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Final Thesis

EMergy and Green Chemistry: do they speak the same language?

An integrated assessment applied to the production of lactic acid

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For some background company while reading:

Abstract

In the world of sustainability assessments, several methods have been adopted, but rarely systematically defined or compared. This can lead to conceptual and operational problems when different languages and approaches are attributed the same semantic valence, related to the concept of sustainability, thus weakening the power of scientific analysis in directing consumption and global development. In this work, two languages, taken from Emergy Accounting (EMA) and Green Chemistry (GC), are compared through the case study of a chemical production process. Furthermore, a more precise definition of sustainability and greenness is proposed.

Two production routes for racemic lactic acid were compared using both approaches: the first based on the fermentation of glucose from biomass and the second based on the fermentation of glycerol, main byproduct of the biodiesel industry.With EMA, the diagrams of the two systems were analyzed and the transformities of the final product and of some reactants (butanol, zeolite) were estimated. For the GC study, some of the main metrics were calculated (atom economy, E-factor, reaction mass efficiency, mass intensity) and a semi-quantitative evaluation with EcoScale was performed. The main features, pros and cons of the two languages were compared, highlighting that EMA and GC provide different, but easily complementary, information about the same system, thus can be used concurrently to deepen the significance of sustainability evaluations.

Chapter 1 - Introduction

1. The issue

In our daily life we hear terms like these all in "one pot" as if they all referred to the same concept, direction or paradigm. They do not.

These are all expressions of a new semantic area that has emerged in recent years in response to a very specific, concerning, yet often dismissed, global issue: climate change. In the non-scientific world, the fruits of research have not been clearly communicated and "absorbed", thus every individual, collective and business has translated their own understanding into words with the vocabulary they had at hand. The result is a messy mix of similar-sounding words which provide a fuzzy image of what the world "should be like" to "respond" to climate change.

Climate change for dummies - some data

While providing a detailed vision on climate change is very far from the scope of this reading, reminding how things are going can help us put the work -and our future efforts- into perspective. Spoiler-not-spoiler: things are going bad. Potentially very bad.

The IPCC (Intergovernmental Panel on Climate Change) stubbornly keeps releasing reports that benefit from more and more reliable science to depict doomer and doomer visions of the future, and it has released its latest update in August 2021, restating that humankind is the main influence of climate change and we will *very likely* experience awful consequences. After the publication of this report, Nature conducted a survey among the 233 authors asking for their opinion about governments' commitment and the future of climate action. Of the 40% of authors that responded to the survey, most expressed skepticism about the capability of governments to reduce global warming, and 60% foresee a +3°C warming by the end of the century. The UNEP (United Nation Environmental Program) does not show much more optimism in its Emissions Gap Report (2021), estimating an increase of +2,7°C with respect to pre-industrial levels. In this same year, after the publication of these two documents, the much praised COP26 took place in Glasgow and established new pledges for the committed Countries with renovated Nationally Determined Contributions (NDCs) and Long-Term Strategies (LTSs). These have not fully convinced everybody though. The Climate Action Tracker consortium, which gathers scientific and academic organizations, estimates that in the most optimistic scenario, in which all Countries implement all the announced targets, including LTSs and NDCs, the planet average temperature will increase by 1,8°C, still above the goal set with the Paris Agreement. Let us just clarify the current state of the climate: we are already at +1°C with respect to 1990 (visualized in figure 1).
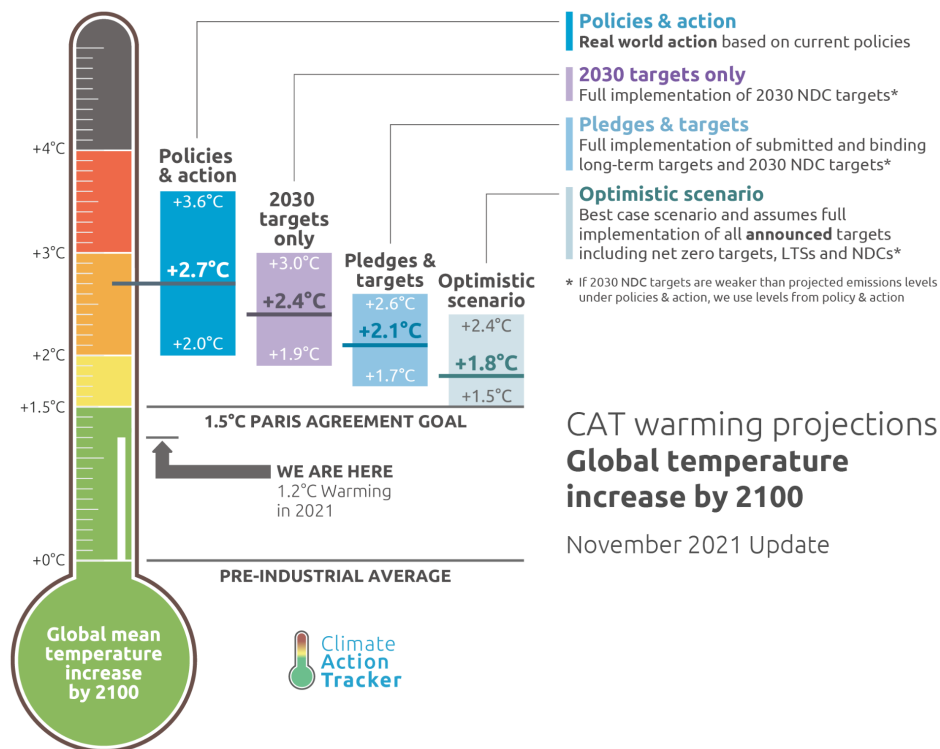
Figure 1: current warming level and possible future scenario. Source: Climate Action Tracker

Since the human mind sometimes has some trouble in visualizing abstract or long-term concepts, we might be tempted to wonder: what would the world look like with this much global warming? An immediately available answer is provided by Prof. Nigel Arnell, who summarizes the results of his team's research on global and regional impacts of climate change at different temperature scenarios. Among the most striking data, they found that "the global average annual chance of having a major heatwave increases from around 5% over the period 1981-2010 to around 30% at 1.5℃ but 80% at 3℃. The average chance of a river flood currently expected in 2% of years increases to 2.4% at 1.5℃, and doubles to 4% at 3℃. At 1.5℃, the proportion of time in drought nearly doubles, and at 3℃ it more than triples".

After decades of daunting data and catastrophic visions, we all know we have a problem that needs a solution. But what solution?

2. What we need

Climate change is not only a menace to our "tangible assets" (cities, food, resources, and many more), but also, perhaps even more, a philosophical and emotional undertaking. For the first time in human history, the survival of our entire species and of several others on Earth is threatened. The human influence on the balance of nature is so heavy that it is modifying the climate of an entire planet. To respond to a challenge that concerns both the physical realm and the human paradigm, we need to intentionally create a novel way of living that can respect the climate pledges adopted with the Paris and Glasgow agreements. And to create a new way of living, we need new words to enable us to think of it.

This is why the semantic world of sustainability was born.

Hints of history in sustainability

Hard is the task of defining when this term -and related ones- were first used, but a few milestones can be highlighted for the sake of contextualization. An early conceptual summary of the evolution of this topic (Kidd, 1992) describes how "Six separate but related strains of thought have emerged prominently since 1950 in discussions of such phenomena as the interrelationships among rates of population growth, resource use, and pressure on the environment" even before the word 'sustainability' appeared. Already in that year, the author states that "literature relating to sustainability is so voluminous that full analysis is not practical". In 1972, "The limits to growth" cast a shadow on the possibility of indefinite increase of population and economic growth: Earth has a finite carrying capacity, thus can support the life of a finite population, and the current economic paradigm founded on indefinite growth cannot be compatible with these premises. Here the authors mentioned the possibility of finding a "condition of ecological and economic stability that is sustainable far into the future". Later came the Brundtland Report (1987) "Our common future", which provided the first definition of 'sustainable development' as the one that "meets the needs of the present without compromising the ability of future generations to meet their own needs." Last in our trinity of imprintings that persist today, in 1994 John Elkington, founder of the consultancy agency 'SustainAbility', coined the term "Triple bottom line", constituted of the 3-Ps of "Profit, People, Planet", to indicate the three fundamental aspects of evaluation of business performance. These were then translated into "environment, society, economy", the three "pillars" of sustainability that we find everywhere today. Many of these ideas coalesced in 2015 in the formulation of the UN Sustainable Development Goals (SDGs) for 2030, which are now considered a benchmark for the evaluation of any kind of human activity, from business to academic curricula. Their Ps became five (Profit became Prosperity while Peace and Partnership appeared) but the SDGs reinforce the concept of measuring sustainable development with quantitative indicators (precisely 17 'Goals' with 169 'targets'). Unfortunately the UN Agenda 2030 does not seem to provide a clear and concise definition of 'sustainable development', but it definitely provides ways to measure it.

So what is sustainability at roots?

"To measure is to know", Lord Kelvin said, and these words carry great wisdom. To be able to see whether our society, or any subsystem of it, is progressing towards our definition of sustainability (or sustainable development), we must be able to measure the changes accomplished. To measure the changes accomplished we need metrics and indicators, and in order to have these we need to formulate a solid definition of what we are studying. To dissipate doubts, blurry evaluations and risks of greenwashing, we have to go back to the roots of the concepts, providing clear and unambiguous definitions. We have to do what philosophers and scientists both do, building solid foundations of our concepts to build a logical reasoning on them, avoiding fallacies due to ambiguities. In this work, we take the concept of 'sustainability' as the foundation of our analysis, and we provide a renovated definition to establish the bases on which to build new knowledge, scientific or heuristic. 'Sustainable' is something that can sustain itself long term, hence something that does not irreparably damage the environment around it. The concept can be applied to any environment, be it ecological, social, economic, political or other; the main "rule" to determine whether a system can perpetuate/preserve itself and thrive in time is that we cannot analyze its single parts, but we must look at the "broader picture" of the system as a whole, and how it interacts with the environment in which it is embedded. From this premise,

sustainability is *"the property of a system that can sustain itself indefinitely in time with no detriment to the surrounding environment"*.

