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The sustainability of phytomass-derived materials: thermodynamical aspects, life cycle analysis and research perspectives

B. Duchemin (1)

Cellulose in particular and phytomass in general are at the heart of our food system. They are also a central energy vector and a vital source of materials. In this article, a multiscale approach to the complex issue of lignocellulose sustainability is developed. Global thermodynamic concepts help to place current biomass exploitation in a global energetic context. In particular, the notion of entropy appears pivotal to understand energy and material fluxes at the scale of the planet and the limits of biomass production. Entropy is, however, best described at the microscopic scale, despite its large-scale consequences. Recent advances in entropy-driven colloid assembly parallel nature's choices and lignocellulose assembly at the nanometric scale. The functional concept of exergy is then developed and a few examples of its concrete use in photosynthesis and biorefinery research are given. In a subsequent part, an evaluation of the relative importance of biomass is performed with respect to non-renewable materials. This discussion helps to explain the interdependence of resources, including ores and fossil fuels. This interdependence has important consequences for current and future biomass uses. Some of these dependences are then quantitatively discussed using life cycle analysis (LCA) results from the literature. These results are of importance to different technological fields such as paper, biobased insulation, construction wood, information and communication technologies, and biobased textiles. A conclusion is then drawn that exposes the research tracks that are the most likely to be sustainable, including self-assembly, exergetically favourable options and low tech solutions

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Introduction

It is scientifically crucial to analyse the use of resources in the long run for ecological reasons. Indeed, human activities cause unsustainable global geochemical redistributions, climate change, soil exhaustion and ore depletion. The extent of modifications to the planet is such that geologists consider this a new geological era, often named the Anthropocene. 1,2 The consequences of mankind on Earth are well documented by the International Panel on Climate Change (IPCC) and in many synthetic academic works.²⁻⁵ For a number of geochemical, biochemical or biological indicators, planetary boundaries have already been reached.² Planetary boundaries are defined as limits within which certain ecological indicators (ocean acidification, biogeochemical flows, freshwater use, biodiversity, etc.) can evolve within a "safe operating space", without irreversibly affecting the Earth system.^{2,6,7} Crossing planetary boundaries does not necessarily mean than the tipping point is surpassed,

even though changes can be abrupt once this boundary is crossed. Rapid climate change and new types of pollution with deleterious consequences for mankind are deeply interconnected with the question of chemicals or materials in general, and biomaterials in particular. ^{262–264} It is therefore important to assess the sustainability of phytomass-derived materials.

So far, most modern experimental developments in materials have been driven by short-term performance, such as mechanical performance, electrical conductivity, or data storage capacity, to name a few examples. This has produced some undiscussable technological advances. Nevertheless, the possibility to use the same technology for thousands of years has systematically been out of scope. One might wonder why materials scientists have largely failed to prioritize sustainability in their daily routine. Shouldn't the role of the materials scientist also be to integrate the future drawbacks of their findings, as did early foresters?8-10 A common approach is to deem research work as being "green" for internal, but self-consistent, reasons. For instance, there is the underlying assumption that lignocellulose-derived materials are environmentally preferable to fossil-based materials because fossil-based materials are not natural nor renewable. Another assumption

Normandie Univ, UNILEHAVRE, CNRS, LOMC, 76600 Le Havre, France. E-mail: benoit.duchemin@univ-lehavre.fr; Tel: +33 2 35 21 71 54 Critical Review **Green Chemistry**

would be that the amelioration of a transformation step in a given multi-step process would enhance the whole process, without looking at the entire process in its physical context. But these are only ad hoc arguments. They clearly need closer scrutiny because they do not acknowledge the complexity of materials' life cycles. These life-cycle aspects include the growth of biomass, the global energetic context, the reliance on non-renewable materials, end-of-life scenarios and sometimes sociological and economic considerations. Therefore, the question should rather be whether materials scientists can prioritize sustainability in their daily routine at all, since sustainability concerns expand far beyond the laboratory gates.

A simple definition of sustainability is the quality of supporting long-term ecological balance. A more thorough definition should acknowledge the tight and dynamic interplay between materials, energy, ecosystems and socio-political aspects. For instance, sustainability can be understood as a hierarchical inclusion of subsets: the industrial economy is a heterotrophic activity included in a human and social subset; this pre-existing social subset is itself included a larger multispecies environmental set.¹¹ This multispecies set comprises plants, animals and bacteria and there are specific interactions between each of these subgroups and humans in general. As a consequence, sustainability is a goal that can be reached only with a deep understanding of the role taken by other species and the reliance of mankind on "multispecies entanglement", or ecosystem dynamics. 11,12 Another functional observation is that sustainability goals are emerging locally and their propagation at the global scale can occur along four different paths: aggregation (local concerns add up at the global scale), compensation (local issues are offset from one region to another), learning (lessons learnt in one place are learnt globally) and contagion (one local event, good or bad, diffuses over the



B. Duchemin

Benoît Duchemin has a Ph.D. in materials science from Canterbury University (Christchurch, New Zealand). He has worked at the national research center Scion (Rotorua, New Zealand), and as a postdoctoral researcher at the University of Luleå (Sweden) and the National Centre French Scientific Research in Caen (France). B. Duchemin has been a research engineer at Le Havre University in Normandy (France)

since 2010. He has mostly worked on cellulosic materials and cellulose nanocomposites, but he also has interest in the shaping of natural materials, low-energy processes and the analytical characterisation of materials by X-rays. The materials analysed are cellulose-based materials, conventional composite materials but also inorganic materials used in the civil engineering context.

globe). 13 As a consequence of these mechanisms, local sustainability can differ but somehow interact due to other local goals or global considerations. Sustainability is therefore an important concept, but also a complex and multiscale one. The understanding of this complexity makes it possible to work out analytical methodologies to decipher what sustainability means in practical contexts, such as that of materials science. A macroscopic understanding can be provided by thermodynamics, and precise case studies can be analysed using exergy analysis or life cycle analysis.

Overall, this article is an attempt to examine when the exploitation of natural materials is the most sustainable and whether it will come up against other physical limits, both theoretically and in practice. This article is also an attempt to sketch the directions taken by the vast materials science community dealing with lignocellulose, as part of a bigger picture involving thermodynamic and ecological aspects. Because the notion of sustainability is intricate and complex, a specific scientific method is developed therein (Fig. 1). Global considerations are best described by thermodynamics, because this discipline seems to encompass most energy and material fluxes due to its inherent statistical nature. These global considerations will be completed by important figures on the interdependency between renewables and non-renewables. Ecological indicators extracted from life cycle analysis (LCA) or other studies will illustrate the ecological footprints of some technologically important materials derived from the phytomass. Case studies on wood, biopolymers, textile fibres, biobased composites, building materials and paper will be presented. This approach will bring a nuanced answer to the question of lignocellulosic sustainability. It will also highlight research perspectives characterized by the most promising sustainability profiles.

Thermodynamic standpoint: the singularity of the phytomass

The Earth is a system in equilibrium with deep space and the energy received from the sun. The energy balance is explained by several factors: Earth captures some of this radiation at its surface (47% of the incoming radiation), after it has gone

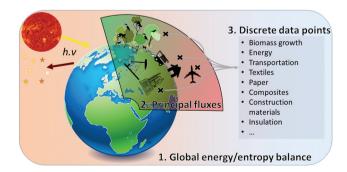


Fig. 1 Conceptual view of the method developed in this article: macroconcepts (1) necessarily contain subsets (2) for which discrete data points from LCA results can be extracted (3).

through the atmosphere and the clouds (absorbing respectively 19 and 4% of the incoming radiation). 14 The clouds reflect 23% of the incoming radiation. The surface of the Earth also reflects some incident sunlight (7%) and this is called albedo. Part of the reflected sunlight is sent back again towards the Earth's surface by clouds in particular. Because the Earth's surface is heated by sunlight, it emits energy in the form of infrared radiation. That is where greenhouse gases (GHG) come into play: they are heated by this infrared radiation and warm up the atmosphere. In the global balance, the Earth sends back slightly more energy than it takes from the sun. 15 The thermal equilibrium and near constant temperature of the Earth (15 °C on average) are explained by the Earth's atmosphere, its steady rotation and the fact that the Earth's core also produces heat due to slow radioactive decay. 15 As is well-known, the current excess of GHG (including CO2 and CH4) due to humans burning fossil fuels intensifies heating of the atmosphere, which provokes "global warming", or "climate change". Biomass plays a role in maintaining the thermal balance of the Earth by fine-tuning the atmospheric CO2 content and the albedo (broadleaf forests, coniferous forests, the seas, deserts or the savannahs have different albedos). Therefore, its exploitation has a very special impact on global thermodynamics.

2.1. An introduction to entropy

The notion of entropy is not often associated with discussions on materials' sustainability, but the concept of entropy can shed a different light on the evaluation of the sustainability of materials, and plant-based materials in particular. The notion of entropy was developed in the first half of the 19th century by Lazare and Sadi Carnot, but it was formalized in its currently used form by Rudolph Clausius in the second half of the same century. The term "entropy" was proposed in 1865 by Clausius to mean that irreversible heat losses are inherent to the system. The use of entropy is associated with the second law of thermodynamics, which is an inequality stating that the entropy of an isolated system never decreases. If the process is reversible, the entropy is constant. The second law of thermodynamics is therefore simply written as:

$$\Delta S > 0$$

where S is the entropy (expressed in J K⁻¹). This notion was introduced to formalise the fact that isolated thermodynamic systems evolve spontaneously and irreversibly in a unique direction to homogenise the energy distribution in a system. This law is "counterfactual" and states what cannot happen; it does not state what precise path a physical system will follow, but it gives a lot of predictive "power". The entropy is maximised at thermodynamic equilibrium for an isolated system and nothing can happen when this equilibrium is reached (due to the irreversibility of the process). It is usually assumed that a given system becomes more random when its entropy is increased; despite being sometimes true, this is not always the case.

A perhaps more functional and mechanistic definition of entropy was given by Ludwig Boltzmann in 1877. This definition is very powerful when backed up by the concept of a phase space,† If \mathcal{P} is this phase space, then the entropy of a state x contained in a box \mathcal{V} of volume V can be written as:

$$S = k \log V \tag{1}$$

where k is usually Boltzmann's constant $(k = 1.38 \times 10^{-23} \text{ J K}^{-1})$, but it can also be taken as a different constant. 15,17 Each box $\mathcal V$ corresponds to a subdivision of \mathcal{P} in which states are macroscopically indistinguishable from each other. The subdivision of \mathcal{P} in \mathcal{V} spaces is somewhat arbitrary and corresponds to an approach called coarse graining, which is developed in the relevant literature. 15 In ordinary situations such as that of a gas in a container, the box \mathcal{V} will be almost the same size as the whole phase space \mathcal{P} , a situation in which thermal equilibrium is reached and entropy is maximised. Due to the use of a logarithm in the Boltzmann definition, the fact that this box is slightly smaller than the whole phase space makes these two states indistinguishable. A more precise Boltzmann's equation can be given for gas systems and this approach gives rise to the field of statistical physics. Other definitions of entropy have been given and they are expressed (in a simplified manner) as a probability of undergoing a process divided by the probability of undergoing the reverse process.17-19 It is, however, important to remember that energy will naturally tend to spread out evenly between particles, and this is what entropy measures: energy dissipation.

2.2. Local entropy: self-organisation of colloidal building blocks

Entropy is often considered to be a measure of disorder: the more disorder, the higher the entropy of the system. This definition is largely imparted to practical uses of the Boltzmann definition of entropy and its application in classical thermodynamics for gases and liquids. However, entropy needs to be understood differently when the particles are confined or subjected to an external force field, such as a gravitational force field. 15,20-22 Indeed, a system with fewer degrees of freedom will have a smaller phase space, and therefore a lower entropy. 15,20,22 Counterintuitively, entropy can thus contribute to the emergence and design of organised colloidal structures, such as packed tetrahedra or hard rods, when atoms, molenanoparticles cules are confined and assembled. 20,21,23-26 This can easily be explained by the higher number of possible configurations provided by some organised structures when confinement is prevalent, in comparison with disorganised structures: when packing occurs, the maximum volume fraction of a disorganised state $(V_{\text{packing}}^{\text{disorder}})$ is

 \dagger A quick definition is given by Roger Penrose: "For a classical system of n featureless particles, (a phase space is) a space $\mathcal P$ of 6n dimensions, each of those points represents the entire family of positions and momenta of all n par-

ticles". ¹⁵ The three positions can be the coordinates
$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$
 in a Cartesian coordinates

nate system and the momenta are
$$m \begin{pmatrix} \frac{\partial x}{\partial t} \\ \frac{\partial y}{\partial t} \\ \frac{\partial z}{\partial t} \end{pmatrix}$$
, where m is the particle's mass.

always lower than that of an organised state ($V_{\rm packing}^{\rm order}$). Therefore, there exists an "organisational concentration window" between $V_{\rm packing}^{\rm disorder}$ and $V_{\rm packing}^{\rm order}$ in which organised particles have more degrees of freedom, a larger phase space, and therefore a higher entropy. Since higher entropy will always be preferred, it becomes thermodynamically favourable to organise a confined colloid so that particles can keep "wiggling" around their mean position instead of percolating against each other and becoming immobile. This explains why

elongated polyhedral particles tend to align and form liquid

crystal-like phases, such as nematic or smectic. 23,24

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So entropy means that, in a fixed colloidal system or in biological systems, rearrangement, biomorphogenesis and growth can occur spontaneously, which means that energy use is optimized. 19,28,29 Entropy-driven processes have suggested to drive a plethora of local phenomena associated with life or not, including RNA self-replication, protein folding, temperature-dependence of contact angles or enzyme selectivity; at a larger scale, entropy can be used to describe the interactions between ecosystems or economics. 10,20,28,30-34 The Nobel laureate Ilva Prigogine introduced the term "selforganisation" to describe these phenomena. Since entropy maximisation can lead to the formation of structures without external work or heat, entropy can form the basis of passive, or energy-efficient, processes. This point is important if one is to draw inspiration from natural biological materials that draw energy from their surroundings, as opposed to heavily processed materials, which need a lot of external energy sources in the form of heat, mechanical pressure or chemical energy.

