of solar exergy are not straightforward. Besides the possible environmental impact, the production of equipment to collect and convert highly dispersed solar energy can require considerable exergy inputs of their own: famous examples are silicon-based solar cells for which the reduction of silicon oxide cuts heavily into the total electrical-energy yield obtained during their life-time. Nevertheless, the biochemical process of photosynthesis clearly shows that the exergy of solar energy can be effectively utilized.

Solar energy and environmental impact

A fundamental objection sometimes raised against the use of solar energy is that it diverts energy away from the earth's natural climatic processes, thereby inevitably creating (severe) environmental impact. It is indeed not difficult to see how the large-scale utilization of solar energy *could* be disruptive (Lems et al., 2002) to the natural energy flows of the planet (e.g. by altering surface heat absorption), but the question is whether this is true in all situations, i.e. whether a disruption of natural energy flows is an *inevitable* consequence of utilizing solar energy for technological purposes.

A thermodynamic evaluation shows that this is not the case. Consider for example the simple situation of solar energy reaching the earth's surface, where one part of the radiation is reflected and another part is absorbed and subsequently released as heat to the atmosphere. As this is the natural situation, a perfectly non-disruptive technological process must ultimately produce exactly the same outgoing energy flows. But does this requirement still leave room for operating any technological process? Judging from the energy flows one may conclude that it doesn't, but it is important to realize that processes are driven by the input of *exergy* and not that of energy. The natural dissipation of solar energy to low-temperature heat is in fact a highly irreversible process, which means that considerable solar exergy can be used to drive technological processes, while still being able thermodynamically to generate the natural outgoing energy flows. In other words, because natural energy conversion is essentially irreversible (see Szargut, 2003), there is thermodynamic opportunity for operating technological processes on solar energy without disturbing natural energy conversion.

It is not a trivial task to retain or recreate all natural energy flows in practical situations: realize for example that natural energy conversion can be very complex (involving heating, air flows, water currents, evaporation and even biomass growth), and that ensuring this energy conversion will itself require processes with unavoidable thermodynamic losses. Nonetheless, the thermodynamic requirements could in principle be met, which proves that the (large-scale) utilization of solar energy is not *inherently* disruptive to natural energy conversion, as is suggested by the fundamental argument against the use of solar energy.

Entropy generation and environmental impact

Entropy generation is often associated with environmental impact. A particularly misleading interpretation of eqn (1) is that the entropy reduction involved with obtaining useful energy and materials must always lead to a larger entropy increase of the environment. While this is essentially true (if at least 'environment' means surroundings in the broadest way possible) it does not mean that technological activities inevitably break down the natural living environment on the planet, and certainly not the ecosphere. The required entropy increase can in principle be achieved by dissipating solar energy, which basically means consuming the exergy of solar radiation, and this is in fact the primary strategy of the ecosphere itself. Furthermore, even if exergy is obtained by burning fossil fuels, the corresponding entropy generation does not imply a breakdown of the ecosphere.

Thermodynamic efficiency

A key result of the thermodynamic analyses of processes is an understanding of the thermodynamic efficiency of the material and energy conversions. It is often thought that the efficiency of industrial processes can hardly be improved, especially when the designs have been optimized with e.g. heat-integration tools. It should be realized however that such tools typically consider only one aspect of the operation of the process, while a proper thermodynamic analysis (e.g. one based on exergy) gives fundamental insights into all aspects of material and energy conversion: all inefficiencies become clearly visible and more effective optimizations can then be performed. In practice, significant efficiency improvements can usually be realized at several points in the process.

In many situations there is no fundamental understanding of the efficiency. Particularly misleading in this regard is the use of energy efficiency, where the total 'useful' energy outputs of a process are related to the total 'useful' energy inputs. The problem with this measure is that it doesn't properly account for the thermodynamic *quality* of the different energy flows, as can be determined with second-law principles. An illustrative example is the use of electricity to heat water. The thermal energy of the heated water is obviously 'useful', and, as the water retains nearly all the electrical energy, the process appears highly efficient. In reality however, the process is highly wasteful: high-quality electrical energy is dissipated to produce an equal amount of low-quality thermal energy, meaning that most of the potential of electricity to perform work (i.e. exergy) has been lost. To make things even worse, electricity is itself generated with considerable thermodynamic inefficiency. A proper thermodynamic analysis would unambiguously show the massive inefficiency of the energy conversion, but note that alternative processes such as heat pumps have their own inefficiencies, which can also be substantial.

The thermodynamic efficiencies of industrial processes are typically quite low, and even with currently available technology significant improvements can be realized. Such efficiency increases directly translate into fewer emissions and less resource use, and at the same time they create new feasible options for material recycling and clean production. In the long run however it will become necessary to fundamentally review the way technological processes are designed and operated, and useful in this regard are the principles of biochemical conversion of energy and material. Our own thermodynamic analyses (Lems et al., to be published) of some key biochemical processes show that the thermodynamic functioning of living-cell metabolism is far superior to that of technological processes, achieving comparable things with much higher thermodynamic efficiencies.

Conclusions

The thermodynamic evaluation of some key issues regarding the feasibility of sustainable technology has led to the following conclusions.

Firstly, material cycles can in principle be closed, although it should be realized (1) that work is required to cover the thermodynamic losses of the processes involved and (2) that some material can dissipate to such a high degree that recovery is not feasible in practice. Since material regeneration can in principle be achieved by dissipating non-material forms of energy, Georgescu-Roegen's 'fourth law of thermodynamics' does not hold generally, but the principle does have practical applicability, especially as current economies are driven mostly by fossil-fuel degradation.

Secondly, solar energy is particularly suitable for driving 'sustainable' technological processes: it is thermodynamically capable of doing considerable work at the natural conditions on earth and its utilization doesn't necessarily require material dissipation on the planet. A main fundamental concern is that of environmental impact, but, despite thermodynamic constraints and some major practical difficulties, solar-driven technological processes can theoretically operate without affecting natural energy conversion. This shows that obtaining thermodynamically useful forms of energy for technological purposes is not always inherently disruptive to the environment. Furthermore, it does *not* follow from the second law of thermodynamics that technological activities (by reducing entropy locally) must necessarily breakdown the natural living environment or the ecosphere.

Thirdly, thermodynamic analyses show that the efficiencies of technological energy and material conversions can in principle be greatly increased. Even with currently available technology, significant efficiency increases can be realized, allowing an immediate reduction of emissions and resource use, and possibly creating new opportunities for material recycling and clean production. Fundamental changes in process design and operation are however required in the long run, and much can probably be learned from the thermodynamic functioning of living-cell metabolism.

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