To put this concept in practice it needs to have an operational definition, that refers to quantities that we can measure and on which we can act. To provide this, we adopt the two principles proposed by Daly, 1990, which are there described referring to resource management for sustainable development, but that can more smoothly be applied to our idea of sustainability, for reasons that will become clear at the end of this journey. The first principle is that, in a sustainable system, the *"harvest rates should equal regeneration rates"*. This means that we should extract and use resources from the environment at a rate that is lower than or equal to the rate at which the environment can replenish these resources. This implies that the rate of use of non-renewable resources, which are considered non-"replenishable" in human time scales, should be equal to zero, otherwise we are depleting resources. The second principle is that *"waste emission rates should equal the natural assimilative capacities of the ecosystems"*, which means that we should produce waste at a rate that is lower than or equal to the rate at which the environment can absorb" and decompose them". This also implies that we should not produce waste that cannot be degraded by the ecosystems. In simple terms, we cannot cut more trees than the forests grow and we cannot dampen more garbage than the land can decompose. These principles are visualized in figure 2 with a symbolic language that will be appropriately introduced in the third chapter.
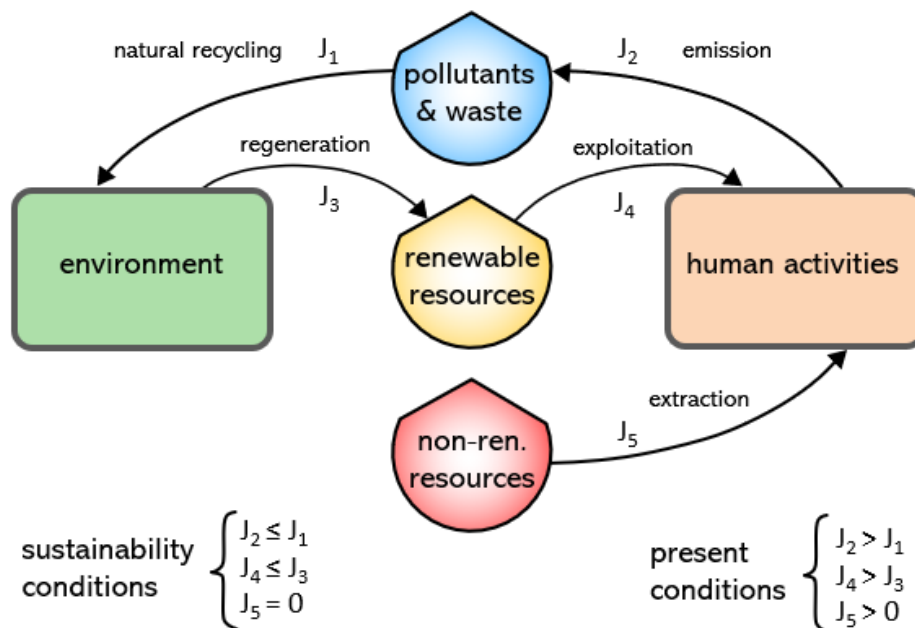

Figure 2: Conditions for sustainability. The environment and human activities are systems that transform energy from one form to another. This energy can be represented in stocks, homogeneous amounts of measurable quantities, and it is available in the form of renewable and non-renewable resources (yellow and red stocks). The environment continuously generates renewable resources (yellow stock) at a rate J_3 which are exploited by human activities at a rate J_4. Human activities also rely on non-renewable resources (red stock) extraction, performed at a rate J_5, and generate pollutants and waste (blue stock) emission at a rate J_2. These pollutants and waste are recycled from the environment at a rate J_1, closing the loop. For a system to be sustainable, the rate of emission must be lower than or equal to that of recycling ($J_2 \leq J_1$), the rate of exploitation of renewables must be lower than or equal to that of their regeneration ($J_4 \leq J_3$) and the non-renewable resources must not be extracted ($J_5=0$).

Needless to say, we are respecting none of these conditions. But at least now we have the picture clear, and we have a common framework to guide our action towards sustainability. In this framework, there is a second aspect of sustainability that needs to be rewritten. When the "three pillars" are discussed, they are always described as equally foundational when, in fact, they are not. Sustainability is said to be the crossroad between economic profitability, social "bearability" and environmental viability. But could an economy exist without a surrounding society? Or could a society exist without a supporting environment? Of course not. Economy needs people to function and people need food (and all the other environmental "services") to survive. Hence, the famous Venn diagram of sustainability should be redrawn as in figure 3, where both society and economy are constrained by environmental limits (more on this will be disclosed at the end of the journey). The reason why we are perpetrating and assisting environmental exploitation and degradation is rooted in a misunderstanding of this framework: we are still pursuing a business model that does not take into account the constraints imposed by the environment. When we will finally rethink our business framework, taking into account these constraints (see Rockström et al., 2009), we will be able to build a really sustainable society.
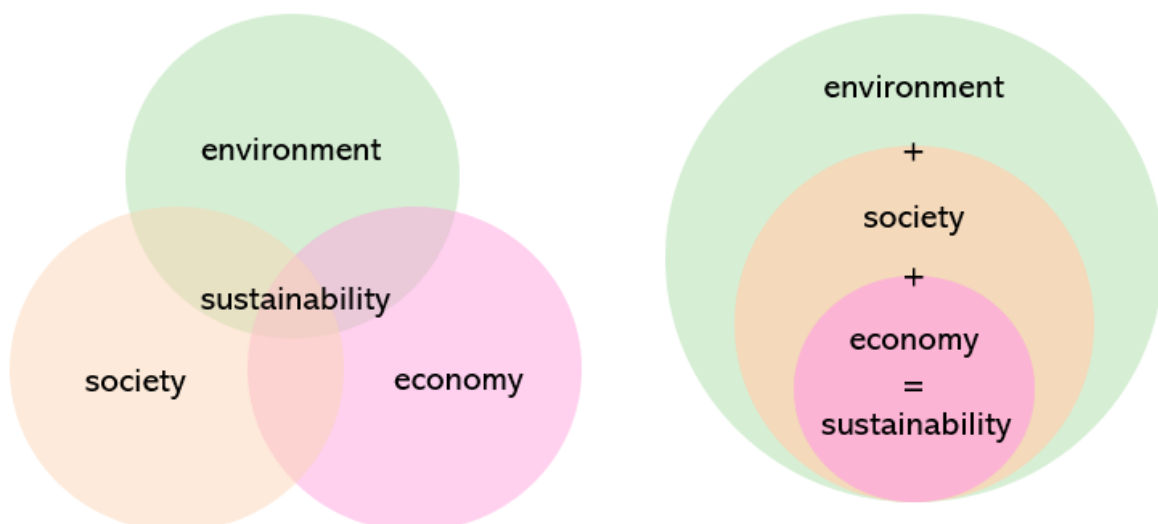

Figure 3: mainstream vision of sustainability (left) vs actual reality of sustainability (right)

This brief excursus puts into perspective what kind of sustainability we are talking about. The concept is more than "My business emits less greenhouse gases than my competitor" or "my product is more *natural* than theirs"; we need a systemic approach, in which we look at the single criteria (emissions, percentage of renewable resources) in the context where they are used: inside their system. Figure 4 tries to summarize the essentials for this journey.

But there is not only that…
Another word often appears in mainstream language with an "eco-friendly" but mysterious flair: "green". In everyday language, and often in marketing narratives, a product is described as "green" if it "sounds sustainable", if one or more aspects of their production or consumption are "better" than competitors from an environmental performance perspective: emissions, "natural products" (what are they really, anyway?) or the percentage of recycled plastics. In the scientific community, a discipline that has utilized the "green" strategy as an

imagery associated with nature is 'green chemistry'. Born as a new way of doing chemistry creating no harm to the environment, it coined the concept of "greenness" to refer to those processes or reactions that respect green chemistry principles. The greenness of processes is measured with several metrics (seen in more detail in the following chapter) which promise to evaluate whether processes "respect the environment" or they do not.

How to navigate the world with these and other myriad similar-sounding terms?
In the process of creating and shaping a "better future" in line with the rest of the life on the planet, it is essential to build reliable assessment tools for "sustainable solutions" -whether we are talking about innovating industrial production, management of ecosystems or a new chemical process. We need methods to evaluate the real sustainability of systems, to avoid "false negatives" (i.e. more sustainable practices that do not get recognition) and "false positives" (greenwashing). This is why a plethora of *environmental assessment methods* have been created and adopted in recent times to evaluate sustainability and environmental impacts: energy analysis, exergy analysis, environmental impacts assessments, LCA, exergoenvironmental assessment… sometimes with the risk of saying the same thing in different languages. They all provide somehow different information, but there might be instances in which results are coherent and "overlapping". In both cases, integrating more than one method can lead to a wider understanding of the sustainability of systems. This is the idea behind *integrated environmental assessment methods*. These include, for example, the adoption of LCA together with one of the aforementioned methodologies.
In this wide world of assessments, how do we know which ones to choose, and whether they will provide the same information and direction for improving systems? This is why, in this work, two of these languages are compared.
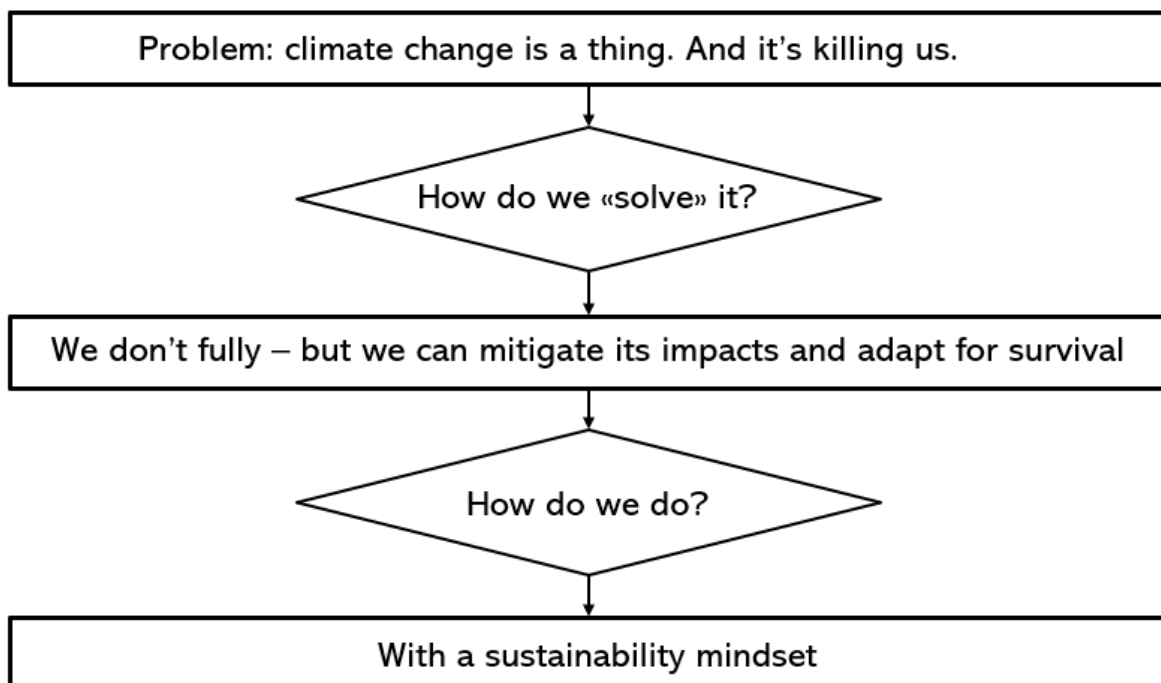

Figure 4: intuitive algorithm - why we need sustainability

3. Why we are here today

The scope of this thesis is comparing two languages, emergy analysis and green chemistry, as assessment tools for the sustainability of chemical systems. This comparison is carried out with a case study which explores two scenarios of lactic acid production.

In the following chapter, the concept and philosophy of green chemistry are introduced, with a focus on the twelve principles of green chemistry. The main metrics used in this discipline are presented and the recent developments in more comprehensive indices are discussed. In chapter three, the main ideas of emergy analysis are introduced, discussing its theoretical framework and explaining its language. The most common emergy indicators and a few specific to this work are described and a comparison between emergy and LCA, widely used environmental impact assessment method, is carried out. The fourth chapter is dedicated to the case study chosen for this work: starting from a reference paper (Morales et al, 2015) which compares two production routes from lactic acid, the same processes are analyzed in terms of emergy analysis and green chemistry. The emergy diagrams of the processes and their extended systems are presented, the UEVs of all the involved inputs and outputs are calculated together with the indicators described in the previous chapter. For both routes the main green metrics are calculated and compared with the results of emergy analysis. The goal of the case study is to draft an answer to the question: "Do green chemistry and emergy analysis provide coherent information regarding the evaluation of chemical processes sustainability?". In chapter five, a more in-depth comparison between the two languages is carried out: green chemistry and emergy analysis are compared in terms of theoretical framework and epistemology, metrics and indicators, and their uses inside and outside the scientific community. Chapter six draws the conclusions to this study, restating its theoretical premises and proposing renovated definitions of sustainability and greenness. Last, chapter seven adds some personal reflections surrounding the topics of this work.