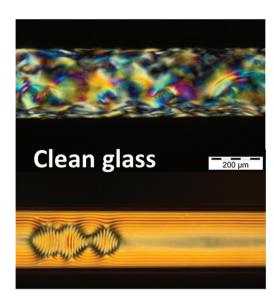
There are limited studies dedicated to the importance of entropy in the colloidal assembly of lignocellulosics.²⁶⁵ Among them, only a few are focused on cellulose itself. In one study dedicated to understanding the temperature dependence of the axial Young's modulus of cellulose I, the crystallite stiffness was found to be influenced by entropy.¹⁷ In the same study, entropy was calculated by determining the relative fluctuations of the atoms around their mean positions, as conceptualised above. This result is interesting in that it shows that, in at least one situation with a hydrophilic organic crystal, the temperature-dependence of the Young's modulus is affected by entropy rather than by internal energy and supposedly weakened hydrogen bonds. Against expectations, these hydrogen bonds account for a relatively small portion of the bonded energy (5-10%) and stiffness (20%). In another recent study, it was found that free volume entropy could favour the formation of kinks (local folds) in nanofibrils placed in slits, an effect attributed solely to geometrical confinement.³⁵ This effect is interesting because, rather than bending, it seems like the nanofibrils prefer to break along a relatively straight line and this could have applications in biomass fractionation.

Other studies focus on the interactions between polysaccharides in the cell wall. It has been shown that the adsorption of xyloglucan (XG) on cellulose surfaces was endothermic, and therefore entropic: the entropy of the whole system (including solvating water molecules) increases if water molecules are freed from the cellulose surface and replaced with portions of XG

chains.^{36,37} The underlying reason is that the polymer state-conformation in solution is restricted by covalent monomermonomer bonds, compared with that of small water molecules with unrestricted conformational space. It is therefore entropically advantageous to replace cellulose–water interactions with cellulose–XG ones. This non-electrostatic adsorption has been demonstrated by molecular dynamics simulations and also experimentally by neutron reflectivity, AFM and surface plasmon resonance spectroscopy.^{36–38} As a consequence, polysaccharide adsorption in this case is driven by entropy rather than chemical bonding (hydrogen bonds or van der Waals forces), as previously assumed.^{37,265} A practical outcome could be the slower and weaker aggregation of hemicelluloses on cellulose at low temperatures, which could have consequences for biomass separation and perhaps biomass growth rates at different latitudes.

There are still relatively few studies related to entropicallydriven self-assemblies of cellulose nanocrystals (CNC), but the field of entropically-driven self-assembly in general is rapidly growing and it should gain momentum in the upcoming years. 20,25,26,39 In particular, this field allows one to reverseengineer colloidal crystals of various shapes, including rods, fibres, and tetrahedra. 23,25 When dealing with macromolecules, this field still faces complex topological issues such as those of geometric frustration and network entanglement, two effects that also shape polymer assembly. 40,41 Nevertheless, CNC can self-organise in the form of tactoids or films over several length scales, an effect that is kinetically and thermodynamically dependent on their concentration, ionic strength, size, aspect ratio and polydispersity. 42-46 The organisation of suspensions seems to be independent of temperature. 24,42 Organisation can also be templated by letting the CNC self-organise in nanogrooves, or in long capillaries (Fig. 2). 39,47 This type of approach can have applications in fields such as papermaking, electronics or textiles, to name a few.

Other works have been dedicated to understanding the thermodynamical interactions of nanocelluloses with different species in solution, a field that has possible applications in water depollution, medical assays, bioethanol production, nanostructured sensors, etc. These measurements usually rely on isothermal titration calorimetry or specific reduced excess determination in batch experiments. In some instances, proof was obtained by molecular modelling. It has for instance been shown that the adsorption of divalent ions to negatively charged CNC was entropy-driven ($\Delta S > 0$) to compensate for unfavourable endothermic enthalpy $(\Delta H > 0)$. This behaviour is explained by the overall entropy gain due to the replacement of surface water by cations, and by the supplementary degrees of freedom gained by the freed water molecules. It was demonstrated than an enthalpy-entropy compensation occurred for the adsorption of a range of moieties on nanocelluloses (Fig. 3). 49,50 These moieties included a large range of cellulose binding modules, bio-macromolecules (expansin, albumin, xyloglucan, lipid bilayers), ions of opposite charges, drugs, dyes and common chemicals such as urea.⁵¹ This compensation meant that the Gibbs free energy of adsorption, which is the force for binding, remained essentially constant. The



Initial conditions

PAH treated 200 µm

After 6 weeks

Fig. 2 Illustration of autonomous, entropy-driven, colloidal self-organisation. The systems were sealed and observed for 6 weeks at T=22 °C. A cholesteric aqueous CNC suspension (6.41 wt%, surface charges 0.128 e nm⁻², $\zeta=-63.7\pm2.6$ mV, Le Maine University)²⁷ was injected into two glass capillaries (5 μ l NMR tubes, $\varnothing_{internal}\sim286~\mu m$). Before injection, both capillaries were cleaned with Piranha solution ($H_2O_2:H_2SO_4~1:1$) to produce a negatively charged surface from the activated silanol groups. The capillary on the right-hand side was further functionalized with a 0.4 wt % aqueous solution of poly(allylamine hydrochloride) (PAH) in order to confer positive surface charges to the glass wall. Both capillaries were thoroughly cleaned and dried under a flow of dry N_2 before being filled with the CNC suspension. Note how the long-range organisation is affected by the boundary conditions of a molecularly thick layer: the cholesteric phase formed large transverse disclinations permitted (lower left) by a repulsive wall and inhibited (lower right) by an attractive wall. Inhibition resulted in small tactoids being formed at the centre of the tube (unpublished results).

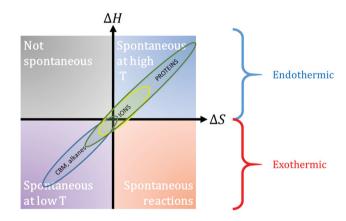


Fig. 3 The adsorption of various moieties on nanocelluloses follows enthalpy–entropy compensation (CBM stands for cellulose binding module). In most cases with ions and proteins (but also with oils in general), the adsorption enthalpy is unfavourable ($\Delta H > 0$) and the successful adsorption of the moiety is therefore driven by entropy. Figure adapted from refs. 49, 50, 56 and 57.

question of adsorption entropy is of course fairly universal and extends far beyond nanocelluloses since it is of relevance to the fields of heavy metal depollution or oil/alkane adsorption by cell wall components. In fact, micron-sized lignocellulosic fragments have often been found to be very efficient for these applications because of their entropic contribution (Fig. 3). This contribution is associated with the release of bound water in order to establish a cellulose–guest assembly.

This is also associated with their more pronounced hydrophobic character at higher temperatures, leading to stronger interactions with all classes of surfactants.⁵⁸ In this framework, the important porosity and hygroscopicity of lignocellulose is a clear advantage, leading to spontaneous adsorption, in the absence of external inputs.

2.3. Global entropy: geochemical cycles and the central role of biomass

As seen in the previous part, living materials and materials in general show a tendency to structure themselves or to respond to exterior stimuli due to entropy-driven processes. In the photosynthesis process, a high entropy resource, atmospheric carbon dioxide, is converted into low entropy materials (glucose, and assembled polymers in the form of starch, cellor other lignocellulosic compounds) through photosynthesis. 59,60 This would contradict the second law of thermodynamics unless one considers that plants draw their entropy from the sun's rays. 15,59-61 The incoming energy is made of high-frequency photons (yellow, visible light) and the outgoing thermal energy leaves the Earth in the form of lowfrequency, infrared, radiation. ¹⁵ Max Planck's formula $E = h\nu$ shows that the incoming energy is made up of high-energy photons, whereas the outgoing energy is made up of lowenergy photons. Because of the total energy balance, number compensation must occur and the incoming photons must come in lower numbers that the outgoing ones. 15,59 As a result, the incoming photons must have a smaller entropy (as

well as degrees of freedom and phase space) than the "exchanged" infrared radiation: the solar energy is absorbed and dissipated. The metabolic pathways involved can be clarified by considering that all living organisms are open thermodynamic systems in an out-of-equilibrium state.^{30,31} Despite the local reduction in entropy associated with the conversion of CO₂ into organic matter (sometimes called negative entropy, or negen-

tropy), the entropy of the universe is increased by the growth

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process and the second law of thermodynamics is respected.

Biodiversity is essential, but plants are specific in that they are by far the most abundant autotrophic‡ primary producers. Plants represent about 82.5% of biomass. Entry are the primary producers of food for all the other trophic levels. Because plants use light energy, they are called photoautotrophic. The most abundant biomass on Earth has thus adapted to convert, by photosynthesis, the only inexhaustible low entropy and high energy source (sunlight) into the organic matter that all heterotrophic organisms rely on. Is, so It is estimated that 100 J of radiative sun energy is required to produce J J of chemical energy in the form of lignocellulose. This has far-reaching consequences since the vast amounts of organic

matter that have accumulated and sedimented over geological

times have produced low entropy fossil fuel reserves. The vast burning of fossil fuels and the associated availability of cheap energy has disturbed normal geochemical cycles (Fig. 4). As pointed out by the economist Georgescu-Roegen, fossil fuels constitute an enormous amount of low entropy material that is rapidly (and quasi-irreversibly) converted into high entropy products (CO_2, SO_2, NO_x) by combustion. ^{10,63} This combustion has for the most part taken place in the last two centuries and its origin is anthropogenic. It has resulted in two major products: (i) as far as matter is concerned, the main product is diffuse, high entropy CO2 massively (and quasi-irreversibly) released into the atmosphere despite land and ocean capture and (ii) as far as energy is concerned, heat being lost into space by infrared radiation. Thanks to cheap energy, three low entropy material resources have been rapidly dissipated or disseminated: non-renewable fossil fuels themselves (self-facilitating their own extraction), non-renewable ores and renewable biomass. These three sources are essentially making the most of the chemical potential of the Earth and they sustain life and humanity in its present form. The reduction of these sources means that the chemical potential is depleting.⁴ At the current discharge rate, only 1000 years of energetic potential would remain to feed the world's population; because of accelerating resource consumption, this potential is alarmingly decreasing by 200 years every 10 years.4 In other words, the current distribution of living species cannot be sustained chemically by the Earth in the long run and species become extinct. Since the "base" trophic level contains plants for the most part, the sus-

‡Autotrophic organisms only require carbon dioxide or carbonates as a source of carbon and simple inorganic compounds (such as nitrogen) for metabolic synthesis of organic molecules (such as glucose). Other than plants, there are some other autotrophic organisms, such as some populations of archaea, that live on chemical energy sources.

tainability of phytomass-derived materials strongly depends on how and why lignocelluloses are used.