Chapter 2 - Green chemistry

1. What is green chemistry?

Leaving definitions to the words of its own creator, Paul T. Anastas, "Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, by-products, solvents, reagents, etc., that are hazardous to human health or the environment." It was also defined as "the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances" (Anastas and Williamson, 1996; Anastas and Warner, 1998). Hence, at the core of this discipline, there is the concept of *preventing hazards* for both humans, non-human species and all the supporting environment. The dream is designing a fully "harmless" chemistry.

2. Brief history of Green Chemistry

Premise
The birth of Green Chemistry is strictly linked to the rise of environmentalism in the late 20th century. The publication of "Silent Spring" by Rachel Carson in 1962 shook the public opinion about the increasing environmental issues in US society: several pesticides used in agriculture were causing detriment to the surrounding ecosystems and ended up accumulating in the food web, and this book was the first strong public denunciation of the toxicity of these agrochemicals. At the same time, the world was witnessing a growing series of environmental disasters related to chemical factories: Niagara Falls, New York, 1978, when deposits of toxic waste buried underground lead to the displacement of an entire neighborhood (Sanderson, 2011); Bhopal, in India, 1984, where a gas leak caused more than 3000 deaths and hundreds of thousands of injuries (ibidem); Times Beach, Missouri, 1982, after a chemical company working on Agent Orange for the US army damped a dioxin-rich mixture in more than 25 locations, which caused illness and deaths both in animals and kids and lead to the displacement of the entire town (US EPA, 2020) - just to name a few. With this awareness, in the late 1980s the focus shifted from waste and pollution remediation to prevention (Sheldon, 2017). The main ideas of green chemistry were included in the 1990 USA Pollution Prevention Act (US EPA, 1990), promulgated as a response to the concerns for environmental issues.

Birth
Soon several milestones in scientific literature followed on this topic, aiming at defining ways to assess the "quality" of chemical reactions with respect to their efficiency and potential environmental harm. In 1991 and 1992 the concepts of atom economy (related to the percentage of atoms used from reactants to products) (Trost, 1991) and E-factor (related to waste generation) (Sheldon, 2017) were proposed as a first approach to "green metrics", while the term "green chemistry" was introduced in 1991 by Paul T. Anastas (Deligeorgiev, 2010), in a program launched by the US Environmental Protection Agency (EPA) to develop a more environmentally-compatible chemistry. The concept started gain popularity in scientific literature and institutions (Wardencki et al., 2005), also thanks to a series of awards and

working groups that were created on the topic. Examples include the first US Presidential Green Chemistry Challenge, announced in 1995, the International Union of Pure and Applied Chemistry (IUPAC) working group on Green Chemistry born in 1996 and the creation of the Green Chemistry Institute in 1997, an international organization aiming at facilitating the collaboration between national agencies, universities and industries to design new technological solutions. The first book was published by Anastas and Warner (1998), who introduced the "12 principles of Green Chemistry". These principles define the main criteria that a process should respect to be defined as "green", and include both aspects related to process efficiency and aspects related to hazard prevention. Not much time later, Winterton (2001) proposed "12 more green principles" to complement the previous and explore the potential of scale-up of newly designed processes, establishing the need for quantification of 'greenness', and the following year the "12 principles of Green Engineering" were also published (Anastas and Zimmerman, 2003). These early publications already stated several major differences between green chemistry and the historical approaches of environmental protection institutions; Anastas & Lankey (2000) point out the main innovations of green chemistry in this regard:

- "It addresses hazard rather than exposure
- It is economically driven rather than economically draining
- It is non-regulatory
- It prevents problems before they occur through avoidance approaches
- It considers the full life cycle impacts at the design stage".

These observations stress that green chemistry introduces an upstream shift in the chemistry focus, from limiting the impacts to preventing them at the source.

Development
In the early 2000s the discipline was already gaining great momentum in chemistry and chemical engineering research (Gonzales and Smith, 2003). Various alternative metrics were proposed, from mass intensity to reaction mass efficiency, and an "updated" version of the E-factor was proposed to take into account the different environmental impacts of different types of waste.

The more the intrinsic complexity of the topic was explored, the more refined methods to assess the "greenness" of chemical processes were developed. Different ways to unify these first metrics in a more comprehensive approach were proposed (Andraos, 2005), and other metrics related to health hazards, persistence, bioaccumulation and ecotoxicity of chemicals were taken into account in the newly introduced Environmental Assessment Tool for Organic Synthesis (EATOS; Eissen and Metzger, 2002). Other multicriteria assessment methods were developed, such as EcoScale (Van Aken et al., 2006), a semi-quantitative tool to evaluate organic syntheses with both environmental impact factors and economic criteria, analyzing yield, cost, safety hazards, work-up and down-stream processing. Meanwhile, the concept of Life Cycle Assessment (LCA) was being developed, first conceived at The Coca Cola Company 1969 (Hunt et al., 1996) and officially acquired its name in 1990 during the first international workshop by the Society of Environmental Technology and Chemistry (SETAC). This tool aims at assessing the environmental impacts of all the phases of production of a set good, including all the industrial processes that convert raw matter to the product (gate-to-gate approach), and possibly also the contributions due to resource extraction ("cradle-to-gate") and the impacts related to disposal and/or recycling ("cradle-to-grave" or "cradle-to-cradle"). These impacts are quantified through several indicators, among which

the Global Warming Potential (GWP, related to greenhouse gas emissions), Cumulative Energy Demand (CED, related to energy consumption) and EcoIndicator 99 (EI99, related to possible toxic effects on humans and ecosystems). Seeing the overlap between the concepts of LCA and green chemistry, Prof. Thomas Graedel (1999) proposed to extend the scope of green chemistry from studying "greener" organic syntheses to designing entire "greener" life cycles. This idea was taken up by several authors, who began to introduce LCA in green chemistry assessments (e.g. Lankey and Anastas, 2002; Gustafsson and Börjesson, 2006). Following this trend, EPA designed its own tool, GREENSCOPE (Gauging Reaction Effectiveness for the Environmental Sustainability of Chemistries with a multi-Objective Process Evaluator), which aimed at evaluating the overall sustainability of production processes. By assessing the processes through the "4 Es" (Environment - Efficiency - Energy - Economics), the tool can compare processes based on different chemical reactions to find the "best" alternative.

At that point, firms started seeing the opportunity hidden in the concept of sustainability assessment, thus several companies began developing their own assessment methodologies to apply to their products - GlaxoSmithKline (GSK), BASF, Chimex (L'Oreal), Mane are a few. From there on, the discipline Green Chemistry gained more and more importance, especially in light of the increasing risks related to climate change, which demand a systemic redesign of our production chains, including the reactions carried out.

It is to be noted that, during the development of the new fields of green chemistry and sustainability, much confusion was present in the definition of the key concepts: "Green chemistry", "sustainable chemistry", "clean chemistry", "environmentally benign chemistry" and similar combination of words were, and still are, often used as synonyms (Eissen and Metzger, 2002), creating a lack of net definitions and a use of different concepts interchangeably. This work endorses the vision of Gonzalez and Smith (2003): "sustainable chemistry not only includes the concept of green chemistry, it also expands the definition to include a larger system than just the reaction. Sustainable chemistry also considers the effects of processing, materials, energy and economics. With this in mind, a researcher must ask the all-important question, "Can a green process be sustainable?"". Any new process proposed as an advancement in green chemistry terms must be evaluated in the broader context of sustainability, and this is part of the reason why we are here today.

Today

Due to the pressure of the environmental crisis, words like "green" and "sustainable" have now become part of the mainstream culture, thus if we asked a random citizen what green chemistry is, they would probably have at least a vague idea of a "chemistry for the environment".

Several types of environmental, sustainability or multicriteria assessments have been proposed and used to evaluate how much a product, a process or a system is sustainable. Tang and coworkers (2005, 2008) also elaborated two acronyms, 'PRODUCTIVELY' and 'IMPROVEMENTS', to help familiarizing with the 12 principles of green chemistry and green engineering, respectively, which can contribute to a popularization of the discipline. Moreover, Green Chemistry has entered several academic curricula already in undergraduate programs, with a specific focus of scientific literature on how to build courses that instruct students on green syntheses assessment and design (see for example Van Aken et al., 2006; Ribeiro et al., 2010).

However, there are not only "positive outcomes". The concerns for the environment are also changing the way consumers choose products, hence firms are increasingly subjected to a marketing pressure to become (or appear) more "sustainable", giving rise to more and more frequent cases of greenwashing (Delmas and Burbano, 2011; De Freitas Netto et al., 2020). This phenomenon corresponds to a communication and marketing strategy of brands which claim to work "respecting the environment" without adopting tangible and measurable actions (Directive 2005/29/EC). Companies that claim that a product is "sustainable" because its packaging is made with "100% recyclable materials" (note: not recycl*ed*, but recycl*able*), or with a fraction of recycled materials (see San Benedetto), or that substitutes plastic with paper (Vaughan, The Guardian, 2018), or uses "organic cotton" while keeping feeding fast-fashion (see H&M, online) is evidently falling into the greenwashing trap. A product cannot be defined as "sustainable" only because one of the aspects of its production seems to be more environmentally-friendly than competitors. To deconstruct an example, a product packed with "50% of recycled plastic" is not sustainable, because the other half of the material is still derived from non-renewable sources, which cannot have space in a sustainable vision of the product chain according to the definitions provided in the first chapter. Even a company that claims to use "100% recycled material" leaves a public note saying that their use of new plastic has not suddenly dropped to zero, but that they reduced its use by 20% with respect to three years earlier - and they do not recycle labels or caps (see CocaCola, online).

Furthermore, when a firm is purposefully using a mixture of vague words that "sound green" without giving detailed information about how they evaluate this greenness, they are probably playing on the blurry line of greenwashing. Unfortunately, the world of commerce does not have a scientific vision of sustainability and some of these "clever" brands are even receiving awards for their claims (see San Benedetto, online). These awards contribute to building a "virtuous" image of the brand on the market, possibly increasing their popularity with two overall detrimental effects: they sell more products which pretend to be "sustainable" without actually being so and they contribute to create a mainstream image of "sustainability" which becomes farther and farther from anything scientifically assessed.

How does this relate to our work?
A valid and scientifically-based sustainability assessment is key to prevent greenwashing and develop a sound culture of sustainability in product design and consumption. Firms need a reliable tool to certify their (real) commitment to the environment, consumers need true-to-life "labels" or certifications to help direct their purchasing decisions and policymakers need a methodology to aid decision-making and evaluate their policies towards real sustainability. At the state of art, several different assessment methods now present in literature and business practice can create confusion and uncertainty when it comes to evaluating "something's sustainability". With this work, we aim at clarifying whether two of these, green chemistry and emergy analysis, communicate the same information or if they provide different points of view. We also aim at proposing a comprehensive environmental assessment method that can embrace a broad variety of aspects related to the impacts of processes on the environment, starting from natural resources and including end-of-life environmental impacts.

3. The 12 principles explained

What are the basic principles that a green synthesis should respect? In the following paragraph the content of the 12 principles is provided as expressed in the original text with a brief comment. A more detailed description with further considerations can be found elsewhere (Deligeorgiev, 2010).

> *1. Prevention. It is better to prevent the formation of waste materials and/or by-products than to process or clean them.*

This is valid both for reagents used in the process and for the solvents adopted, whose function is primarily to create an environment where reactants can come in contact. Solvents especially, which are used in high quantities with respect to reagents, can create non-negligible environmental impacts if not recycled. Following this principle, the field of mechanochemistry, or "grinding chemistry", has seen growing interest, aiming at creating synthetic methods that avoid the use of solvent and combine reactants, often just grinding them in the same pot with a mortar (Gečiauskaitė and García, 2017). However, if a solvent has to be used, it is better to operate with concentrations as high as possible to avoid the burden of solvent recycling or disposal.

> *2. Atom Economy. Synthetic methods should be designed in such a way that all products participating in the reaction process are included in the final product.*

Atom economy is one of the most widely used metrics in green chemistry, explained in the following paragraph. It proposes that all the atoms of the reagents involved in a reaction must be utilized in the structure of the product - or, at least, as many atoms as possible.

> *3. Avoidance or Minimization of Hazardous Products. Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.*

The reagents, solvents and auxiliaries used during a synthesis should present the lowest level of hazardousness possible. The less the hazardous materials used, the less the risk of detrimental effects to humans or to the ecosystems.

> *4. Designing Safer Products. The design of products should be safe in terms of human health and the environment.*

The same idea of the third principle must be valid also for the products of the synthesis, which must not create harm to humans or ecosystems.

> *5. Safer Solvents and Auxiliaries. The solvent chosen for a given reaction should not pollute the environment or be hazardous to human health.*

Organic solvents are often used in organic syntheses. These can present moderate or high risk for the operators or for the environment, if discharged without proper disposal. Thus, alternatives to organic solvents should be adopted wherever possible, first of all the use of water. Several reaction environments have been developed as substitutes: supercritical CO_2, ionic liquids, water with surfactants creating micelles for non-polar compounds, expanded solvents being the most common (Gonzales and Smith, 2003).

> *6. Energy Efficiency. The energy requirements involved in the chemical processes should be accounted for, in view of their influence on the environment and the economic balance, and the energy requirements should be diminished. If possible, the chemical processes should be carried out at room temperature and atmospheric pressure.*

Energy production and consumption is likely to create a non-negligible environmental burden. Burning fossil fuels to generate heat or steam produces greenhouse gases

emissions and several byproducts, whereas electricity also contributes to these impacts if not fully generated from renewable sources. In chemical syntheses, heating, cooling and maintaining systems under pressure or in vacuum is a considerable energetic expenditure, which should be reduced or eliminated wherever possible.

> *7. Use of Renewable Feedstocks. The intermediates and materials should be renewable rather than depleting (which is the case with, e.g., crude oil) whenever this is technically and economically advantageous.*

According to the definition of sustainability provided in the previous chapter, no amount of non-renewable resources should be used in a truly sustainable system. It is evident that reaching this goal is not possible in a short amount of time, but reducing the fraction of non-renewable resources used in processes is necessary until abating them is feasible. One example of this substitution is the production of chemicals from fermentation of organic matter, such as the case study of lactic acid here examined.

> *8. Decrease and/or Elimination of Chemical Stages. Derivatizations, such as protection/deprotection and various other modifications, should be decreased or avoided wherever possible since these stages require additional amounts of reagents and waste products could be formed.*

Some chemical syntheses require additional steps of derivatization to avoid the formation of byproducts. However, these steps also require matter and energy expenditure that increase the overall impact of the production system. Chemical syntheses should be rethought, changing reactants if necessary, to avoid these extra steps.

> *9. Use of Catalysts. It is well known that catalysts increase substantially the chemical process rates, without their consumption or insertion into the final products.*

Several syntheses require the use of stoichiometric amounts of reactants whose structure do not end up in the final product (e.g. a stoichiometric acid or base), contributing to the production of waste. This issue is completely bypassed by the use of catalysts, which increase reaction rates and can usually be recycled for more than one use, avoiding waste generation.

> *10. Design of Degradable Products. The design of the final chemical products should be such that, after fulfilling their functions, these products should easily degrade to harmless substances that do not cause environmental pollution.*

In the current design mindset, attention is given to all the phases of the concept and development of goods until the utilization by the end user, but little concern is given to products' end of life. Most of them are designed to be "immortal", thus not to degrade once their useful life is over. Non-degradable products must be disposed of in some way, and when the quantity of waste disposed is higher than what the environment can absorb, its permanence in the environment creates an issue of waste management. Shifting the design perspective from "immortal" to "durable" products, as reported in the 12 principles of engineering (Anastas and Zimmerman, 2003), would relieve this burden: at the end of their life cycle, degradable products would decompose into harmless chemicals which would be taken up by the environment, feeding back matter into ecosystems and preventing pollution issues. This includes, for example, the synthesis of biodegradable polymers from fermentation products, such as poly-lactic acid (PLA) from lactic acid derived from processes like the ones analyzed in the present work.

> *11. Real Time Analysis for the Avoidance of Contamination. Increase in the Role of Analytical Chemistry in Green Technologies Analytical methodologies should be developed in such a way that the process can be monitored in real time.*

In the traditional approach to chemical synthesis, characterization and analyses are carried out at the end of the process. However, if harmful chemicals are formed during a reaction, this will be discovered only a posteriori, thus byproducts will have to be disposed of. By implementing real-time analyses this risk is eliminated, and in the case toxic substances are detected during a synthesis, the process can be immediately interrupted. This is a call to action for analytical chemistry to focus on developing such detection methods. A promising field is that of sensors and biosensors, small devices that can be placed in situ (whether in batch or in a continuous reaction) and connected to an external software.

> *12. Inherently Safer Chemistry for Accident Prevention. The reagents used to carry out chemical processes should be chosen with caution in order to avoid accidents, such as the release of poisonous substances into the atmosphere, explosions and fires.*

Safety of chemical products is key not only for the health of daily workers and users. Mindful of previous environmental disasters due to chemistry-related accidents, the risk of similar episodes in the future must be minimized. Safer chemicals mean less risks both when the system is correctly managed and when "something goes wrong".

4. Main green chemistry metrics - a chronological perspective

The creation of green chemistry metrics is a relatively recent area of research and still an ongoing process. In the following paragraph, an overview of the most relevant metrics is given following the chronological order of their proposal, highlighting the novelty and shortcomings of each to understand the direction of green metrics development. Their equations are summarized in Table 1 in alphabetical order. Note: several papers refer to reactant and reagent as different terms: the first refers to the raw materials directly involved in the structure of the product, whereas the second refers to any mixture or solution aiding or taking part in the reaction. We adopt this same vocabulary referring to green metrics.

- *Chemical yield*. As long as quantitative chemistry has existed, chemists have always calculated yield and taken this metric as a first assessment of the "convenience" of a reaction. The chemical (percent) yield is the percent ratio between actual yield (number of moles of product actually obtained) and theoretical yield (the number of moles of product that result from the stoichiometry of the chemical equation). Knowing that the number of moles corresponds to the mass-to-molecular-weight ratio, yield is directly related to the mass and molecular weights of limiting reactant and product. It provides a first measure of how much of a reactant is converted into the desired product, but does not provide information regarding all the surrounding conditions (efficiency at molecular level, waste, energy use among others).
- *Atom Economy* (AE, 1991). Ratio between the molecular weight of the product and the sum of molecular weights of the reactants. As a "molecular-level efficiency", it aims at determining how efficiently atoms of the reactants are used in the product: the more, the better. It is considered the first example of green metrics, and it paved the way for the development of the class of mass-based metrics. Being focused on the molecular level, it lacks considerations on other aspects of process efficiency, such as stoichiometry, solvents, and waste production.
- *Environmental-factor* (E-factor, 1992). Mass ratio of waste to product. Conceived as a tool for "efficiency in organic synthesis", the focus on the mass of waste per kg of product highlighted a systemic difference between various sectors of industrial production: while syntheses of bulk chemicals resulted in E-factors in the range 1-5

kg/kg product, pharmaceutical processes could reach values higher than 100. This stimulated research towards more efficient processes especially in the field of drug production, which now has become one of the most prolific in terms of green metrics. In its original formulation, E-factor was calculated excluding water, since it is considered to have a negligible environmental impact, but the recent trend in pharmaceutical industry is to include it in the calculation, thus both values of E-factor with and without water can be found in literature. Together with Atom Economy, this indicator became a milestone that sparked interest and awareness in the idea of a greener chemistry. Although in the concept of E-factor part of the energy consumption is included in waste as CO_2 (derived from burnt fossil fuels), this indicator does not provide complete information regarding the energy use of reactions, since electricity is not accounted for and emissions related to heat or steam production can be difficult to keep track of. The other notable shortcoming of this metric is that, in its terms "all waste is born equal", i.e. it does not take into account the different environmental impact of different types of waste.

- *Environmental Quotient* (EQ, 1999). Introduced by Sheldon as a revision of the E-factor, recognising the lack of distinction between different types of waste. It is the product of the E-factor and of Q, "an arbitrarily assigned unfriendliness multiplier", an integer number from one up which defines the overall toxicity of the substance. The EQ is still, by definition, quite arbitrary, since it is not related to ecotoxicity or human toxicity studies, but it brought attention to the need to create quantitative measures of toxicity in order to achieve a truly "green" chemical.

- *Effective Mass Yield* (EMY, 1999). Defined as "percentage of the mass of desired product relative to the mass of all non-benign materials used in its synthesis". It aims at complementing and deepening the information contained in the E-factor, since the non-benign materials used in syntheses translate in non-benign byproducts (i.e.: waste), which makes EMY correspond to 1/E, including only hazardous waste (not all waste like in E-factor).

- *LCA* (1999). When Prof. Graedel proposed to add life cycle assessment to the methods of green chemistry assessment he claimed that "adding a life-cycle perspective to green chemistry enlarges its scope and enhances its environmental benefits". Indeed, LCA is an environmental impact assessment method that allows to quantify not only matter and energy consumption of a process but also its impacts in terms of toxicity on humans and ecosystems, greenhouse gas emissions and much more, through several impact indicators. Given that the attention to green metrics was mainly focused on mass-based tools, LCA can add a broader perspective on how to assess processes' greenness holistically.

- *Reaction mass efficiency* (RME, 2001). Percent ratio of the mass of product and the total mass of reactants. Proposed by GlaxoSmithKline (GSK) for their internal greenness evaluation procedure, it represents a more complete indicator than AE since it takes into account stoichiometry, yield and excess reagents. However, it does not consider the use of solvents, energy consumption and environmental impacts of the synthesis.

- *Mass Intensity* (MI, 2001). Mass Intensity is the total amount of mass required to produce a unit of product (the equivalent of energy intensity) in a reaction step excluding process water, expressed in a weight/weight basis. It corresponds to the E-factor+1. Another metric proposed by GSK, it was later adopted by the Green

Chemistry Institute Pharmaceutical Round Table and renamed Process Mass Intensity (see below). When MI was suggested, the authors performed a correlation test between atom economy and MI of their chemical syntheses and found no evident correlation between the metrics. This means that the two indicators provide different information, thus atom economy alone cannot be viewed as a sufficient tool to evaluate the greenness of a reaction. This highlights the need of finding complementary metrics or developing more comprehensive ones for more holistic evaluations.