Whereas the case of fossil fuel combustion and biomass depletion is relatively straightforward to understand in an "Earth versus universe" battery schematic, the diffusion of condensed chemical elements on the planet seems more relevant when dealt with in terms of inter-regional patterns. Good examples are those of nitrogen and phosphorus. Common food and textile crops need both nitrogen and phosphorus to grow effectively, since both elements are essential for photosynthesis. 2,64 Phosphorus cannot be found in the atmosphere but only in the hydrosphere or in the lithosphere. It is generally extracted from non-renewable reservoirs. These P reserves are low-entropy P. When P is extracted and irreversibly scattered on arable land, planetary P becomes of higher entropy since it is mixed with other elements and diffused in the lithosphere and in the hydrosphere, which increases its phase space volume. These P reserves are limited and peak phosphorus could soon be reached (Fig. 6). 65,66 In contrast, N can be fixed by legumes from the atmosphere to the lithosphere. In most situations, however, N is brought in the form of synthetic fertilizers, which are produced using fossil fuels. Geological quantities of nitrogen-containing moieties such as NH₃ and NO_x are therefore released into the environment through the use of fertilizers produced by the Haber-Bosch process (~120 Mt N per year) or by combustion of fossil fuels (~40 Mt N per year). This diffusion of nitrogen fertilizers into the environment is estimated to sustain about half of the food production worldwide and it promotes carbon sequestration. Yet, it has deleterious consequences for the climate (nitrous oxide, N2O, released from the lithosphere and the hydrosphere is a GHG), for biomass (through eutrophication of the hydrosphere and acid rain) and for human health, because ozone production from NO_x increases the oxidizing ability of the atmosphere, and because of aerosols. The coupling of the nitrogen cycle and the carbon cycle is extremely strong and current atmospheric N2O levels are at levels never seen before. 67,68 Phosphorus is currently estimated to be the limiting factor in the N:P ratio that enables optimal biomass growth. Its diffusion in a non-usable (high entropy) form therefore means that artificial biomass growth acceleration will be limited in time.⁶⁹ Similarly to N and P, the metabolic processes of plants rely on freshwater; on a number of other chemical elements, including S, K, Ca, and Mg; and on micronutrients, such as Cl, Fe, B, Mn, Zn, Cu, Mo and Ni. The spatial distribution of these elements also requires close monitoring because their phytoavailability is important with respect to plant growth and human health, especially in the case of food crops. 70,71 However, other elements are toxic and their confinement in low entropy, high concentration forms is desired.262 For instance, P fertilization comes with trace amounts of heavy metals, such as cadmium, that have deleterious consequences in the long term due to accumulation in soil, and migration to food. Consequently, the high levels of cadmium in French or Canadian durum wheat needs to be monitored.72 The example of cadmium shows how toxic

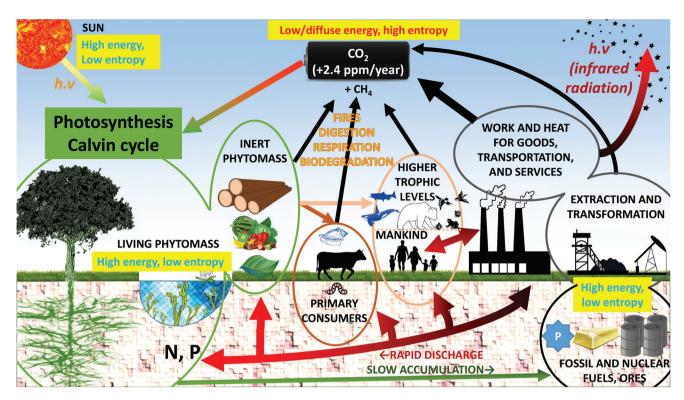


Fig. 4 The carbon cycle can be reinterpreted in thermodynamic terms by stating that low entropy/high energy resources (non-renewable fossil or nuclear fuels, non-renewable ores and renewable biomass) are being rapidly depleted. The energy from these three sources is rapidly transformed into CO₂ (+3-4 Gt C per year; +2.4 ppm per year in the atmosphere over the 2010-2020 period). CO₂ is a form of diffuse, low grade and high entropy chemical energy. Man cannot use it efficiently. In contrast, CO2 capture by phytomass produces the only form of low entropy chemical energy readily usable by the phytomass itself, by mankind and by higher trophic levels in general. This process (photosynthesis) is fuelled by the only inexhaustible low entropy energy source (sunlight) and it provides most former (fossil) and current (heat, biomass) energy. Photosynthesis acts by condensing highly diffuse atmospheric CO₂ and it induces local entropy drops. The limited efficiency of photosynthesis (~-2 Gt C per year) provides a slow discharge of the atmospheric CO₂ chemical potential and it cannot compensate for the +5-6 Gt C per year emitted from fossil resources. Fossil fuels and other non-renewables currently sustain most life processes by permitting the speeding up of biomass growth (N, P) and exploitation, including deforestation (~+1.9 Gt C per year). Part of this non-renewable and renewable energy is definitely lost because it is dissipated to outer space in the form of high entropy infrared radiation. Whereas biomass is required for basic needs (food, clothing, heat), the thermodynamic cycle is in a temporary out-of-equilibrium state thanks to the chemical and energy potentials of ores and fossil fuels. These two potentials sustain the current biomass distribution and humanity. However, these potentials are rapidly discharging because they are not replenished by biomass growth and sedimentation, which are slow processes. The danger is that of a planet in a "post-modern" state with a depleted fossil potential and a massive, non-exploitable, CO2 potential. In other words, the danger is that of a planet that has quickly and irreversibly gone into a high entropy state. Slowing down this unsustainable cycle involves limiting the use of fossil fuels and elaborating conservation or restoration strategies to optimize CO2 capture by biomass. It also involves a strategy to use biomass at a more "natural" rate. [N.B.: Annual atmospheric CO2 capture by the hydrosphere is not represented but it is equivalent (~2 Gt C per year) to that of the biosphere (the phytomass, for the most part) in the absence of deforestation. The hydrosphere acts as a buffer that slowly captures CO2 in the form of rocks by sedimentation of calcium carbonate or fossilization of ocean biomass. No usable energy is produced in the conversion process.]

elements that are concentrated locally (low entropy) can be scattered to levels that are unsuitable for the health of humans, other animals and plants. The same reasoning applies to nuclear wastes (actinides, depleted uranium, etc.), plastics (microplastics, environmental release of hormone-like moieties such as bisphenols) or other heavy metals. The issues of groundwater depletion and salination are also pivotal. 73,74

The danger is that of a planet in a "post-modern" state with an irreversibly depleted low-entropy potential. This potential is constituted of highly usable biomass in addition to non-renewables, either in the form of fossil fuels or minerals of interest. In this post-modern state, the only low entropy, highly exploitable energy sources are the remaining biomass and sunlight. Slowing down

this unsustainable cycle involves quickly limiting the use of fossil fuels, minerals and ores, and elaborating on conservation or restoration strategies to optimize CO2 capture by biomass.5,75-78 It also involves conservation strategies to use biomass at a rate that is entropically compatible with the health preservation of some ecosystems and the restoration of other ecosystems.

2.4. Entropy in conversion processes: exergy

Entropy, in the engineering sense, can precisely be used to tell how much energy is not available in a conversion system.⁷⁹ The concept of exergy combines the first and the second laws of thermodynamics in that it couples energetic considerations with inevitable energy dissipation: exergy is therefore the Critical Review Green Chemistry

optimal work that can be produced by a system.80 This optimum point is reached when the system is at equilibrium with the environment. In fact, a very simple definition of exergy (unit: J) can be given for an irreversible process occurring in a reference environment (sink) with a temperature T_0 and it states that the total exergy B available is:§

$$B = H - T_0 S_{\text{gen}}$$

where S_{gen} is the entropy generated by the process (it is the sum of all entropies, including that of the system, the atmosphere, and a heat reservoir) and H is the enthalpy of the system.80 Exergy destroyed by the system (I for irreversibility or "exergy consumption") is proportional to entropy that is created:80,81

$$I = T_0 S_{\text{gen}}$$

By definition, an ideal reversible process consumes zero exergy. Whereas energy is conserved (first law of thermodynamics), exergy is consumed due to process irreversibility. An important aspect lies in the consideration that the system operates in an infinite and stable atmosphere with a sink temperature T_0 . It is not affected by the process. 81,82 Exergy is therefore a "real world" measure of energy quality (or potential), distinct from energy, which is a measure of quantity: exergy analysis shows how much energy can be utilized in a given context.80 Exergy has also been called the availability function, availability, available work or essergy. 63,81,83 More precise definitions of exergy have been given for chemical reactions, adiabatic flows (no heat reservoir external to the cycle), sunlight absorption, electron transport chains, evaporation, condensation or kinetic processes. 63,81,82

This tool is, according to some thermodynamicists, the only relevant unit to assess the sustainability (or "thermo-ecological cost") of technological solutions. 63,80,84 Let's explore the example of a combustion engine. Exergy analysis takes into account the fact that combustion of high exergy fossil fuels produces two main streams, other than high exergy work. First, there are the low exergy combustion residues that are chemical in nature (CO_2 , NO_x , soot, etc.). Secondly, there is the low exergy heat dissipated to the surroundings. The exergy balance is quite different from the energy balance because it shows that 90 to 95% of the exergy input is wasted. Indeed, the input energy is transformed without loss: according to the first principle of thermodynamics, the fuel yields the mechanical work, but also heat and the energy for the chemical reactions involved in the production of exhaust fumes. The output energy comprises low grade energy in the sense that low temperature heat and combustion wastes are poorly usable once diffused in the environment (high entropy, low exergy).

§ For the sake of simplicity, this functional definition omits potential exergy sources, such as kinetic exergy, electro-magnetic or gravitational potential exergies. This definition is largely operational since it can safely be assumed that all the transformations of relevance for us occur on Earth at constant altitude, at zero velocity relative to the planet and in the absence of a strong electro-magnetic field.

Generally speaking, exergy analysis can be a powerful tool to quantify the loss of energy quality, and a high exergy efficiency will mean both higher sustainability and lower environmental impacts, because less energy will go to waste. 63,80,83,85

It is thus beneficial to express process efficiencies both in terms of energy efficiencies (output energy/input energy) and exergy efficiencies (output exergy/input exergy). Exergy efficiency is always lower than energy efficiency in the actions of fuel or electric heating, or electric cooling, due to thermodynamic irreversibility. 80,83 One can therefore immediately see the specific role that biobased materials can play in sustainable development in terms of thermal insulation or any use of these materials for energy co-generation: direct incineration with energy recovery, by-product incineration in a biorefinery context, or more advanced energy conversion via biomethanation or hydrogenation.

Exergy analyses have been undertaken to better understand the efficiency of plant metabolism and photosynthesis in particular. Photosynthesis is a complex two-part process that is well-described in modern textbooks or in relevant publications. 12,82 The question of photosynthesis efficiency is central and the chemical reactions involved use 32% of the light captured by the chlorophyll, which has an extremely high efficiency, near quantum limits. 12,86-88 It has also been found that the theoretical energy efficiency of photosynthesis as a whole is ~35-37% when the definition considers the Gibbs free energy of one mole of glucose divided by the energy contained in photons. 12,82,89 Yet, experimental measures usually point to much lower energy efficiencies, in the 1-4% range for the whole plant. Detailed analyses of the photosynthesis sub-processes have shown that exergy is lost at several steps of the process and explain the observed low efficiency. 82,89 In particular, light absorption is restricted to a narrow photoactive region (400-700 nm) and part of the radiation of interest is reflected by the leaf. Another major loss of efficiency is attributed to the electron transfer chains, which are the channels through which the highly excited electrons are transferred away from their nucleus of origin. These studies shed light on a limiting factor of plant growth, and therefore biomass availability.

Exergy is also a natural candidate for comparing technologies in which low grade heat can be drawn from the environment or re-used within a process. It has for instance been used to compare different heat pumps. 90 Another obvious application could be the study of phase change materials (PCM) used for latent heat storage since low temperature heat is extremely valuable in terms of exergy.⁹¹ Biobased solutions exist: cellulosic materials such as wood, spun filaments or cellulose nanofibres can be used as scaffolds for PCM stabilization and PCM materials such as myristic or palmitic acid enable the production of fully biobased composites for heat storage. 92-95 Closer to the thermodynamics of industrial processes, exergy analysis has been used to characterize the exergy efficiency of biomass conversion in several biorefinery contexts. This type of study can help to identify the most exergy deficient organs of the biorefinery to improve its global efficiency. 85,96 The example of a sugarcane mill producing simultaneously lactic

acid, steam and electricity was investigated; in this case, a steam boiler was the most deleterious to exergy because the fast thermochemical reactions occurring within the boiler were a source of irreversibility.85 In another study, a wholecrop safflower biorefinery was studied and the exergetic efficiency of the process leading to ethanol and biodiesel production was found to reach ~73%.97 This result demonstrates the important reduction in waste generation due to the biorefinery concept, with the ability in particular to recover metabolic CO2 from saccharification and fermentation. This CO2 recovery maximises the process exergetically while minimizing pollution. In this study, the largest exergy destruction rate was that of the water treatment unit, a unit characterized by the high irreversibility of its subunits (oxygen consumption by aerobic processes, desalination, electrodialysis and reverse osmosis); this unit alone accounted for ~70% of the process's irreversibility and future efforts should therefore be aimed at

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improving this unit.

The analysis of processes using exergy is thus very useful to quantify the depletion of energy quality and the consumption of resources. Nevertheless, it is relatively ill-suited to the analysis of materials due to the complexity of the sink definition: the use of resources that need mining and heavy extraction processes are difficult to deal with. 63,98 For instance, chlorine is used for paper fibre bleaching and it is disseminated into the environment. This dissemination is problematic for exergy analysis of the pulp and paper industries since the ground state (or zero state) of natural chlorine presence is not easily defined: the three most important environmental sinks (the atmosphere, the hydrosphere and the Earth's crust) thermodynamically balance each other, away from equilibrium.⁶³ A more thorough exergy analysis would require the inclusion of the exergy cost of the other life cycle aspects, such as transportation, mining, harvesting, pre-treatments, use and disposal. This holistic approach has not been performed in exergy analysis because of the complexity problem. A holistic vision can nevertheless be provided by semi-quantitative approaches and by LCA.