- *Process Mass Intensity* (PMI, 2006). Equivalent to mass intensity but for entire processes, PMI is the total amount of mass required to produce a unit product including all the inputs of a reaction. When PMI was adopted by the GCI Roundtable, it became a benchmark for greenness assessments in the pharmaceutical industry. Some groups consider PMI "the most complete mass-based metrics" because it considers all the chemicals involved in a reaction -reagents, solvents, catalysts, auxiliaries and work-up chemicals, including process water- with respect to the mass of product, whereas a different opinion endorses the use of E-factor rather than PMI, claiming that PMI does not add value with respect to the E-factor. "The ideal PMI is 1, whereas the ideal E factor is 0, which more clearly reflects the ultimate goal of zero waste. The E factor also has the advantage that, in evaluating a multi-step process, E factors of individual steps are additive but PMIs are not because PMI doesn't discount step products from the mass balance." On one hand, the E-factor does provide a more immediate measure of "wastefulness" of a reaction. However, since the first formulation, the calculations of this tool assume that 90% of solvents are always recycled (hence only 10% contributes to waste), an estimate often seen as too optimistic and that might result in misleading values. PMI, on the other hand, accounts for all the inputs needed for a synthesis, thus it is a more complete metric, but it does not provide immediate information about the recycling of solvents. Regardless of disputes, as the other mass-based metrics, PMI does not take into account energy consumption, hazardousness of chemicals and environmental impacts.

Several other mass-based metrics have been proposed to evaluate process efficiency, reported in table 1. It is evident that most of them contain the same information rearranged in various fashions, hence calculating each of them for every reaction seems redundant. A choice regarding which to calculate might depend on the scope of a particular analysis.
As previously mentioned, the main shortcoming of these metrics is that (except LCA) they do not provide information regarding energy consumption and environmental impacts of the products and waste generated. To obviate this lack, some mass-based metrics have been proposed (Curzons et al., 2001), but LCA is still one of the most comprehensive tools for environmental impact evaluation, providing also information about energy consumption through the Life Cycle Inventory (LCI).

metric	symbol	equation	unit measure	optimum value	ref.
atom economy	AE	$\dfrac{MW\ product\ (g/mol)}{\Sigma\ MW\ reactants\ and\ reagents\ (g/mol)} * 100$	%	100%	(a)
carbon efficiency	CE	$\dfrac{mass\ of\ carbon\ in\ product\ (kg)}{\Sigma\ mass\ of\ carbon\ in\ reactants\ (kg)}$	%	100%	(b)
chemical yield	CY	$\dfrac{mass\ of\ product\ (kg) * MW\ reactant\ (g/mol)}{mass\ of\ reactant\ (kg) * MW\ product\ (g/mol)} *$	%	100%	(b)
E-factor	E	$\dfrac{\Sigma\ mass\ of\ waste\ (kg)}{mass\ of\ product\ (kg)}$	kg/kg	0	(c)
effective mass yield	EMY	$\dfrac{mass\ of\ product\ (kg)}{\Sigma\ mass\ of\ non-benign\ reagents\ (kg)} * 100$	%	N/A	(d)
env. quotient	EQ	$E\ (kg/kg)\ *\ Q\ (dimensionless)$	kg/kg	0	(c)
mass intensity	MI	$\dfrac{\Sigma\ mass\ of\ all\ inputs\ (kg)}{mass\ of\ product\ (kg)}$	kg/kg	1	(b)
process mass intensity	PMI	$\dfrac{\Sigma\ mass\ of\ inputs\ (incl.\ process\ water)\ (kg)}{mass\ of\ product\ (kg)}$	kg/kg	1	(e)
reaction mass efficiency	RME	$\dfrac{mass\ of\ product\ (kg)}{\Sigma\ mass\ of\ reactants\ (kg)} * 100$	%	100%	(f)
solvent intensity	SI	$\dfrac{\Sigma\ mass\ of\ solvents\ (kg)}{mass\ of\ product\ (kg)}$	kg/kg	0	(b)

Table 1: most widespread green metrics. (a)=Trost, 1991; (b)=Roschangar et al., 2015; (c)=Sheldon, 2017; (d)=Hudlicky, 1999; (e)=Monteith et al., 2020; (f)=Curzons et al., 2001.

5. Then "sustainability assessments" came…

Soon after the development of these metrics, it was clear that the information provided by them was not sufficient. The complexity of chemical syntheses, especially in the pharmaceutical sector, require tools that can embrace this complexity "from a holistic perspective", and this became a common phrase in the area. The limits of mass-based indicators make them not suitable as stand-alone measures of greenness in this holistic sense. For this reason scientists started applying LCA and developing more complex "sustainability assessment methods", i.e. combinations of indicators and procedures to reach a wider evaluation of the sustainability of a process. Green chemistry metrics were combined with energy consumption measures, toxicity indicators and several other factors that influence a synthesis to obtain new tools, with the goal of providing more reliable analyses via still easy-to-use methods. With the creation of these tools, the line between 'green chemistry' and 'sustainability' became more blurred, and several other terms such as 'environmental assessment' started to be widely used in literature. Hence, it is now hard to draw a net line between green chemistry metrics and sustainability or environmental assessment methods. Tickner and Becker (2016) divide the broad world of green chemistry assessments into four categories: progress can be measured at "the molecular level, the

product/chemical level, the firm level, and the societal/policy level" (Blake, 2015). The mass-based metrics examined so far belong to the first category, but several tools at the other levels have been developed both in academia and within companies, both as general evaluation or for specific types of products, many examples of which are reported in the paper. In the following paragraph, a brief overview of the first tools that paved the way to today's variety of assessment tools is provided in chronological order.

EATOS (2002). The Environmental Assessment Tool for Organic Syntheses (EATOS) is a software developed by Eissen and Metzger (2002) at the University of Oldenburg and is used to perform calculations of greenness for reactions at laboratory scale. Since performing a complete LCA or retrieving data about energy consumption and investment is often difficult for reaction at an early stage of development, this tool uses mass index (i.e. Mass Intensity, MI) and E-factor as green metrics to calculate the Potential Environmental Impact for mass unit (PEI/kg) of each compound of feed (named $Q_{m,in}$) and waste (named $Q_{n,out}$) on a 1-10 scale (1=no impact, 10=max impact). The value of $Q_{m,in}$ is established from the R-phrases of chemicals and their cost, whereas $Q_{n,out}$ takes into account potential human and ecotoxicological effects. From these data, the environmental indices EI_{in} and EI_{out} for inputs and waste are calculated as the product of Q and mass intensity (for inputs) or E-factor (for waste). This tool does not introduce substantial innovation in the calculation method (the environmental index EI_{out} corresponds to Sheldon's EQ), but the paper restates the need of quantifying both masses of compounds involved and their environmental impact. Moreover, the authors highlight the necessity of a shift of perspective: while "most chemists tend to focus on the chemical reaction to improve the chemical yield" (ibidem), studying how to reduce the amount of material used and the mass of waste produced is crucial to develop a really green chemistry.

GREENSCOPE (2003). The following year, EPA launched its own tool: Gauging Reaction Effectiveness for the ENvironmental Sustainability of Chemistries with a multi-Objective Process Evaluation (GREENSCOPE) (Gonzales and Smith, 2003). This methodology uses a series of indicators drawn from the Waste Reduction Algorithm (WAR) to evaluate the sustainability of processes dividing indicators in four categories - the four Es: Environment, Efficiency, Economics, Energy. For each indicator, the software calculates a value which is converted into a percent 'sustainability scale' (from 0% to 100% sustainability). In two following papers, the list of indicators and the data needed to calculate them are given (Ruiz-Mercado et al., 2012a, 2012b). Although it is not a life-cycle approach like LCA, GREENSCOPE offers some degree of flexibility in the definition of boundaries, leaving to the operator whether to assess the sustainability of the reaction only or to expand further (Gonzales and Smith, 2003). Given the quantity of indicators used, the tool provides a wide range of information, but it does not appear as immediately intuitive or easy to understand.

EcoScale (2006). On the other hand, EcoScale is an intuitive, easy-to-use semi-quantitative assessment for laboratory-scale reactions. It "evaluates quality of the organic preparation based on yield, cost, safety, [temperature and time] conditions and ease of workup/purification" (Van Aken et al., 2006). Each of these features is assigned a range of 'penalty points' to assign depending on the reaction conditions, then these points are subtracted from a benchmark of 100. The remaining score corresponds to the EcoScale measure, hence the higher the score the "greener" the reaction. This tool succeeds in being easy-to-use, (it has been proposed as a framework for undergraduate green chemistry teaching, as in Dicks et al., 2018), but it has some evident limitations due to the way penalty

points are assigned to each category: the presence of, e.g., expensive reactants, toxic chemicals or energy-consuming workup or purification steps, is penalized with weights assigned with no rigorous, data-based procedures. Hence, the total score of reactions is rather subjective. Another interesting highlight of the paper is that these weights vary when the reaction scale changes, taking into account restrictions on the use of certain reagents or previous regulation. For this reason, this methodology must be carefully applied to avoid scores that do not reflect the real greenness of reactions.

Green Star (2010). Another tool developed for teaching purposes is Green Star (Ribeiro et al., 2010). Conceived as complementary to mass-based metrics, this semi-quantitative method starts from the 12 principles of green chemistry to evaluate a synthesis 'benignness'. Each principle is assigned a criterion (e.g. safety, human toxicity, degradability), measured on a weighted scale from 1 (lowest benignness) to 3 (highest benignness), and the scores of each reaction are graphically represented in a star-shaped scheme - the wider the area, the greener the reaction. The main green metrics were calculated for comparison -yield, E-factor, atom economy and others- and the results of these and Green Star were compared. The authors concluded that Green Star and green chemistry provide "different but complementary indications" about greenness and the two metrics together provide fuller insight into the quality of a process. As for the previous tool, a semi-quantitative metric is useful in an academic environment to teach the overall approach of green chemistry, but cannot be applied to industrial processes for in depth-evaluations.

CHEM21 'Metrics Toolkit' (2015). CHEM21 is the title of a EU project (Chemical Manufacturing Methods for the 21st Century Pharmaceutical Industries, see CORDIS, European Commission) dedicated to create more sustainable alternatives for chemical intermediates in the pharmaceutical industry. After a review of the main green metrics, the project developed its 'Metrics Toolkit' aimed at assessing reactions "from discovery, through scale-up, towards commercialisation" (McElroy et al., 2015). The tool was proposed to assess the state of art, identify bottle-necks and improvements but also become an educational instrument. After defining 10 'key parameters' of a sustainable reaction (e.g. renewability, safety, LCA, energy), a number of metrics were selected to evaluate each parameter. Then, for each metric, the reactions are scored in a system based on flags (green = best 'score', amber, or red = worst score), with the goal of producing a tool with a holistic view. The evaluation is structured on four levels: Zero, First, Second and Third Pass. Each of them corresponds to a stage of research of the synthesis (discovery for Zero and First, scale-up for Second and potential industrial applications for Third) and is related to certain metrics of increasing complexity, to have a level of detail commensurate with the stage of development. This toolkit brings the novelty of a differentiated assessment from laboratory to industrial contexts in a unified system, which can be useful to distinguish the most suitable metrics for each priority. Nevertheless, the flag-based scoring system does not allow immediate quantitative comparisons, which makes the tool effective in a training or teaching environment but not necessarily the most suitable for an industrial system.

Green Aspiration Level (GAL, 2015). The GAL concept is a benchmark developed by Sheldon and coworkers to address sustainability in the drug production sector. In the field of green chemistry, the pharmaceutical industry faces peculiar challenges: having the highest average E-factors among the chemical productions (Sheldon, 2017), the main focus for improving processes greenness is reducing waste production. Moreover, the sector suffers from the lack of standardization of green metrics. For this reason, Sheldon and coauthors proposed a list of suggestions to standardize the methodology of greenness assessment for

pharmaceutical applications. As a first point, they recommend to adopt a series of metrics based on the E-factor concept, one of the few to capture the dimension of waste production; to dissipate uncertainties around the inputs to consider as 'waste', they introduce two E-factor measures, one including all process inputs ("complete E-factor", cEF), and one which discounts water and solvents ("simple E-factor", sEF). Secondly, they claim the necessity to define a benchmark 'starting point' of reactions to avoid falsification of E-factors by externalization of process steps ("one can dramatically reduce the process E factor overnight by purchasing an intermediate rather than making it", see Roschangar et al., 2015); they suggest to define the 'starting point' of a synthesis as the first step from "commonly available starting materials". Then, the concept of 'process complexity' is introduced, defined as the sum of the number of 'construction reactions' (in which C-C or C-heteroatom bonds are formed, creating the skeleton of the molecule) and 'strategic redox reactions' (that establish the correct functionality for the final product). After establishing the bases, the Green Aspiration Level is introduced, as "an unbiased metric of green process performance relative to industry", with the goal of standardizing green metrics in the pharmaceutical sector. GAL is calculated from "average development phase-dependent E factors for the pharmaceutical industry as a whole from the PMIs" multiplied by the relative complexity of the process considered (i.e. complexity of the examined synthesis divided by the average complexity of pharmaceutical industry). The GAL is not based on the evaluation of the environmental impact of the waste produced (in fact, as the original E-factor, it lacks an assessment on the hazardousness of that waste), but on an "internal" comparison between the current state of art of industrial syntheses and the new paths proposed. For this reason the application of this methodology has the potential to stimulate dramatic improvements in the pharmaceutical industry. However, the disposal of the waste still generated by processes must be monitored in order to minimize its environmental burden. Another promising point of the paper is the focus on the concept of process complexity; since molecules require a high number of process steps, its application seems more suitable for drug production, but the notion can be exported to other sectors of chemistry to improve their greenness by reducing the number of non-essential steps. The GAL concept was later revised with the introduction of the 'innovation GAL' (iGAL) in 2018 (Roschangar et al., 2018).

6. Firms' metrics: proactivity and shortcomings

Soon after the development of the first green metrics, companies started seeing the potential competitive advantage of adopting this 'green attitude' in their business practice. To communicate their efforts and results to reduce their environmental impacts, firms began incorporating green metrics or developing their own. A few examples include SEEbalance© (BASF, 2004), GREEN MOTION™ (MANE, 2012, see Phan et al., 2015) and Chimex's Eco-footprint (L'Oreal, 2014, see Leseurre et al., 2014). The first encompasses the 'three pillars' of sustainability, evaluating costs, environmental impacts and social effects of products or processes. The second is a semi-quantitative tool similar to EcoScale that starts from the 12 green chemistry principles and assigns to all MANE's production processes a score from 0 to 100; this score is determined from a 100 baseline by subtracting a number of penalty points proportional to every "non-green" production feature (e.g. non-natural raw materials, toxic inputs or products, energy-intensive steps etc.). The third tool is similar to GreenStar, since it presents ten indicators (e.g. water consumption, synthetic pathway efficiency, valorization of used solvents etc.) that are evaluated on a 1-4 scale, using a

graphical representation where the wider the area, the 'greener' the process. Extending its effort to share its method, MANE also designed a user-friendly interface on its website that allows other firms to evaluate their 'GREEN MOTION™ score' after signing in, through a series of yes/no or multiple choice questions. This is a promising step forward in broadening the adoption of green metrics and rendering their calculation easy for non-specialized users.

On the other hand, the fact that several companies are creating their own sustainability or greenness assessment methods generates ambiguity in the green metrics panorama: if each firm uses a different evaluation scheme, it is impossible to compare results from different sources, hence to delineate a broader perspective in terms of "who is the greenest". Instead of aiming at standardization of results, "branded" metrics promote a competition not based on comparison with competitors, but exclusively on the amelioration of internal procedures. Thus, if all the information regarding greenness assessment were fully public, the final consumer would be overloaded by too much information from too different frameworks. Another risk related to individual indicators is greenwashing. Industrial assessment procedures might not be completely transparent to the public due to commercial purposes; this could lead to pernicious practices of hiding or misrepresenting evaluation methods and results, so to appear "greener" than real. It would be beneficial for firms to agree on common metrics and adopt a shared assessment framework, both in terms of progress in knowledge and in terms of ease for the final consumer.

An interesting case showcasing the risk of diversified industrial metrics is presented in the following lines. In 2016, a group of academics and representatives of the biggest pharmaceutical companies gathered to establish a common framework to evaluate greenness in their production processes, aiming to "unify the many metric-based approaches and transform them into tangible and uncomplicated goals" (Roschangar et al., 2017) and "create a good communication strategy for alignment across the pharmaceutical industry" (ibidem). Starting from the GAL, the group streamlined a methodology and defined common indicators in the GAL framework, in a discussion that was later published on *Green Chemistry*. Only three years later, a group of chemists at Novartis published a paper on Chimia, a journal of the Swiss Chemical Society, about a novel "Green Chemistry Process Scorecard" (Onken et al., 2019) used to evaluate all the firm's processes, with no relation to the previous GAL tool. The paper presents an innovative approach to defining metrics: to ensure that their method is easily understood from all areas of the organization, the group organized a brainstorming session to engage the organization in designing their label, involving both technical and managerial personnel. During this session, the need of a "common currency", a simple metric which could be easily understood by non-specialists, emerged, and the choice fell on 'carbon dioxide release'. According to the authors, all the firm's contributions that can cause environmental impacts can be translated into a carbon dioxide release measure, hence this quantity "can be used as a universal unit of measurement for the ecological footprint" of their products. An overview of internal chemical processes highlighted four main contributions to CO_2 emissions: incineration of organic waste (>90% of total), wastewater treatment, energy consumption and "other" (transport, plant operation, packaging, process development etc, not considered in their analysis). After this investigation, the team started proposing possible indicators to use as their "green label" until "a couple of specific advanced options were identified"; then, they asked their "global chemical development" organization" to vote which indicator to implement. The outcome is a Scorecard that rates processes from A (lowest impact) to E (highest impact), where the boundaries between the letters were "defined a priori and refined

within a couple of years". This Scorecard rate was applied to all the syntheses in the company's portfolio, which were later 'calibrated' to the amount of each product needed at peak volume, to explore where the highest absolute amount of waste is produced, regardless of the single process score.

The methodology that led to the elaboration of this Scorecard is peculiar enough to deserve a comment. First, the amount of carbon dioxide released can hardly be considered a "universal" measure of ecological footprint. As a proxy, it can provide an indication of higher or lower use of fossil fuels or incineration of organic matter, but it cannot take into account other types of environmental impact (e.g. eutrophication, ecotoxicity etc). Taking an example from the paper, which says that solvents disposal constitutes the major fraction of CO_2 released, it would be enough to stop disposing of solvents by incineration and instead releasing them in wastewaters to drastically reduce the CO_2 release without abating (instead, skyrocketing) environmental impacts. Moreover, although the paper refers to the 12 principles as a reference for process improvement, this indicator alone cannot give a measure of process greenness, because it is not related to several of the principles - to the number of steps, to the toxicity of substances used or to renewability of feedstocks, for example. Considering carbon dioxide emissions as a proxy for the "intensity" of a process can be a good first approximation, but taking it as a measure of total impacts can be misleading. On the other hand, the choice of calibrating the scale on the absolute amount of product needed at peak volume is a smart way to find areas of improvement in terms of overall waste reduction, but the A-E scale (associated with green-to-red colors) does not allow the same identification inside each process, to find the most intensive steps. As for the decision-making process, involving the company's diverse population in creating their greenness indicator is indeed a groundbreaking novelty that could bring benefit inside the company, in terms of employees cohesion and ownership, and to communication and dissemination of results with stakeholders and the audience. However, the democratic methodology of voting leaves space for uncertainty from the scientific side. A "voted" indicator does not necessarily represent the most effective choice from a technical perspective. An effort should be made to avoid moving in the direction of a "populism in science", where all votes (specialists and non-specialists) are made equal, to aim instead to a "dissemination of scientific culture", in order to give everybody the essential technical concepts to understand the basics of sustainability assessment. Last, the group made the interesting choice of naming their tool "Eco-label", which sounds vaguely similar to the widely adopted EU Ecolabel certification (European Commission, online).

Considering the overall context of the two papers, it is difficult not to notice that this latter was published after Novartis had agreed with other firms to evaluate sustainability with a common method within the GAL framework. Unfortunately, it is not clear whether the companies currently use the shared GAL-based methodology or any other metrics, since, to the best of our knowledge, no information was available from their websites.

Of course it is not possible to know the exact dynamics behind the two publications, which perhaps reflect a natural chronological progress in scientific research, but what we see leaves the impression of opportunistic behavior, riding the "greenness" wave to attract attention on their own firm. It is to be noted that, rather than "for reputation building, innovation and competitive advantage" (Roschangar et al., 2017), environmental protection should be seen as a necessity for human (therefore business) survival.

7. Summing up

Greenness and sustainability are related, but are not the same thing. Sustainability is a broad concept that incorporates elements of environmental preservation, social justice and economic feasibility, at different levels of relevance, as expressed in the first chapter. In order to ensure the perpetuation of a system as the definition says, sustainability of all three components must be accomplished. Greenness, in relation to green chemistry, is a concept born within a specific field of science. It aims at quantifying the ecological burden of chemistry on the environment, hence it can be seen as a form of process efficiency. Even though the 12 principles encompass a broad range of relations between chemistry and the environment, most metrics measure how materials and/or energy are used in a production system. Green metrics do not answer the question "Can this system sustain itself indefinitely?" but "How much does this process consume/produce/emit?". They focus on specific aspects of reactions to quantify resource consumption efficiency. For their formulation, they are effective and extremely helpful to evaluate and improve a chemical process' performance, but cannot capture the broader view of how the process (or single step, or entire chemical plant) interacts with the surrounding environment, being ecological, social or economical. Green metrics do not investigate whether the energy required to extract raw materials is less or more than that embodied in the products, nor whether the environmental impacts of the process and the waste are high or low (see the shortcoming of E-factor); this is why LCA is often associated with green metrics or sustainability assessment methods. For this reason, they are certainly comprehensive tools, exploring several aspects at one time, but it is hard to define them as 'holistic'. Even though some green chemists might feel disrespected in their efforts, the reason for this claim, and the motiv to go further with elaboration of sustainability assessment methods, is explained in the following chapter.

Chapter 3 - Emergy analysis

1. Emergy? Is it spelled wrong?

The word "emergy" (spelled with an "m") derives from "embodied energy", a concept related to systems ecology, thermodynamics and complex systems science that has been used to study the dynamics of self-organizing systems, and consequently improve decision-making to achieve sustainability (Gaudreau et al., 2010). Most books and papers report the original definition: "*emergy is the available energy (exergy) of one kind that is used up in transformations directly and indirectly to make a product or service*" (Odum, 1996) - but to understand what this means in depth we have to dive into the context behind its birth (Brown and Ulgiati, 2004).