3. Phytomass: availability and environmental context

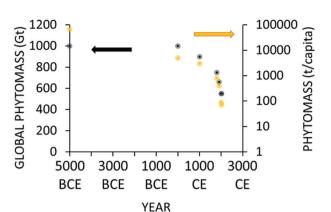
3.1. The availability of biomass and phytomass-derived materials

Plants represent about 82.5% of biomass; other taxa are bacteria (\sim 12.8%), fungi (\sim 2.2%), archaea (\sim 1.3%), protists¶ (\sim 0.7%), animals (\sim 0.4%) and viruses (<0.1%). ⁶² Among plants, only a small fraction (\sim 0.2%) is found in marine environments (green algae and seagrass). Forests cover 31% of terrestrial land and they amount to 60 to 75% of continental

biogenic carbon.⁹⁹ How much phytomass can be used? Phytomass has been divided in two since the advent of agriculture and it is currently estimated that mankind consumes biomass at a rate that is much higher than biomass can sustain (Fig. 5).4,77,100 In particular, one notices that the amount of phytomass per capita has been decreasing exponentially as it amounted to ~70 000 t per capita in 5000 BCE, ~800 t per capita in 1800, ~400 t per capita in 1900 and to ~71 t per capita in 2020 (Fig. 5). In contrast, modern agriculture has been able to provide more food than ever and production has increased by ~50% over the last 40 years, despite crop productivity reductions (Fig. 5). 101,102 As of today, it is estimated that the amount of food produced annually is ~1.27 t per capita. Nevertheless, this increased food production is exogenic and anthropic as it is maintained by the use of fossil fuels, for mechanization, nitrogen production or phosphorus extraction. This increase has thus only been possible thanks to the additional use of non-renewable low entropy sources (fossil and nuclear fuels, ores) or to the exploitation of slowly built-up low entropy sources (massive deforestation). The other side of the coin is the low (< 2.9%) proportion of ecologically "intact habitats", and the fast disappearance of wilderness areas in general. 75,78 In contrast to food production, the production of textiles can hardly cope with the demand worldwide and it has been steadily decreasing over the last 60 years (Fig. 5). A rough estimate shows that ~1.5 kg per capita of biobased textile fibres are currently produced annually, if viscose is added to the production of primary textile fibres (cotton, flax, jute, etc.). 101,103-105 Several factors can explain this trend and the production of cotton fibres is a good example. This production accounts for roughly 1/3 of the global natural textiles but it is threatened by several environmental limitations such as high water consumption and a high vulnerability to pests. 106,107 Furthermore, this cultivar is strongly sensitive to climate change; the threat is particularly strong in rain-dependent regions such as some parts of India. These figures show how little phytomass is currently available when compared to the past and they also demonstrate the growing importance of essential food crops in phytomass use, which should be a warning to the overuse of lignocelluloses in the form of nonessential items with planned or built-in obsolescence. Relatively modest textile production is a reminder that these crops in the form of biocomposites will probably not be able to replace steel or wood for large-scale structural applications.

Looking towards the future, it is difficult to extrapolate how climate change and mankind will further affect biomass availability. ^{5,62,77,100} The effects of climate change can already be felt through price and yield instabilities of common crops, as well as increasing wildfires. ^{108–110} While biomass could respond favourably to increased CO₂ levels provided that N and P were available, the effect of heat stress is negatively impacting on plant metabolism by (i) decreasing the activity of photosynthetic enzymes, (ii) increasing evapotranspiration and decreasing irrigation and/or (iii) decreasing CO₂ capture by stomatal conductance reduction. ^{67,110–112} Heat stresses lower crop yields. It is therefore not a surprise to learn that climate

[¶]Protists are predominantly one-celled eukaryotic (cells with a nucleus) organisms that are not animals, plants or fungi. The protist domain includes protozoa, some algae, and slime mold.



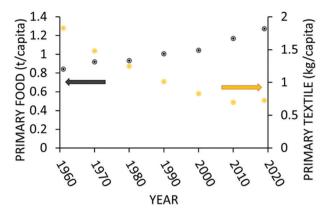


Fig. 5 Left: Global amount of phytomass (black dots) and the amount of phytomass per capita (orange dots); data adapted from Smil (2011). Right: Primary food production (black dots), including cereals, root vegetables, sugar, dry legumes, nuts, fruits, vegetables and oil seeds, and primary textile production (orange dots) between 1961 and 2019; data from FAO. 101 Annual viscose production is not represented, but it has been fluctuating between 0.5 and 0.8 kg per capita since 1950, and it currently amounts to \sim 0.75 kg per capita. 103

change has decreased crop productivity by 21% between 1961 and 2021. 102 Structural choices also threaten some cultivars and biodiversity, such as the hevea used for natural rubber or palm tree monocultures for palm oil. 113,114 In this context, man has an important role to play in land care and biodiversity preservation. 5,8,9,76,115 Novel agricultural practices, such as agroforestry, intercropping, the use of perennials, organic farming or permaculture, are attempts to address durability issues. 16 Beyond the quantitative availability question, one certitude remains: biomass will remain readily available and universal in the long term.

3.2. Energetic considerations

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What is the relative importance of biomass in comparison with crude oil for energy needs? With an annual production amounting to 4 to 5.5 Gt (cumulating dry wood and crops such as cereals, oils and sugar) and a total use of fossils amounting to 15 Gt (including coal), the replacement of fossil fuels with phytomass seems very unlikely. 76,116 The addition to the mix of 3.3 Gt of grazed dry biomass used for livestock does not change the imbalance.⁷⁶ Furthermore, 3 t of biomass from wood or agricultural residues only contains as much energy as ~1 t of oil. Therefore, attempts to produce energy from lignocellulose will inherently be limited by the biomass growth rate. 117-119 Biobased energy can be obtained by direct combustion or conversion into CH₄ (biogas), H₂ (in a pure form or mixed in syngas), ethanol, biodiesel (transesterified oils or fats) or electricity. The case of biofuels is well-documented in the scientific literature and debated in terms of environmental effects. 76,120,121 The conversion of lignocellulose into H_2 is the subject of active research worldwide due to political incentives to replace fossil fuels with H₂. It can be performed by pyrolysis followed by steam reforming, gasification in supercritical compressed water, photocatalysis. 118,122-125 However, H2 is already mass-produced, generating 2.5% of global CO₂ emissions; it is currently an inefficient energy vector (reservoir leakages, limited yields)

and an important source of GHG. ^{63,122,123,126,127} About half of the total H₂ production is used for ammonia production. ¹²⁷ The limits to biomass availability and H₂ production yields mean that it will be a limited answer to the global energy demand; comparisons should also be made with more mature techniques that are less energy demanding, such as direct incineration or methanation in bioreactors with methanogenic archaea (landfill gas). Looking back in history, the quasi-abandonment of wood-gas generators in the mid-20th century is an interesting case study. It is largely attributed to an insufficient wood supply with respect to demand from the transportation sector for countries like France. Other disadvantages such as high maintenance, fire risks, long starting times or widespread carbon monoxide poisoning led to the abandonment of the technology in countries like Finland and Sweden. ¹²⁸

3.3. Carbon storage potential and the importance of forest management

Biomass growth is an important step because wood, algae or industrial crops emanate from very different environments (namely, forests, sea and agricultural land) with different carbon storage potentials. While forests store 45% of organic carbon in their tissues and in the soil, the complete conversion of all existing forests to grassland or cropland would increase atmospheric CO₂ by 130-290 ppm. 115 To establish a comparison, the current CO2 amount in the atmosphere is ~410 ppm (280 ppm in 1750, 315 ppm in 1958), with a current annual increase of ~2.4 ppm. At the current rate, it is estimated that the combustion of fossil fuels yields 5-6 Gt C per year whereas phytomass captures about 2 Gt C per year (Fig. 4). The carbon mitigation potential of phytomass is therefore very limited as long as fossil fuels are as widely used as they are today. Current estimates show that large scale forest plantations could reduce atmospheric carbon by 15-60 ppm, but this storage capacity would take about 100 years to be reached due to the time needed for the forests to reach maturity. 115 At longer timescales, from centuries to millennia, trees

will enrich the soil carbon content through organic matter transfer in the rhizosphere and *via* litterfall; this is how atmospheric carbon can be mitigated in the long term. Litterfall means a strong interaction with an incredibly rich soil ecosystem composed of xylophage fungi (rots), other fungi, shrubs, xylophage and non-xylophage insects, earthworms, *etc.* (some of these organisms are working symbiotically). In this context, one understands the beneficial role that forests could play in carbon mitigation and the ambiguous part of intensive agriculture for annual crop production.

Biomass stored in the permafrost could play a dramatic role in atmospheric CO₂ release. Rapid permafrost thaw is currently considered a high threat to climate goals (such as the Paris Agreement) because it could cause massive release of CO₂ and CH₄ into the atmosphere (and mercury into the oceans) in a few decades. These two greenhouse gases are either stored in the ice or produced by decomposing biomass that was previously stored in the ice; the resulting warming effect is not currently included in models but this permafrost carbon feedback could lead to temperature increases 10–40% higher than estimated. Methane has a GWP 84 times that of CO₂ over the first 20 years in the atmosphere, 25 times over a 100-year period and 7.6 times over a 500-year period. The limited lifetime of methane is explained by its photodissociation under UV radiation.

The complexity of natural forests means that their carbon storage capacity is higher than that of plantation forests. 115 Yet, plantation forests can be beneficial and they are most efficient carbon sinks in tropical regions; nevertheless, afforestation can have a negative effect at high latitudes, on peatlands or in grassland or savannahs. 115 For existing plantation forests, it is generally agreed that sustainable forest management, in contrast to abandoned plantations, can better mitigate carbon emissions. 133,134 For instance, prescribed fires are recognized as beneficial treatments that increase the resilience of stands to wildfires and the carbon storage capacity of the forest. 135-137 The carbon storage capacity of forests also depends on the use of the forest products. In terms of net CO₂ emissions, a scenario in which forests are left untouched is less interesting than a scenario in which wood products are used to replace fossil fuels: untouched forests are not an optimal carbon sink as long as fossil resources are burnt. 133,138 Some authors state that the substitution of fossil fuels and "fossil-intensive" materials by wood may be the best single opportunity for carbon mitigation.¹³³

Paradoxically, it is often suspected that forestry operations are ecologically detrimental and cause long-term soil fertility losses due to old tree cuts and intensive management for pulp or biomass use. ^{133,139,140} This perception is not senseless in the context where 99% of new plantation forests over last fifty years are monocultures, and where lots of them require the heavy use of fertilizers and pesticides, a little-known fact. ^{115,141–144} To provide an example related to soil fertility, it has been estimated that heavily utilized stands with 15-year to 30-year rotations could induce important soil organic matter and nutrient losses; these losses translate, in the case of

Douglas-fir stands on Vancouver island (Canada), to recovery times lasting up to 8 centuries. These suspicions should be considered carefully and they can be addressed with selection forestry and other sustainable management practices. 8,9,115,139 For instance, it is recommended to plant mixtures of species. Nevertheless, intensive practices can sometimes have benefits: it has been shown that soil fertilization in nitrogen-deficient soils could increase the biomass yield and carbon storage capacity of European forests and heathlands. 68,133,145

3.4. The interdependence of biomass and non-renewable resources

It has recently been estimated that man-made materials, including steel, concrete, glass, plastics, paper, wood and textiles, have outweighed the whole living biomass in 2020 (± 6 years), reaching about 1.1 Tt.⁷⁷ These colossal amounts of anthropogenic materials were produced because energy and ores were cheap and abundant. One might, however, question this trend. Indeed, it is now generally agreed that we are on the brink of peak oil (its annual production in 2020 was ~ 4.5 Gt). Peak coal is now almost a decade ago and peak gas is still to come. The offset of cheap energy abundance will cause a price increase and rarefaction of all materials, since the prices of extraction, processing and transportation will be cascaded and increased themselves. This will apply to biomass-based materials (construction wood, paper, etc.) as well.

The rarefaction of metals, and therefore rare earths, is well established. 63,146,147,266 This rarefaction is expected to come rather soon for zinc, silver, nickel and copper (Fig. 6). Many of these strategic materials are currently listed by the EU as being critical for the EU's economy. 114 In a similar manner to peak oil, these "metal peaks" will mark the time point after which the rate of extraction will decline due to diminishing ore grades and identifiable reserves. For instance, the approach of a "copper peak" is a threat to the wide-scale and long term deployment of microelectronics and large scale power installations. Semi-conductors are particularly threatened as they are used everywhere today in information and communication technologies. Metal rarefaction in conjunction with fossil fuel depletion is therefore expected to result in a change to the landscape with respect to materials in general, and electronics in particular, over the next centuries. 146,148 What's more, these metals are omnipresent in the current technological context and serve all stages of biomass transformation to useful materials.80 This anthropogenic transformation inevitably brings a certain amount of non-renewable resources to their life-cycle.

Advanced phytomass-derived materials exist with applications ranging from partly bio-based batteries to "tougher-than-steel" composites and lab on chips or medical assays (paper microfluidics) and they have a role to play in the future of materials science. However, forthcoming developments will need to be mindful of the interdependence of resources. To be sustainable, these developments have to minimise the use of non-renewables in the life-cycle of these advanced "green" materials. This also forces us to design

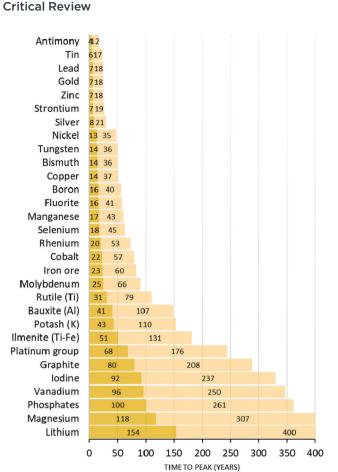


Fig. 6 Projection of the basic availability of chemical elements (essentially metals and common rare earths) according to current demand (light colour) and with a projected boom (10% per year) in demand (dark colour). Figure adapted from ref. 266.

materials that integrate a frugal circular bioeconomy to decrease the pressure on biomass production for material needs, so that biomass can be further exploited for energy and food.⁷⁶

4. Life cycle analysis and relevant quantifications

The previous parts helped to provide a global view of material and energy availability based on thermodynamics and data indices. In this part, life cycle analysis will be introduced to get a better insight into precise environmental aspects of phytomass use.