2. Short philosophical history of the emergy language

The concept was proposed by H.T. Odum (1924-2002), an ecologist who worked on systemic analysis of ecosystems, energy systems and social-economical systems. Over the course of his ecological studies in the 1950s and 1960s, he focused on quantifying energy flows in ecosystems and how these affect ecosystem functioning. From here, he started reflecting on the idea of '*energy quality*': different types of energy have different ability to perform work, depending on how "concentrated" the type of energy is. Furthermore, he pointed out that the actual possibility of utilization of energy depends not only on its availability, but also on the cost of extraction and/or concentration. The quantity of energy of one kind required to make a quantity of energy of a different kind was defined through ratios called 'quality factors'. The first definition of energy quality is dated 1973: "The ability to do work for man depends on the energy quality and quantity and this is measurable by the amount of energy of a lower quality grade required to develop the higher grade" (Odum, 1973).
Another concept derived from his ecological background and energy source observation is that of '*net production*'. Odum suggested that an energy source must provide a net energy contribution to the larger system it is used in, which means it must provide more energy than that spent for extracting and processing it. This net energy constitutes the true value of energy. The inputs spent for extraction and process of energy include not only material sources, but also environmental and human services. This attention to all the energy, material, labor, services and information spent for producing a good is what characterizes all emergy analysis, whose name was born in 1983 (Brown and Ulgiati, 2004).

3. So what is so special about it?

Breaking down the definition helps gaining some insight:
"*emergy is the available energy*" = Available energy (exergy) is the 'net energy' that remains after subtracting the energy dissipated in heat due to the second law of thermodynamics, i.e. the energy that can be actually used to generate work;
"*of one kind*" = all the contributions needed to create a product, whether in terms of matter, energy, labor, services or information, are accounted for, converting each input in the same unit measure: solar emergy.

"used up in transformations directly or indirectly" = all the steps necessary to obtain a product or a service are taken into account: to produce a jar of jam, all the inputs, expressed in terms of solar energy, from the solar irradiation needed to grow fruit to the silica used to mold the jar, the work of the employee supervising the production chain and even the cost of waste disposal of the factory are accounted for.

"to make a product or a service" = this accounting method can be applied to physical goods, but also to human services, ecosystems, industrial districts and any other complex system.

Innovations

The emergy concept introduces some radical innovations in the way we conceive systems, first of all in how we think of the '*value*' of things: instead of a market price determined by the perceived utility of a good (*user-side perspective*), value is now quantified through emergy, which is the sum of all contributions of energy, matter and services that were necessary to produce that good (*donor-side perspective*). Emergy quantifies the *memory* of the investment for its production, not an actual energy quantity; it is "a measure of the past and present environmental support to any process occurring in the biosphere" (Brown and Ulgiati, 2004). Another aspect of this revolutionary approach is the possibility of quantifying different inputs with the same unit measure. Even though we were taught that "we cannot sum apples with pears", the emergy accounting method allows us to do so through its specific algebra. All the "pears", "apples" and other contributions are quantified in emergy, measured in *emjoules* (emergy joules). Since solar energy is usually taken as a reference form of emergy, all the emergy inputs are expressed in terms of solar emergy, which corresponds to the amount of solar energy required to obtain that specific input. The unit measure of solar emergy is the *solar emjoule* (sej).

Although these two aspects already make the emergy method unique with respect to other sustainability assessments, the sharpest paradigm shift is definitely the 'completeness' of this accounting: this analysis considers not only the matter and energy inputs traditionally included in other assessments (e.g. fossil fuels, raw materials, electricity), but also the contribution of environmental and human inputs. The solar energy needed for plants to grow, the rain and the rivers providing water in ecosystems, the geothermal heat of Earth, the labor of workers, and all the services of the economy, from electricity provision to waste disposal - everything is accounted for in emergy analysis. Each of these inputs, expressed in different units measure, can be transformed into emergy quantities through the use of 'conversion factors' named Unit Emergy Values (UEVs, the previous 'quality factors'), which quantify the amount of emergy corresponding to one unit of input. etc. These UEVs are defined starting from a global emergy baseline (GEB), which is the annual amount of direct available energy that supports the geo-biosphere, given in solar equivalent joules (Perosa et al., 2019).

Language

Within the framework of emergy analysis (also referred to as emergy synthesis or emergy accounting, the latter being a statical analysis of a stationary system operation, aimed at calculating sustainability indicators), systems are described through the 'energy systems language', adapted from electronic circuits in energy networks, whose symbols are represented in figure 5 and described in the following paragraphs. These symbols are used to draw the diagrams that represent the systems under study.
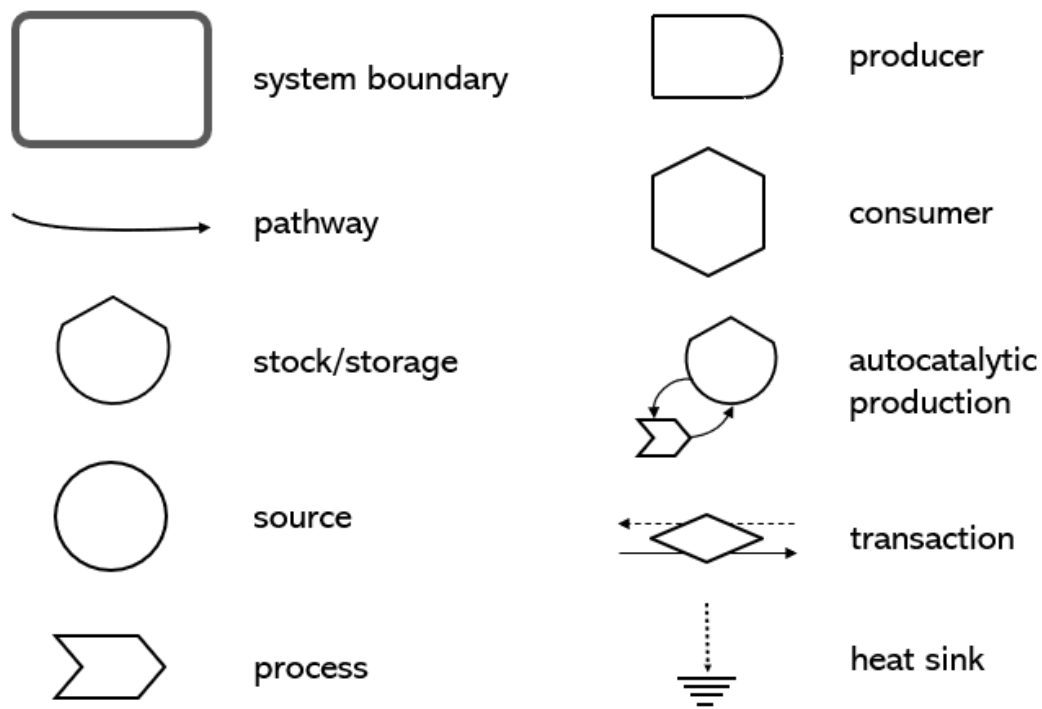
Figure 5: energy systems language

System boundary. The limit that separates the system from the surrounding environment. Since there is often no physical separation between "inside" and "outside" of a system, the boundary is defined by the authors depending on the scope of the study. It includes a three-dimensional spatial and a temporal dimension. For this study, the boundary coincides with the physical space of the (modelized) production plant, both in height and area, and refers to one year of production, set to 1 ton.

Pathway. Flows of energy, matter or information (solid lines) or money (dashed lines). It represents a flow that moves from a system component to another.

Stock/storage. Store of energy, matter, information or money. Stores in a system are linked to each other through pathways (inflows and outflows) of the same "substance".

Source. Source of energy, matter, information or money from outside to inside the system. It can be not-limited (sources that can be used with no limitation in quantity or rate, e.g. goods or information) or flow-limited (which have a maximum rate of inflow, e.g. solar radiation).

Interaction/production function (process). Process in which two or more flows of various energies or materials interact to generate different products. The most common type is the multiplicative interaction, where the output equals the product of the inputs.

Producer. System component characterized by a photosynthetic production function, which can convert solar radiation to organic matter (e.g. a plant, a grassland, a crop field).

Consumer. System component that consumes energy, material or information generated by a different component (e.g. a herbivore feeding on grass, a predator feeding on prey).

Autocatalytic production. Feedback loop composed by a storage and a process connected, in which the outflow of the stock is fed to the multiplicative interaction and, increased, enters back into the storage. The larger the storage, the greater the feedback.

Transaction. Exchange of a money flow for energy, materials or information flow.

Heat sink. Visualization of the energy dissipated in heat due to the second law of thermodynamics.

Epistemology

Another remarkable aspect of emergy is its *philosophical framework*. Odum's production went far beyond the mere definition of a scientific, technical concept: through his several publications, he framed emergy in the context of the current environmental change, expressing the need for a paradigm shift for humanity. Through diagrams and systems language, we can aim at gaining a deeper understanding of nature, humanity and the economy and society we have built. He explored the "epistemological values of explaining (theoretical), accounting (analytical) and understanding (epistemic)" through three levels of analysis (Perosa et al., 2019) :

- a 'model' ('Modell', from the German), a mental construction created by humans to facilitate the study of parts of the surrounding world, that does not aim at explaining reality but to address the analytical need of 'accounting', measuring, calculating;
- an 'image of the world' ('Weltbild'), the "set of definitions, axioms and theorems which has the pretension of telling how the reality is" (ibidem), i.e. what we call a 'scientific theory', to explain the events we witness and predict new events;
- an 'intuition of the world' ('Weltanschauung'), a mental view that aims at giving meaning to reality, not a scientific construct but a perspective with "metaphysical, ethical, aesthetical, ontological principles" (ibidem) with which each human approaches their understanding of the world.

Thus, emergy is much more than a tool to evaluate sustainability - it provides a new perspective to enrich our understanding of reality, of which the language used (the energy systems language) is an intrinsic component.

Formally, emergy is neither an extensive nor an intensive quantity, but a 'memory' of the energy invested to create something. It is not a state function, because the emergy of a product depends on the process through which it was generated. The more energy was spent in producing a good (or service, or other), the more energy is 'embodied' in that product, hence the higher the emergy content. A high emergy content can be linked to either a high inefficiency in resource consumption for the good's production or to a high level of complexity of the product.

Among the theoretical contributions, Odum proposed the '*maximum empower principle*' as a potential fourth law of thermodynamics. In the early 20th century, Lotka proposed the 'maximum power principle' to explain the behavior of complex systems (i.e. systems capable of self-organization) such as ecosystems. He stated that self-organizing systems tend to maximize the power extracted from the surrounding environment, and that those which prevail in the competition of natural selection are the ones that are most capable at maximizing this power. The survivors are not the most efficient (where efficiency is the ratio between the work the system performs and the energy taken from the environment) or the fastest (i.e. the ones with highest rate of energy consumption and production), but the ones that generate the highest power (where power is the energy per unit of time). Odum reinterpreted this principle in emergy terms, stating that the systems that win in competition are the ones that maximize their empower (emergy per unit time, measured in emjoules per second) (Odum, 1996).