4.1. A succinct introduction to LCA

Life cycle analysis (LCA), sometimes referred to as "life cycle assessment", is a set of tools aimed at quantifying the total impact that a given material, technological implementation or service has on the environment. LCA emerged in the 1960s due to a rise in environmental concerns. In practice, the results are used to rank or evaluate services or processes in terms of

their environmental footprint. The results can be used to reduce the environmental cost, to compare two solutions, to inspire technological developments, to modify a product's design or to phase out outdated practices. 148 LCA can also be used to document environmental impact reports. LCA can reveal positive outcomes in terms of health, ecosystems or employment. To do so, a LCA integrates the physical fluxes (matter and energy) embodied in the different life stages of a product. There are thus three important aspects that define LCA: energy fluxes, matter fluxes and life stages. Firstly, the energy fluxes should accurately reflect the type of energy and the amounts that were used. In general, the energy comes from three different sources: fossil fuels (coal plants, gas turbines, petrol and diesel generators or combustion engines), uranium (nuclear energy) or renewable energy (biomass, hydroelectric power, solar panels, wind energy). These three sources have very different environmental footprints in terms of resource consumption, greenhouse gas emission and water footprint. In some cases (sawmills, pulp and paper plants), the energy comes directly from biomass by-products (sawdust, lignin) through incineration. Regardless, the energy used at each stage of manufacture is highly dependent on the location of the plant and so are the modes of transportation (trucks or container ships, air freight, trains, cars, etc.). Secondly, the fluxes of matter take into account steps such as mining used for ore extraction, pulping for cellulosic materials, oil extraction for synthetic polymers, refining, transformations, synthesis, enrichment, land management, etc. Thirdly, the description of the different life stages (and their boundaries) is paramount in the description of the working hypothesis. These stages are commonly fractionated into manufacturing steps, transportation, use and disposal scenarios; the study can be narrowed down to any of these subsets. Therefore, LCA can make a global "cradle to grave" assessment but it can also serve to estimate pollution produced by different life stages of a given item or by the item in different life scenarios (for instance, by adjusting the primary energy source or by envisaging different end-of-life scenarios). Various categories of truncated (or partial) LCA have been identified in the literature: the "fence line approach" (product use on site), the "cradle to gate" (from the resource to the factory gate), the "cradle to cradle" in the context of recycling, the "gate to gate" when only one manufacturing/modification step is concerned, the "well to wheel" in the context of transportation or the "field to fork" in the context of food production. 148 LCA has been normalized through a set of norms ranging from ISO 14040 to ISO 14049. These harmonized practices are important for interoperability reasons, since each subpart of an LCA has its own set of scenarios that might have been assessed using independent LCA and included in databases. The use of these databases permits the construction of complex scenarios and emphasizes the importance of LCA normalization and interoperability. In practice, LCA has been employed in various situations to assess how beneficial it would be to use electric powered vehicles instead of diesel engine vehicles, to insulate houses, to recycle construction wood instead of putting it into landfill, to recycle paper instead of burning it for energy recovery, to travel by train instead of travelling by air, to recycle batteries instead of

manufacturing new ones, etc.^{76,148,153} LCA fundamentally questions the design of technological items, industrial processes and even political choices. Many counterintuitive results have shown that "common sense" is not an appropriate approach to evaluate environmental policies. Moreover, modern LCA can evaluate the social dimension of a technological system through relevant impact categories and provide information in terms of health and safety (work-related injuries or cancers, psychological stress), discrimination (salary fairness, forced sterilization), restrictions of freedom and associations (child or forced labour), security of living conditions, delocalization, corruption, social benefits, etc.^{154–156} These are very relevant categories when dealing with agricultural resources shared on a global market.

In general, the LCA is built in a four stage process. 157 This four step process is a direct implementation of the ISO14000 norm and it differs from earlier methodologies with a narrower focus on improvement analysis. 139,148 In the first stage, the objectives and boundaries of the study need to be declared. This declaration will first and foremost include the use of the study (ecoconception, comparative assessment, environmental impact) and the functional unit (a car bonnet, a shopping bag, a kilogram of polymer, etc.). The calculation methods, data sourcing and the boundaries of the study (geographical validity, temporality, raw materials, energy sources, manufacturing, formulation, processing, transportation, distribution, use, reuse, maintenance, recycling and waste management, cases not included) are also indicated at this stage. The second stage is named the life cycle inventory (LCI) and its goal is to make an exhaustive report of the quantitative fluxes associated with the case study. The fluxes can conveniently be expressed through a flow diagram. These fluxes will be expressed in the same physical unit(s); they can be calculated from first principles or extracted from the relevant scientific literature, from public or free databases (US DOE, ADEME, USDA, lcadatabase.com, agribalyse), from restricted databases (Idea, ALCIG, DATASMART LCI package, etc.) or from database aggregators (OpenLCA Nexus, for instance). LCIs include, if relevant, inputs (raw material supplies, energy consumption, fossil fuels, etc.) and outputs such as atmospheric, land and/or water emissions (CO2 equivalent, CH₄, NO_x emissions, other greenhouse gases, PO₄ diffused in water, cumulative radiative forcing, etc.). Interestingly, it is possible to integrate thermodynamic aspects (such as exergy) in conventional LCA.80 The output streams are often classified in various categories such as human health (organic or inorganic carcinogens, ozone layer, etc.) or ecosystem quality (eutrophication, acidification, land use, ecotoxicity, water footprint, etc.). Experimental data and actual on-site measurements can be inaccessible and therefore missing from the LCI. In the third phase of the analysis, the impacts will be evaluated by convoluting life scenarios and the LCI. In the fourth stage, the results will be interpreted and discussed in the light of restrictions (boundary conditions) imposed at the start of the study. In particular, potential biases and incompleteness, various limitations due to restricted data availability and methodological sensitivity should be discussed, as it is not uncommon to find contradictory results (positive or negative footprints, values one order of magnitude different, *etc.*).^{132,133} This last step is critical because the complexity of fluxes involved in any LCA is such that the analysis will inevitably be incomplete, as discussed in the introduction of this part.

Subsequently, a critical review can be made by certified experts to check its validity with respect to the norm. The experts should be recognized for their competency in both the field of study and LCA in general; their task will be to verify the different stages of the analysis in terms of methodology (adequacy with the norm, possible conflicts of interest, scientific and technological plausibility) and in terms of data sourcing and calculations. They will also verify the interpretations (coherency with the hypothesis and limits of the study, likelihood of the extrapolations) and transparency of the study.

4.2. LCA and other environmental indicators of biobased materials

This subchapter will report some interesting results from the literature that are related to biobased materials. In general, these studies are used to make comparisons between different life scenarios or between biobased materials and non-renewable ones in the context of a life service. The case of materials used in medicine will not be treated because the services rendered are invaluable. When relevant, LCA data are completed with data from the literature. For instance, supplementary figures related to carbon emissions are given.

4.2.1. Biopolymers. About 4% of fossil fuels are used for the production of plastic materials, and 99% of the feedstock used for their production comes from fossil fuels.²⁶³ Because of their environmental persistence in the form of macroscopic or microscopic entities, plastics are a major source of pollution with disruptive effects on organisms and the environment. As a consequence, plastics have been considered as an important subcategory (named "novel entity") in the planetary boundary safe operating space, aside more traditional geological boundaries such as ozone depletion, freshwater use or N and P flows. 2,262 Therefore, it is of major interest to study biobased and biodegradable alternatives. There are many LCA works on biobased polymers and there are no clear trends for whether these biobased alternatives are environmentally beneficial (Table 1). 159-165 The goal of this paragraph is thus to paint a simplified portrait of the main results through representative examples.

PLA is often cited as an example of a biobased polymer. It is repeatedly claimed to be biodegradable, whereas it is in fact biodegradable only in industrial composting facilities. ¹⁶⁴ Being produced from corn or sugarcane, PLA is a typical example of a biobased material in competition with food resources. ¹⁶² In a study dedicated to the cradle to gate analysis of PLA from sugarcane in Thailand, it was found that this polymer resulted in 500–800 kg CO₂ eq. emissions per ton, about half of that of PP or PET. ¹⁶⁶ In this context, the primary energy demand is similar to that of comparable synthetic polymers. Since PLA is based on an agricultural system, it has trade-off contributions to acidification, photochemical ozone creation, eutrophication and farmland use. Its human toxicity potential was found to be similar to that of PE, PET, PP or PS. These results were later confirmed

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and similar trends in comparison with their fossil-based equivalents were found for other biobased polymers such as PHA, thermoplastic starch, biobased HDPE or biobased PET. Therefore, the advantage of biobased polymers in terms of global warming potential (GWP) and their disadvantages in terms of eutrophication, acidification or ozone depletion seem rather universal, since this trend is reported in a wide range of peer-reviewed articles or book chapters, including literature reviews. 160-163,167-170 The mentioned drawbacks largely stem from the use of nitrogen-rich fertilizers in intensive agriculture. Regarding different end-of-life scenarios, it was assessed that the compostability of biobased polymers was not necessarily advantageous when compared to recycling of traditional polymers, because recycling strongly mitigates the GWP associated with the production of new plastics, as well as fossil fuel depletion. 161 Furthermore, there are lots of uncertainties regarding methane emissions associated with end of life scenarios of PHA and PLA when they are sent to landfill or composted; these uncertainties can translate to a greatly increased GWP. 161,163,166 The other main reproach that could be addressed for these analyses is their tendency to minimize the environmental burden associated with the "stochastic" fate of polymers in the environment: polymers in general cannot go through a strictly controlled end-of-life. Some accidently end-up in the environment and generate microplastic pollution in soils, animals or water; others will be burnt in an uncontrolled manner, generating toxic fumes. Both outcomes suggest very different impacts than initially predicted by LCAs. They underline the need for continuous research on true biodegradability, a domain that could benefit from advanced techniques such as isotope-ratio mass spectrometry or FTIR microspectroscopy. 171,172 Overall, there still are uncertainties about the environmental benefits of biobased polymers with respect to fossil-based polymers, and there is room for more comparative studies with consistent methodologies. Furthermore, this domain will certainly benefit from

4.2.2. Textile fibres. Cellulosic fibres are very widespread due to their use in the textile industry, as reinforcements in composite materials but also for other uses such as air or liquid filtration. Cellulosic fibres include natural bast fibres from hemp, from flax or from plants belonging to the Urticacea family (ramie, nettle); they also include cotton wool or man-made fibres. Cellulosic man-made fibres are sometimes called artificial silk and they are made of wood pulp. These fibres are usually categorized in different groups depending on their manufacturing process. Historically, these fibres were made by the viscose process and they are found under the trade names Viscose, Rayon or Modal. The viscose and modal processes rely on the reagent CS₂ to form cellulose xanthate during the process. The viscose process is also used for the production of cellophane, dialysis membranes and household sponges. A more recent process in which cellulose is dissolved in aqueous N-methylmorpholine N-oxide (NMMO) without derivatisation has been proposed to address some of the toxicity issues inherent to the viscose process. A thorough presentation of the NMMO technology can be found in a previous work. 176 The fibres made

more thorough social life-cycle assessments. 173

using this process are found under various trade names such as Lyocell, Alceru, Newcell or Tencel, but "lyocell" has gained acceptance as a generic name. As to the viscose process, it is universally recognized as being a polluting process from its early uses to the present day. 177-179 This is in large part due to the use of CS₂, a known powerful neurotoxin. This strong reactant is known to cause deleterious health effects to the workers who are exposed to it, such as skin colouration, paralysis, cardiovascular diseases, impotence, teratogenicity and hysteria. 178 Many cases of CS₂ intoxication were reported in Britain at the start of the 20th century in the viscose industry, and in more recent times in the USA. 178,180 Sadly, carbon disulfide's acute health effects still affect dwellers living near viscose plants today, such as those living in Nagda (Madhya Pradesh, India), due to air, water and crop pollution. 179,181,182 Since these side-effects are not thoroughly documented, they have not been integrated in current LCA. Such effects could be accounted for in terms of human and ecosystem ecotoxicity due to the chemicals used during the manufacturing process. They also have a high social cost.

Shen and coworkers have proposed a "cradle-to-factory gate" LCA of man-made cellulose fibres in comparison with three commonly used textile fibres: cotton, PET and PP fibres. 183 Whereas Austrian viscose or modal plants make use of the byproducts (black liquor and bark) for energy needs, similar representative factories located in Asia rely on fossil fuels or electricity from the local grid. This difference is due to the integration of dissolving-grade pulp preparation in the Austrian plants, as opposed to pulp import. Therefore, these plants are good examples of integrated processes in which biomass is used both for material and energy needs. In comparison with the viscose process, the NMMO process has the benefits of functioning in a nearly closed-loop cycle, thereby greatly reducing the amount of residual chemicals to be treated or recycled. 184,185 A level of uncertainty in these results is induced by the non-inclusion of potentially deleterious forestry practices and their potential impacts on the ecosystem (rotation period, soil nutrient depletion, use of pesticides, etc.). Nevertheless, the LCA demonstrated that the primary energy requirements for Tencel and Austrian viscose were of the same order of magnitude as that of cotton (2.0 CO₂ eq. per t fibre, the least energy intensive fibre in this study), with a lower amount of non-reusable energy (oil, gas, coal or uranium) needed. Older Tencel processes or Asian viscose required more primary energy than more controlled and recent alternatives, in large part because of the non-integrated pulp production and inherent transportation costs; nevertheless, all man-made fibres relying on renewable energy (often biomass) for their processing were emitting ~100 times less CO2 per t of staple fibre. Furthermore, man-made cellulose fibres use 100-500 times less water than cotton if cooling water is ignored, and 10-20 times less water if cooling water is taken into account.183 Because irrigation water is often pumped underground (70% estimate), its intensive use for cotton growth can come in conflict with freshwater for basic human needs. 105,183 Furthermore, cotton has an estimated freshwater and terrestrial ecotoxicity about 100 times higher than any other man-made fibres, including PET and PP, and this is due

Table 1 Life cycle analysis of various biobased and fossil-based polymers. List of abbreviations: GWP: global warming potential; TE: terrestrial eutrophication; FE: freshwater eutrophication; OD: ozone depletion; HT: human toxicity; ET: ecotoxicity; DCB: 1,4-dichlorobenzene; CTU: comparative toxic unit; CFC-11: trichlorofluoromethane

Product	Impact analysis	Interpretation or additional information
PLA from corn ¹⁶³	GWP: 3.1 kg CO_2 eq. per kg granule; eutrophication: 0.024 kg N eq. ; acidification: $0.62 \text{ mol H} + \text{eq.}$; OD: $3.5 \times 10^{-7} \text{ kg CFC-11 eq.}$; HT carcinogens: $1.5 \times 10^{-7} \text{ CTUh}$	A meta-analysis showed that whereas on average the GWP was around 0.7 kg CO ₂ eq., it could increase to 3.3 kg CO ₂ eq. when the end of life was included
PHA ¹⁶³	GWP: 0.4 kg CO ₂ eq. per kg granule (meta-analysis)	A meta-analysis showed the GWP could increase to 3.1 kg CO ₂ eq. when the end of life was included
Thermoplastic starch ¹⁶³	GWP: 2.0 kg CO ₂ eq. per kg granule; eutrophication: 0.009 kg N eq.; acidification: 0.53 mol H + eq.; OD: 2.9 \times 10 ⁻⁷ kg CFC-11 eq.; human health carcinogens: 8 \times 10 ⁻⁸ CTUh	A meta-analysis showed that whereas on average the GWP was around 1.1 kg CO ₂ eq., it could increase to 1.3 kg CO ₂ eq. when the end of life was included
Fossil-based HDPE ^{163,166}	GWP: 1.9 kg CO ₂ eq. per kg granule; eutrophication: 4×10^{-4} kg N eq.; acidification: 0.33 mol H + eq.; OD: 0 kg CFC-11 eq.; human health carcinogens: 6×10^{-8} CTUh	Synthetic HDPE used as benchmark
PLA from sugarcane ¹⁶⁶	GHG emission: 0.5 to 0.8 kg CO_2 eq. per kg granule depending on the energy mix; acidification: 2.1×10^{-2} kg SO_2 eq.; Eut: 5×10^{-3} PO ₄ ³ eq.; ozone creation: 3.4 $\times 10^{-3}$ kg C_2H_4 eq.; HT: 8.5×10^{-3} kg DCB eq.	If PLA is incinerated, its GWP would reach 2.33 kg CO eq. per kg of granules. In the same study, HDPE is cor sidered less favourable in terms of GWP, but more favourable in terms of acidification, eutrophication, ozone creation or human toxicity
Biobased HDPE from sugar beet ¹⁶⁹	GWP: 1.6 kg; acidification 10.6 mmol H $^+$ eq.; TE: 38.6 mmol N eq.; FE: 2.61 g P eq.; fossil fuel depletion: 520 g oil eq.; for ethylene production only: OD: 3.3 × 10^{-4} g CFC-11 eq.; land use: 2.37×10^4 g C deficit; mineral depletion: 60.19 g Fe eq.	
Biobased HDPE from wheat ¹⁶⁹	GWP: 1550 g; acidification 16.5 mmol H $^+$ eq.; TE: 62.2 mmol N eq.; FE: 0.75 g P eq.; fossil fuel depletion: 460 g oil eq.; for ethylene production only: OD: 3.4×10^{-4} g CFC-11 eq.; land use: 8.28×10^4 g C deficit;	
Fossil-based HDPE ¹⁶⁹	mineral depletion: 100.11 g Fe eq. GWP: 4050 g; acidification 3.2 mmol H ⁺ eq.; TE: 7.5 mmol N eq.; FE: -1.2 g P eq.; fossil fuel depletion: 1280 g oil eq.; for ethylene production only: OD: 2.9 × 10 ⁻⁷ g CFC-11 eq.; land use: 5.82 g C deficit; mineral	
Biobased PET from woody biomass ¹⁶⁸	depletion: 0.64 g Fe eq. For many categories (climate change CO_2 eq., acidification kg SO_2 eq., TE mole N eq., human health particulate PM 2.5, smog kg 03 eq., ET CTUe, OD kg CFC-11 eq.), the impact increased in the following order: fossil based TA < wood-based TA < corn stover-based TA; for each subset, the impact increased according to fossil $EG \ll corn EG <$ wheat straw $EG \ll switchgrass EG$; only fossil fuel depletion was generally lower for all biobased alternatives (up to 22%)	If carbon sequestration is hypothesized due to biogent carbon stored in biobased PET, then biobased alternatives could have 21% lower GWP
Biobased epoxy (super entropy) ¹⁶²	GWP: 4079 g CO_2 eq.; abiotic depletion: 0.01 g Sb eq. ; acidification 25 g SO_2 eq.; Eut: 6.9 g PO_4 eq.; freshwater aquatic ET 66 g DCB eq. ; terrestrial ET: 229 g DCB eq. ; cumulative energy demand: 1.90 kJ eq. ; OD: $0 \text{ g CFC-}11 \text{ eq.}$; HT: 545 g DCB eq.	Comparison with a petroleum-based epoxy resin: GWF 6663 kg $\rm CO_2$ eq.; abiotic depletion: 59.4 kg Sb eq.; acic fication 40 kg $\rm SO_2$ eq.; eutrophication : 6.6 kg $\rm PO_4$ eq.; freshwater aquatic ET 246 kg DCB eq.; terrestrial ET : 29 kg DCB eq.; cumulative energy demand: 2.16 MJ eq OD: 1.26×10^{-6} kg CFC-11 eq.; human toxicity : 490 kg DCB eq.
Biobased polyamide Vestamid® Terra DS ¹⁷⁴	GWP: 4 kg CO_2 eq.; abiotic depletion: 0.0639 kg Sb eq.; acidification 0.0748 kg SO_2 eq.; Eut: 0.0848 kg PO_4 eq.; freshwater aquatic ET 0.0342 kg DCB eq.; marine aquatic ET 4030 kg DCB eq.; terrestrial ET l: 0.0132 kg DCB eq.; primary energy demand: 231 MJ; OD: 2.58 × 10^{-7} kg CFC-11 eq.; HT: 1.12 kg DCB eq.	This polyamide is 100% based on castor oil
Cellulose acetate from corncob from a green approach ¹⁷⁵	GWP: $176 \text{ kg CO}_2 \text{ eq.}$; abiotic depletion-fossil: $2.56 \times 10^4 \text{ MJ}$ eq.; terrestrial acidification 10.1 mol H ⁺ eq.; TE: 17.1 mol N eq.; FE: 0.411 kg P eq.; marine Eut: 1.61 kg N eq.; OD: 8.46×10^{-3} kg CFC-11 eq.; terrestrial ET: 0.0132 kg DCB eq.; freshwater ET: 32.4 CTU ; HT noncancer: $2.27 \times 10^{-4} \text{ CTU}$; HT cancer: $6.05 \times 10^{-5} \text{ CTU}$	

to heavy pesticide use. Eutrophication and land use also disfavoured this cultivar. Asian viscose, PET and PP fibres had the highest GWP, due their reliance on fossil fuels. Data of manmade cellulose fibres in terms of CO2 emissions and low water consumption were also confirmed in a metastudy by other authors. 186 In a subsequent study, Shen et al. compared PET fibres, biobased PET fibres, recycled PET fibres, recycled PET, biobased PET fibres and PLA. They found out that the GHG emissions were ranked according to: PET > bio-based PET > PLA > recycled PET > recycled and biobased PET > man-made cell-ulose fibres.

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Ionic liquids (ILs) have been an intensive research topic in the last 20 years. These liquids can be tailor-designed and some of them have proved to be very efficient cellulose solvents. Imidazolium-based solvents have been particularly scrutinized. 188-190 In a study aiming to compare the potential use of the IL BmimCl with NMMO (Lyocell process), it was found that BmimCl was less favourable in terms of GWP, abiotic resource depletion, acidification potential, photochemical ozone creation potential, freshwater aquatoxicity potential and volatile organic compound emissions. 191 Nevertheless, the developmental toxicity of ionic liquids has been assessed and the results of this LCA could benefit from available toxicity data. 192-195 It is also well-known that the purity of ILs is a sensitive issue and that "real world" industrial ILs could depart from "academically perfect" laboratory-grade quantities. This study shows how hard it is to use LCA in a prospective way because of the unknowns persisting when a process has not been upscaled, including the EU REACH registration of the chemicals themselves.262 The development of biobased deep eutectic solvents could potentially improve the health track of ILs without compromising performance. 196,197

The case of natural fibres other than cotton should be mentioned. There seems to be no consensus on the overall $\rm CO_2$ emissions of flax, hemp or jute fibres, but these fibres require much less irrigation than cotton, if any. 105,186 The $\rm CO_2$ footprint of wool varies greatly across studies and it can amount from 1/2 to as much as 20 times that of cotton, because sheep are ruminants that emit methane. 186 If sheep's wool is considered a byproduct of meat production, the carbon footprint can be negative since wool production is a way to avoid waste generation. 186

As of today, the textile industry remains heavily polluting. 105,198 Post-finishing treatments (bleaching, scouring, dying and water-repellent, flame-retardant or antibacterial treatments) also contribute to their environmental impact. One ton of textile pollutes 200 t of water and the textile industry is responsible for $\sim 8-10\%$ of global CO₂ emissions. 105,179 In this context, it is important to prioritize, in descending order, actual textile use (30% of garments are not even sold or worn), durability, reuse and recycling. 105,132,186,199 Incineration and landfill are not desirable and reuse is relevant only if the environmental cost of it (advertising, internet sale, transportation, etc.) does not exceed the cost of production and distribution of equivalent garments. 105,132,200 Other options, such as textile renting, updating or repairing, are of course expected to be eco-efficient. Researchers also explore textile recycling and the separation of polyester blended fabrics by selective dissolution of cellulose or wool using ionic liquids, or by selective degradation with keratinases to separate wool from polyester. 199,201-203 These approaches have the advantage of dealing with biodegradable/non-biodegradable blends. These blends could otherwise not be recycled as textiles.

4.2.3. Composites for lightweight applications. Fibrereinforced composites are often considered as the pinnacle of modern materials as far as mechanical properties are concerned. It is therefore interesting to evaluate the performance of biobased alternatives in terms of their life cycle. For instance, a study has been conducted on carbon fibre parts for automotive applications (a floor pan), to replace steel.²⁰⁴ Pyrolytic recycling of the carbon fibres was part of the scenario. The manufacturing of carbon fibre composites is about 14 times more energy intensive than steel, but this energy cost is somewhat compensated for by the weight savings in the vehicle that result in lower emissions (84% of the energy is engaged during the use stage), resulting in equivalent primary energy uses and slightly lower CO₂ emissions (9.5% at best). However, the use of lignin based carbon fibres was advantageous when compared with synthetic PAN-based fibres, both in terms of CO₂-equivalent greenhouse gas emissions (-22%) and primary energy (-5%).204 Another interesting study reported the replacement of steel by wood-based materials (made of a viscose fabric and hardwoods) in the side impact beams found in the doors of passenger cars; environmental benefits (ecosystem, human health and resources) in the order of 20% were largely due to weight reductions. 154 The study also pointed out that the wood solution resulted in increased land use (+30%) and similar marine eutrophication but social, political and economic benefits by promoting local employment and secure living conditions. Kraft pulp or wood fibres can advantageously reinforce PP and reduce the GWP of neat PP by 14% to 35%. 205,206

It has long been suspected that the replacement of glass fibre-reinforced polymers with natural fibres such as hemp fibres could lower CO2 emissions and decrease crude oil consumption because natural fibres have outstanding mechanical properties along the fibre axis.²⁰⁷ In a recent study, the use of jute fibres instead of glass fibres was studied for buggy bonnets.²⁰⁸ This study revealed that the use of jute had moderate environmental benefits that were essentially due to weight savings and to the production stage. A reduction of ~10% in fossil fuel use was achieved. However, jute had large social advantages since jute cultivation promoted local farming and limited exodus from rural areas. In a more general study, it was found that natural fibre reinforced composites generally had a lower environmental impact when compared with glass fibre automotive parts for four main reasons: (i) their production pollutes less and acts as temporary carbon storage, (ii) the fibre volume fraction is higher when natural fibres are used, which means that less of the more polluting resins are needed, (iii) lighter weight means a better fuel efficiency of the vehicles during use and (iv) incineration of these parts permits energy recovery. 209 However, the use of agricultural crops can have disadvantages too, as the use of fertilizers is known to induce water pollution (acidification and eutrophication).²⁰⁹ It is worthwhile to note that conventional surface treatments performed on natural fibres do not significantly weigh on their LCA outcome: they are much less energy intensive than the processes used for nanofibre production. 208 Since the matrix is

contributing a significant part of the environmental footprint, another idea would be to replace "virgin" polymers with recycled ones for automotive parts. In this case, LCA has proved the absence of environmental benefits due to lower mechanical performances of the matrix, meaning no weight gain. 210 Very different results are obtained in the context of larger vehicles (buses or trucks) where larger structural steel parts can be replaced with pultruded glass fibre composites. 211 In this context, the energy savings in use (i.e. during the service life of the vehicles) are very significant due to induced weight savings and fuel efficiency; however, it is not clear whether pultruded glass fibres can compete against aluminium, because aluminium can be recycled while providing similar weight savings. 211

Generally speaking, natural fibres can result in 10 to 20% lower environmental load for automotive parts due to their strength and stiffness. One would think that the opportunity provided by nanocelluloses in terms of mechanical performance could be even greater for the LCA.²¹² Nevertheless, energy demanding manufacturing processes can tip the balance backwards. Despite their excellent mechanical properties, both bacterial cellulose and nanofibrillated cellulose (NFC) suffer from the high energy cost and low yield of their production stage. 212-214 This burden weighs heavily on their life cycle. As a result, these technological solutions are presently less favourable than that of glass-fibre/polypropylene composites or neat PLA in an automotive context.²¹⁵ In a gate-to-gate approach solely taking into account the manufacturing process, the production of cellulose nanowhiskers can be equivalent to or better than carbon nanofibres in terms of GWP or human toxicity (DCB).²¹⁴ However, these results ignore the lifetime uses of the products and the end-of-life scenarios, but the expansion of nanocelluloses should be accompanied with an updated LCA.

4.2.4. Insulation. Dealing with insulation, the use of dynamic LCA is of prime importance because buildings have long lifespans, and the large amounts of carbon stored in the form of insulation will be released at the end of life. In the meantime, plants will have grown and stored more carbon. 216,217 However, this carbon cycle depends on the plants studied: for instance, trees grow slowly and the amount of carbon stored after growth equals the amount initially credited once a forest rotation is over. A forest rotation can last a century, and it typically ranges from 45 to 120 years. 217,218 In contrast, fast growing annual plants (crops) essentially regenerate the amount of carbon stored within a year. In practice, dynamic LCA shows that some technical solutions could appear beneficial for mitigating global warming in the short term (20 to 100 years), whereas biogenic carbon cycles and methane decomposition mean that the real impact should be estimated for longer time intervals, ranging from 500 to 1000 years, especially when wood is used.216,217,219 As a result, climate impact assessments can appear contradictory depending on the choice of static or dynamic LCA treatment. 217,220

It is demonstrated using dynamic LCA that biobased walls insulated with straw, a very frugal technology, are preferred over conventional insulating materials (such as glass wool or

expanded polystyrene insulation) because no matter how efficient these modern materials are, they always contribute a emission and ever-increasing forcing. 216,218,219 Since CO₂ emissions are purely cumulative (as opposed to CH₄), the climate impacts of these synthetic materials measured in terms of radiative forcing are most detrimental in the long term. Furthermore, the use of fastgrowing lignocellulosic crops such as flax, barley, oat, wheat, corn, or hemp can yield interesting by-products (shives, straw) that can directly be integrated into wall insulation, which offers the chance to rapidly sequester CO2 in building materials.216,218 A scenario in which building facades are extensively renovated in 28 European countries with straw shows that ~500 to 700 Mt CO₂ eq. can be stored in the next 200 years and carbon neutrality would be almost immediate.218 In contrast, insulation with timber and glass wool would take about 150 years to reach carbon neutrality and a classical expanded polystyrene solution would yield 300-400 Mt CO₂ eq. by the 2220 horizon. The net difference between these two material choices is about 1 Gt CO₂ eq.; as a comparison, it was estimated that the GHG emissions of the oil industry due to gas flaring (such as methane leaks) and thermal extraction of heavy crude oil was ~1.7 Gt CO2 eq. in 2015 alone.221 The total GHG emissions due to combustion are about 20 times higher (the contribution of methane is important).

Another idea would be to green-up the building envelope because this practice could be beneficial in terms of ecological diversity, air quality, psychological well-being, sound reduction and thermal insulation. Green facades (a.k.a. "vertical gardens") are known to trap a layer of air against the facade, which helps to insulate the building in windy conditions, but they also provide some cooling effects in warmer conditions because they protect the facade from direct sunlight and help to cool it by evapotranspiration.²²² In a LCA performed on different types of technical solutions, direct greening (natural growth of Hedera helix, commonly named ivy) had a negligible environmental footprint in its implementation, while providing significant savings for cooling in a Mediterranean climate. More advanced solutions, such as living wall systems with planter boxes or felt supports, provided better insulation for both cooling or warming, in temperate (Netherlands) or Mediterranean climates. Unfortunately, their environmental benefits in terms of insulation were largely offset by the energy required to produce the materials used for structural supports (steel profiles, HDPE boxes, PE fleece, etc.), the irrigation system and the use of tap water and nutrients to maintain these walls.²²²

A lot of research is devoted to the manufacturing of light-weight cellulose materials, such as nanocellulose foams, for thermal insulation or sound absorbance.²²³ However, these materials often rely on supercritical drying or freeze-drying, two energy intensive processes that are too long and costly to replace mass-production techniques. These remain laboratory achievements that cannot yet be transposed in an environmentally desirable way to commercial uses, but future enhance-

ments are expected to solve the challenge of drying under ambient conditions.

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4.2.5. Structural applications in building. Despite its green aura, construction wood is also heavily dependent on the use of fossil resources. Furthermore, the end-of-life of these products, whether being sent to landfill, used for methane production or re-used, is paramount with respect to their environmental footprint. 133 A study has been performed to evaluate the cradle-to-gate energy use of 1 m³ of construction wood in a North American context; several types of products were considered, such as glue-laminated timber, green and kiln-dried lumber, laminated veneer lumber, softwood plywood and oriented strand boards (OSB). 139 The results showed that a third of the energy used for manufacture originated from biomass, while the remainder originated from non-renewable resources. A margin of improvement can be found by exploring energy-efficient drying and hot-pressing processes, alternative resins, lower resin content and by maximising the use of biomass for energy production. Another study focused on the quantification of CO2 and greenhouse gas (GHG) balance due to the use of wood or concrete frames for the construction of a multi-storey building. 138 The main outcome of this study is that the GHG balance of wood frames will be very undesirable (i.e. positive) if the construction material is sent to landfill. This is due to the emission of methane. The emissions are then comparable to that of concrete frames. Whereas concrete frames will initially release about 1.5-2 times more CO2 due to cement production, the carbonization process in-use (and reabsorption of atmospheric CO2) will eventually halve that total emission. Unsurprisingly, the scenarios in which wood is reused will be more desirable (slightly positive emissions). If biomass is re-used for energy purposes (biogas collection or burning), the GHG balance will be minimal. Improvements for better GHG mitigation include the use of logging residues, sawmill wastes and used wood frames to replace fossil fuels. 138 This study can nevertheless be criticized because the time between the start of the service life and the end-of-life is sufficiently long to justify the use of dynamic LCA.216,219 A dynamic LCA of a complete bio-based wall made of a timber frame and insulating straw bales tends to prove that the long term (200 to 800 years) cumulative GWP of the wall that is composted at its end-of-life is lower than the same wall that is incinerated.219 This counterintuitive result is due to the fact that radiative forcing is due essentially to CO2 and CH4. However, CO₂ emissions are cumulative over time, whereas atmospheric CH_4 more dynamic due is photodissociation.^{2,219}

4.2.6. Paper and its connection to digital uses. An oftencited green example is that of disposable plastic carrier bags over paper bags. Surprisingly, the answer is that plastic bags "cost" less to the environment than their "natural" paper counterparts when they can be recycled, in large part because they are lighter but also because paper manufacture and recycling are energy intensive and generate chemical effluents. ^{148,224} It is also interesting to compare scenarios in which paper is recycled (in a closed-loop scenario) or inciner-

ated, or in which the "untouched" forest, spared due to recycling, can be used for something else, such as biofuel production as a replacement for fossil fuels, or simply as an energy source. 225,226 Unsurprisingly, the latter scenario is the most advantageous in terms of energy use, CO2 emissions and SO₂ emissions. In contrast, since 1 kg of corrugated board sent to landfill leads to the emission of approximately 130 g of methane, the landfill scenario is the least desired one.²²⁶ Paper incineration with energy recovery is an interesting option as well. Paper grades have different environmental footprints: thermomechanical pulping is less energy intensive than chemical pulping (resp. 42.5-45 GJ t⁻¹). Nevertheless, thermomechanical pulping emits more CO₂ (1450 kg CO₂ per t) than chemical pulp (300 kg CO₂ per t) and it is both more energy-intensive and CO₂-emitting than recycled pulp (resp. 13 GJ t⁻¹ and 800 kg CO₂ per t). ²²⁵ Unfortunately, the choice of paper grade depends on the final product (printing paper, newsprint, sanitary paper, corrugated board, etc.). Life-cycle energy breakdowns show that sanitary paper is the most energy intensive paper grade (~15 GJ t⁻¹ of paper) because the fibres cannot be recycled or incinerated at the end-of-life. 225 Reducing the filler content in printing paper enables better energy recovery and it alleviates the environmental burden of filler processing (calcium carbonate or kaolin are not renewable resources and need to be extracted from geological resources). In the context of the Netherlands, a 75% recycling rate of mixed board and paper is estimated to induce a saving of ~ 1.1 t of CO₂ per t of paper, in comparison with a scenario without recycling.225

There exists a strong connection between printing paper, information storage and the digital world. Information and communication technologies (ICT) have a huge ecological footprint that is largely ignored because the material aspect of ICT is hidden away from the user. Data consumption is out of control, as it was estimated that each individual on Earth was associated with ~1.7 Mo per s in 2020.227 ICT used ~3-4% of primary energy and emitted 3-4% of GHG in 2017; the use rate was increasing ~9% per year by early 2019. 228-230 It is projected that ICT could contribute 20% and as much as 51% of electricity demand in 2030.229 In the worst case scenario, ICT would account for as much as 23% of GHG emissions in 2030. Post-pandemic projections cannot yet be established with clarity.²³⁰ As a comparison, airplanes, which are often blamed for being heavy polluters, accounted for 2% GHG and the rate of flight commutes was estimated to increase by 5% per annum in 2017. Digital services in general, and data storage in particular, are therefore considerable GHG emitters and cannot be ignored when discussing sustainability.

Is it more sustainable to use interconnected, digital objects, rather than printed paper? Conflicting estimates show that decisive conclusions can hardly be made due to the fast evolution of ICT.²³¹ Other results show that the environmental burden of paper is higher in terms of GHG or energy use when paper is not recycled, but falls in the same range as that of pure digital alternatives when paper recycling is included in the scenario.^{232,233} It has been found in other studies that the

environmental impact of e-readers depended on the content read: they were less disadvantageous when replacing "long term prints" such as books, in contrast with newspapers. Nevertheless, these studies ignore at least part of the digital equipment production in their inventory, whereas this production phase is usually dominant in these LCAs since they include the important energy consumption and environmental burdens induced by rare earth or metal extraction. 234-236 For instance, the environmental footprint (eCO₂) of smartphones is 80-90% associated with the extraction, production and transport phases.²³⁵ It has been estimated in a separate study that the carbon footprint of a book was ~1.3-7 kg eCO₂ whereas that of the most common tablets or e-readers was in the 130-170 kg eCO₂ range, meaning that between 19 and 130 books could have the same environmental footprint as the necessary hardware used for reading them electronically.²³⁶ Moving beyond GHG, the manufacturing of these devices depletes rare earths and metals and results in high human toxicity.235

However, there might be some domains where progress in paper science can be applied to introduce more sustainable alternatives to digital storage. Historically, paper was used in the form of punch cards to store data. Modern laser or printing techniques could mean printing data at 100 000 DPI (meaning one dot is 0.25 µm). If each dot is a bit of information (black and white scenario), then an A4 paper sheet could contain at least 60 Go of information. With 16-bit encoding, 1 To of information could be held on one cellulosic substrate the size of a standard paper sheet. Current experimental efforts have produced impressive results since nanocelluloses ~3 nm in diameter mean very low roughness substrates. Existing nanolithography techniques or nano-embossing have achieved well-defined pillars about 7.5 µm in diameter spaced 4.5 µm apart, virtually resulting in an estimated information density of 54 Mo per A4 paper sheet.²³⁷ Cellulose nanocrystals cross-linked with citric acid have been imprinted with features as small as 140 nm (lines) or hole patterns with a periodicity as small as 800 nm. In the latter case, the information density would reach 12 Go per A4 paper sheet (the equivalent of 8000 scientific journal articles in pdf format, each 1.5 Mo on average).²³⁸ Patterns with features above ~100 nm could easily be read at high rates using modern optical devices.²³⁹ One needs to remember that cellulose acetate has long been used for TEM imaging too, with the ability to replicate much smaller features. Therefore, cellulose could be used for long term passive storage. Cellulose 250 million years old has been found intact in halite crystals, giving an idea of the durability of cellulose when preserved under the right conditions and what a long-lasting passive storage it could be.240

5. Perspectives

There are many things to conclude from this review. Perhaps, first and foremost, fundamental thermodynamic considerations should be placed back at the centre of the discussion on sustainability. It is evident from a rough study of entropy

levels on Earth that photosynthetic organisms and their sophisticated machinery have extracted high entropy CO2 from the atmosphere over geological periods and turned it into low entropy resources in the form of fossil fuels and the entire biomass, including phytomass. This constitutes the chemical battery of the Earth. This chemical battery is the root of our biological existence, but also that of our current economy. The second law of thermodynamics shows that resource depletions are equivalent to a battery discharging, which translates into quasi-irreversible atmospheric chemical changes (CO2 levels). The carbon mitigation potential of phytomass-derived materials is modest (at best) in comparison with our unreasonable use of fossil fuels: if storing carbon in buildings by insulating Europe for 200 years with straw could lead to the storage of 1 Gt CO₂ eq., a gigantic 1.7 Gt CO₂ eq. was emitted by the oil industry in 2015 through flaring alone. Without massively reducing the burning of fossil fuels, the carbon mitigation power of phytomass will be insignificant. Phytomass will not be the miracle remedy to CO₂ emissions. The biomass capital is also declining due to overexploitation and climate change; it is currently at its lowest since 5000 BCE. Even worse, when biomass and crops are impacted by climate, consequences can be bleak. It is estimated that recent social conflicts in the Middle East or in Africa have been triggered by unusually warm and dry summers, or by abundant rainfall.241,242 Economic pressures due to lumber shortages on the wood market are currently felt worldwide due to a higher demand for wood in construction. Therefore, it is very important that technological developments do not alter the phytomass budget any further.

Technological developments should also be mindful of non-renewable resources, such as freshwater, and basic chemicals used for fertilization, such as phosphorus and nitrogen. Water, nitrogen and phosphorus are planetary boundary indicators in a critical state; furthermore, the global nitrogen geochemical cycle is out-of-balance due to massive and inefficient use of fertilizers. 2,4,68 Nitrogen availability, and synthetic fertilizers containing nitrogen in particular, are known to boost food production. Yet, they are currently present in excess due to favourable fossil fuel availability, a situation that cannot be sustained indefinitely and that will be critical to address with respect to global food demand.^{2,64} The use of phytomass for food first will become paramount. Consequently, biomass needs to be taken care of in the long term through better agricultural practices, such as agroforestry or permaculture. These practices can have social benefits: the development of local crops in rural areas can put a brake on rural exodus and promote wealth, education and safety. Looking further at the interdependence of resources, other worrying facts emerge. In particular, the depletion of non-renewable resources means that there is no backup plan for a wide range of technologies (including agriculture) once peak oil, peak coal, peak metals or peak rare earths are reached. That is where renewables from biomass have a particular role to play, along with more abundant geological resources such as calcium carbonate, quartz or clays. The exponentially increasing consumption of materials

and energy over the last two centuries hides a more optimistic result: that of efficiency. Indeed, whereas technological progress has enabled man to use more and more resources at a higher rate, technological progress has also enabled a much higher efficiency. As a result, fossil fuel consumption per dollar of gross domestic product has been halved between 1965 and 2015. The increase in global consumption is therefore attributed to two things: the increase of the world's population and that of its global well-being, thanks to the rebound effect||. The rebound effect is spectacular in the digital world in which remarkable innovations in energy efficiency or data storage have led to more mass-production. ^{243,244}

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Nevertheless, the entropic aspect of biomass production is in itself inspiring to produce more efficient technologies. The quantum exergy efficiency of photosynthesis is remarkable and it has long been recognized in academic works.82,86-88 Consequently, it is doubtful whether atmospheric carbon capture technologies will ever achieve better light-to-chemical energy conversion in such an environmentally innocuous way. 245,246 Bioinspired processes should therefore follow the same path in trying to use solar energy and entropic paths. Closer to feasible research subjects, low-grade and diffuse energy sources should be used as much as possible, as shown in the exergy subchapter. This approach will give processes a net advantage in energy efficiency and sustainability from the ground up. These energy sources can be chemical (H₂O, CO₂, NO_x, etc.), kinetic (wind, river or ocean currents) or thermal (low grade infrared, convective heat in water streams). Examples therefore include the use of biomass in techniques such as windmills, phase change materials or passive desalination membranes. 92,247 Another interesting lesson from this thermodynamic study is that entropy can actually be a driving force for materials self-assembly, meaning autonomous or lowenergy processes, potentially with minimal environmental footprints. Existing examples in the domain of cellulose science include xyloglucan/cellulose self-assembly as well as spontaneous adsorption of a vast array of chemicals on lignocellulosic substrates.

Because resources are finite, "low tech" processes have an important role to play. They display inherent frugality because they rely on simple technologies and do not require external energy sources (such as electricity or fossil fuels) to function; instead, they rely on passive or low-grade sources such as solar energy, wind power or human power. Examples include the washing line or the shower bag, borrowing books from the library instead of downloading ebooks on a tablet, or more recently as seen during the COVID-19 pandemic, personal pro-

|| The rebound effect, also known as the Jevons paradox, states that sometimes consumption increases due to a weakening of the factors limiting the use of a given technology. As a result, the energy or materials economies that result from improved technology are partially or fully compensated for by a behavioural change in society with respect to this technology. For instance, when cell phones become easier to produce thanks to progress in the semi-conductor industry, their price drops and more people can afford them.

tective equipment in the form of home-made face masks/ shields, or long exposure to natural light for fabric disinfection. 236,243,248 Low tech processes contrast with those that are high tech (hydrogen production, hybrid vehicles, solar panels, etc.) in that they do not follow a high consumption lifestyle and growth-oriented macroeconomics; growth-oriented consumption is increasingly pointed out by modern economists as being unsustainable, both in terms of social and physical limits. 10,244,249 Ideally, low tech solutions should have the advantage of being easy to implement in all areas, including isolated ones, with limited transportation involved. In the COVID-19 case, staying home was the most efficient option selected by most governments worldwide, and this change in attitude is a reminder that solutions to modern issues are not always technological. Nevertheless, the danger with low tech solutions, as well as environmental innovations in general, is once again the rebound effect. The rebound effect can translate into exacerbated resource consumption, an outcome in opposition to biomass availability. A bias would be to ignore that some low-tech realizations are scientifically challenging, as illustrated by hygromorphic materials (cladding, for instance) that can be used in passive responsive architecture. 250-253 Since the sustainability of bio-based materials is fundamentally dependent on transformation processes, one solution could be to focus on low-tech transformation processes as well. Field retting is such an example in which wind, rain and naturally occurring soil microorganisms help to fractionate stem fibres prior to further processing and defibrillation.

Life cycle analysis and exergy analysis both produce some very interesting results on precise aspects of materials or processes. For instance, they show how polluting the textile industry is, but also which parts of this industry need to be addressed and how they can be addressed. They also show that the LCA of biopolymers or biofuels usually suffer from the footprint of intensive farming: intensive farming serves to produce dedicated crops, but also emits large amounts of NO_x, contributes to freshwater depletion and leads to the acidification and eutrophication of water streams. In that sense, LCA demonstrates that sustainability is not obtained through the use of phytomass-derived resources alone. Dynamic LCAs are of particular relevance when dealing with carbon storage, a track that seems relevant in the building industry with phytomass-derived structural and insulating materials. LCA also serves to evaluate the environmental cost of recycling, an option that is generally favourable in the paper industry, for instance. A specific mention should be made of nanocelluloses since these materials are the subject of intense research efforts worldwide. Their production is currently rather process-intensive and a lot of work still remains to cleanly and efficiently deconstruct biomass into nanocelluloses.²⁵⁴ Perhaps it is not a surprise to see a shift in the nanocellulose community to top down approaches, rather than bottom-up ones. 149,255,256 There will be some advantages in dealing with relatively bulky entities such as energy savings due to the absence of heavy refining. However, as far

as delignification, densification or bleaching are required, the treatment of thick samples will be limited by heat and liquid diffusion kinetics; these two limitations will translate to other energy costs that are not as important for heavily refined samples with much smaller dimensions.²⁵⁷ Alternative techniques such as microwave ovens instead of conventional convective ovens, or an understanding of bulk chemistry for biomass functionalization will play a decisive role in the optimization of these processing paths. 257,258 The scientific orientations and possibilities are extremely numerous, and a recent article by Jinwu Wang et al. echoes the 1999 article by Josef Schurz that has opened many avenues, many of them still to explore. 259,260 In this manuscript, a rapid assessment of current nanolithography techniques shows that cellulosics are extremely promising for passive data storage. Sustainable data storage will without a doubt be a major challenge in the upcoming decades and important reductions of CO2 emissions could be obtained while tempor-

arily storing carbon. As a final conclusion, the question of materials sustainability, and ecological economics in general, will not have a single answer.261 In the context of lignocellulose, the absence of a single answer means that it does not suffice to use biobased materials to contribute sustainability. Regardless of the chosen strategies, the use of biobased materials will have to be relevant and unwasteful; the materials produced will need to be durable, re-usable, multifunctional, ideally upcyclable or recyclable. In particular, it is generally agreed that recycling, reuse and efforts in energy efficiency contribute to reductions in material and energy usage. 76,225,244 There is therefore no difference from the sustainability standpoint between biobased materials and non-renewable materials such as ores, metals or synthetic organics: both are intertwined in the same technological framework. Whereas these conclusions will come as no surprise, the scale of the task is colossal if society is to comply with sustainability goals such as those defined by the Paris Agreement on Climate Change or the European Union and United Nations common goals for a sustainable future.

Abbreviations

Evenory (in I)

Green Chemistry

B	Exergy (in J)
BCE	Before common era
Bit	Binary digit
BmimCl	1,3-Butyl methylimidazolium chloride
°C	Degree Celsius (unit)
CE	Common era
CFC-11	Trichlorofluoromethane
CH_4	Methane
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibres
CO_2	Carbon dioxide
CO_2 eq.	Carbon dioxide equivalent
CS_2	Carbon disulfide

CTU	Comparative toxic unit
DCB	1,4-Dichlorobenzene
DNA	Deoxyribonucleic acid
DPI	Dots per inch
E	Energy
ET	Ecotoxicity
FE	Freshwater eutrophication
GHG	Greenhouse gas(es)
GWP	Global warming potential
h	Planck's constant ($h = 6.62607015 \times 10^{-34} \text{ J Hz}^{-1}$)
Н	Enthalpy (in J)
H_2	Dihydrogen
HDPE	High density poly(ethylene)
HT	Human toxicity
ICT	Information and communication technologies
IR	Infrared
J	Joule (unit)
k	Boltzmann's constant ($k = 1.38 \times 10^{-23} \text{ J K}^{-1}$)
K	Kelvin (unit)
LCA	Life cycle analysis
LCI	Life cycle inventory
ν	Frequency of light (in s ⁻¹)
N	Nitrogen
NFC	Nanofibrillated cellulose
NMMO	<i>N,N</i> -Methylmorpholine oxide
0	Octet (1 o = 8 bit)
OD	Ozone depletion
OSB	Oriented strand boards
\mathcal{P}	Phase space
P	Phosphorus
PE	Poly(ethylene)
PEEK	Poly(ether ether ketone)
PET	Poly(ethylene terephthalate)
PHA	Poly(hydroxyalkanoate)
PLA	Poly(lactic acid)
ppm	Parts per million
PVC	Poly(vinyl chloride)
RNA	Ribonucleic acid
S	Entropy (in J K ⁻¹)
$S_{ m gen}$	Entropy generated by the process (in J K ⁻¹)
T_0	Heat bath temperature (in K)
TE	Terrestrial eutrophication
TEM	Transmission electron microscopy
UV	Ultraviolet
\mathcal{V}	Box in \mathcal{P}
V	Volume of V
L ∕celluloseI	Maximum volume fraction of cellulose I at packing
packing	(unit cell volume/monomer)
VcelluloseII	Maximum volume fraction of cellulose II at packing
packing	(unit cell volume/monomer)
Vdisorder	Maximum volume fraction of a disorganised state at
packing	packing
Vorder	Maximum volume fraction of an organised state at
packing	packing
	1 0

State

Xyloglucan

x

XG

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Conflicts of interest

There are no conflicts to declare.

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