Energy hierarchy

Another paradigm shift introduced by the emergy framework is the concept of *energy hierarchy*. As a "formalization" of energy quality, Odum suggested that types of energy with different qualities act at different levels of complexity inside a system. Larger inputs of lower energy quality generate smaller outputs of higher energy quality, which in turn generate even smaller outputs of higher quality. Matter, energy and information of lower quality converge to give rise to more complex structures of higher quality, through parallel and hierarchical processes. This energy quality is linked to the "position" of energy in the hierarchy of the system and to the ability of energy to exert a control function on the system it acts upon. Figure 6 (Brown & Ulgiati, 2004) explains the concept of hierarchy in a generic system. In (a) several units with different levels of complexity are viewed together; in (b) these levels are seen individually, separated by their level of complexity from the lowest to the highest. In (c) a representation of these levels in energy systems language is shown: on the left side, the energy source feeds low-quality energy into the system, which is used by the lowest-complexity units (A-E, producers, plants which perform photosynthesis), whose energy in turn feeds a higher-complexity level (J-L, consumers who feed on plants) that produces higher quality energy, energy that is transferred to a higher level (S-T, consumers who feed on consumers) which elaborates it into a higher-quality energy transferred to a higher-complexity level (Z, consumer) and so on to higher complexity levels and higher quality energy. From left to right, the complexity of the levels and the quality of energy increase, while the total energy and the number of units of high complexity that a system can support decrease. From right to left, higher-complexity units exert a control function on lower-complexity levels through feedbacks, flows of energy that regulate the functioning of lower units (e.g. mechanisms of population control through predation). In (d) the 'transformation series' of the system is shown: the scheme reports the orders of magnitude of energy transferred for each level of complexity, starting from the most abundant (the Sun, energy source) to the most scarce (unit Z, highest complexity); energy flows are reported in solar empower (emergy per unit time, sej/t). In (e) the relationship between power and complexity levels is represented, passing from the lowest level (lowest energy quality, highest net power) to the highest (highest energy quality, lowest net power). Scheme (f) reports the relationship between complexity levels and transformity, the UEV that quantifies the amount of emergy per unit energy (measured in solar emjoules over joules, sej/j): the lowest level is characterized by the lowest energy quality, hence lowest transformity (i.e. one unit emergy corresponds to a low amount of energy), whereas the highest level has the highest energy quality, thus highest transformity (one unit emergy requires a high amount of energy, which is all that is accumulated from the lower levels).
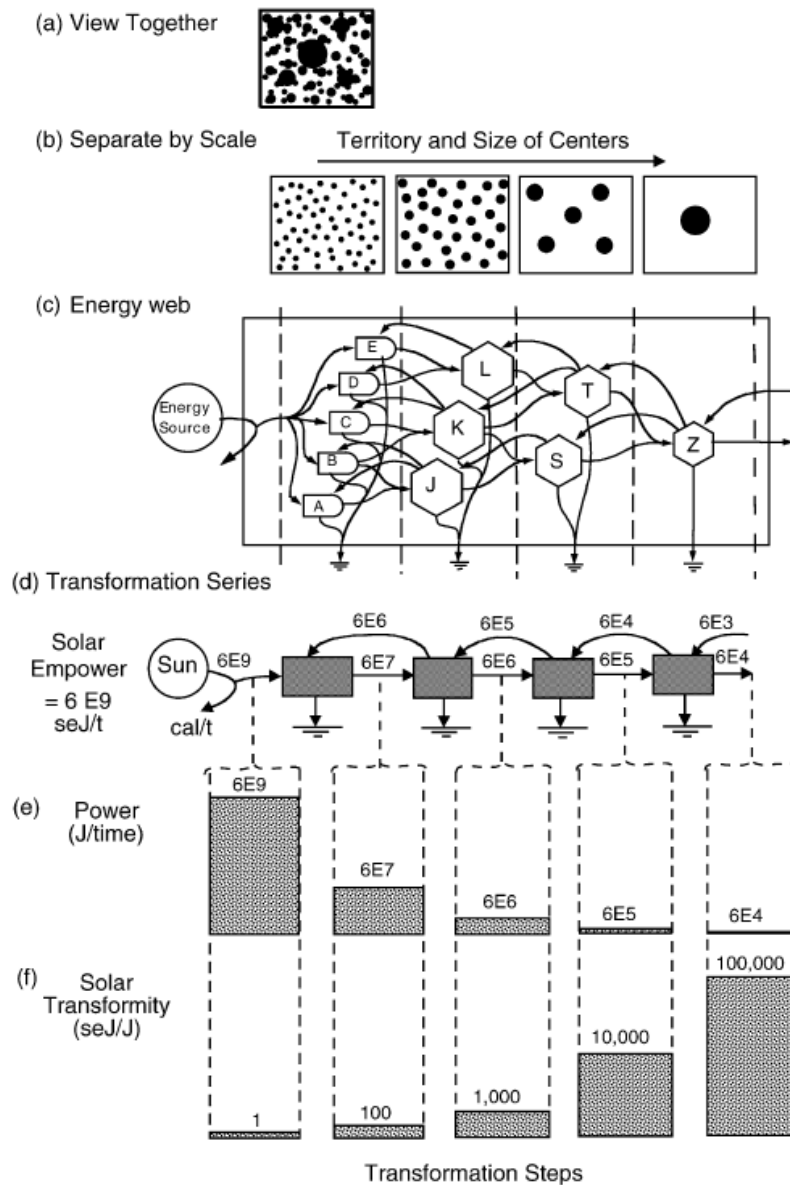
Figure 6: Concepts of energy transformation hierarchy. (a) All units viewed together; (b) units separated by scale; (c) the units as a web of energy flows; (d) units shown as a transformation series with values of energy flow on pathways; (e) useful power flowing between transformations; and (f) transformities (Brown and Ulgiati, 2004).

4. How emergy analysis works

No matter how different systems may appear, there is always a common methodology to perform emergy analysis:

1. *Diagramming*. The system under study is first verbally described in all its components, defining its main scope, main process, main product and temporal and spatial boundaries. With this information, the diagram of its structure and its relationships is drawn using the energy systems language;

2. *Inventory*. All the flows acting inside the system are listed in a table and quantified. For each of them, the correspondent UEV is determined, allowing to calculate the

total emergetic contribution of each flow and the total emergy output of the system (related to its mass or energy output);

3. *Indicators*. After quantifying all the emergy flows, indicators are chosen and calculated according to the scope of the study. These give a measure of the environmental load and of the sustainability of the system.

The first phase is a peculiar trait of emergy analysis and it has a twofold function: it allows to visualize and quantify the flows acting on and inside the system, including feedbacks, for the following quantitative step of the inventory; and it highlights the cause-effect relationships between flows and stocks of energy, matter, information and money, disclosing a level of understanding of the intrinsic functioning of systems not always possible in other assessment methods.

The second step is the determination of the emergy flows. From the emergy diagram, all the flows that enter the system are listed in an emergy table, each input described with its amount and unit measure. These flows are then converted into emergy flows through the corresponding Unit Emergy Values (UEVs), which represent the amount of emergy per unit input. The UEVs quantify how much emergy is needed to produce one unit of input or output, whether this is energy, matter, information, etc. Each flow in the table is multiplied by the respective UEV to obtain the emergy flows, which are then summed through the emergy algebra rules to obtain the total emergy involved in the process. As a last step, the UEV of the output(s) is (or are) calculated by dividing the total emergy flow by the quantity of output(s). Usually, output(s) UEVs are calculated both with and without the contribution of labor and services (L&S), to allow easier comparisons between the same products in Countries with different economies. Comparing two outputs obtained from different processes, the one with higher UEV is related to the process with lower efficiency, since more emergy was needed to obtain the same product. In the following lines the main UEVs used in emergy analysis are reported.

Transformity. Emergy per unit of available energy (exergy), measured in solar emjoules over joules (sej/J). The transformity of solar energy is 1 sej/J by definition, because solar energy was chosen as a reference for emergy measurements.

Specific emergy. Emergy per unit mass, measured in solar emjoules over grams (sej/g).

Emergy cost of labor. Emergy per unit labor. This unit labor can be measured either in solar emjoules over currency (e.g. sej/$, sej/€) related to the stipend provided to the worker, or in solar emjoules over time (sej/year, sej/hour), related to the amount of time needed for a specific task. If the labor is manual, some studies report it in solar emjoules over joule or calories (sej/J or sej/cal), linked to the amount of physical work (in a thermodynamics sense) provided by the workforce. This UEV represents the emergy spent for a worker's sustenance, education, commuting etc.

Emergy per unit money. Emergy used to generate one unit of an economic product, expressed in emergy per unit currency (e.g. sej/$, sej/€). It is obtained by dividing the total emergy of a system for its currency used (e.g. the GDP for a nation), and it represents the emergy linked to a system's purchasing power.

To calculate the total emergy involved in a system, assigning to each flow its corresponding emergy value, the emergy analysis follows its own algebra. Five rules dictate how to combine emergy flows.

1. The total emergy of a process is the sum of the products of each input flow and its UEV:

$$Em_Y = \Sigma_i^n (E_i \cdot UEV_i) \quad i = 1, \ldots, n$$

where Em_Y is the emergy of the output (yield) of the process, E_i is the i-th input flow and UEV_i is the UEV of the i-th input flow;

2. If a process has one output, all independent emergy flows are assigned to the output:

$$\Sigma_i^n Em_i \Rightarrow Y$$

where Em_i is the emergy of the i-th input flow, "$\Rightarrow$" is "assigned to" and Y is the output (yield);

3. When a flow splits, its emergy is assigned to each branch based on the ratio between available energy (or mass) on the split pathway and available energy (or mass) on the pathway before the split:

$$Em_j = (E_j/E_T) \cdot Em_T$$

where Em_j is the emergy on pathway j after the split, E_j is the available energy on pathway j after the split, E_T is the total available energy on pathway T before the split and Em_T is the total emergy of pathway T before the split. As a result of this rule, all split pathways have the same UEV;

4. If a process has two or more coproducts, all independent emergy flows are assigned to each coproduct:

$$\Sigma_i^n Em_i \Rightarrow \forall Y_i \in \{Y_1, \ldots, Y_n\}$$

where Em_i is the emergy of the i-th input flow, "$\Rightarrow$" is "assigned to", "$\forall$" is "for all", Y_i is the i-th co-product and "$\in$" is "belonging to the set of" all the coproducts (from Y_1 to Y_n).

5. Emergy from feedbacks and reunited coproducts cannot be double-counted; only independent flows are summed to yield an emergy flow never greater than the emergy flow from which the feedbacks or coproducts derive:

$$\cup_i^n \{Em_i\} \Rightarrow \forall Y_i \in \{Y_1, \ldots, Y_n\}$$

where "$\cup$" is the union operator of set theory, which takes only the distinct elements of two sets (i.e. all the elements without repetition).

This last rule in particular clarifies a possible misunderstanding of rule 4, in which the total emergy seems to increase as a result of the production of coproducts. Coproducts are defined as products that cannot be obtained one without the other from one process, hence the same energy input invested for the production of one coproduct is also invested for the production of the other, whether the second product is desired or not, thus the total emergy is assigned to both. When merging flows that include coproducts of the same process, only the product with the highest emergy flow is counted.

The last step is the calculation of *emergy indicators*, which help interpreting the results of the analysis. Regardless of the type of system (ecosystem, industrial system, etc), indicators provide immediately readable information regarding resource utilization, load on the environment and long term sustainability of the system. In a generic system (figure 7), few main emergy flows can be identified: local renewable resources (R), natural nonrenewable resources (N) and nonrenewable resources from outside the system (F), which includes purchased energy and services. The total emergy yield of the system is Y = R + N + F. The following paragraph illustrates the most used performance indicators in emergy accounting.
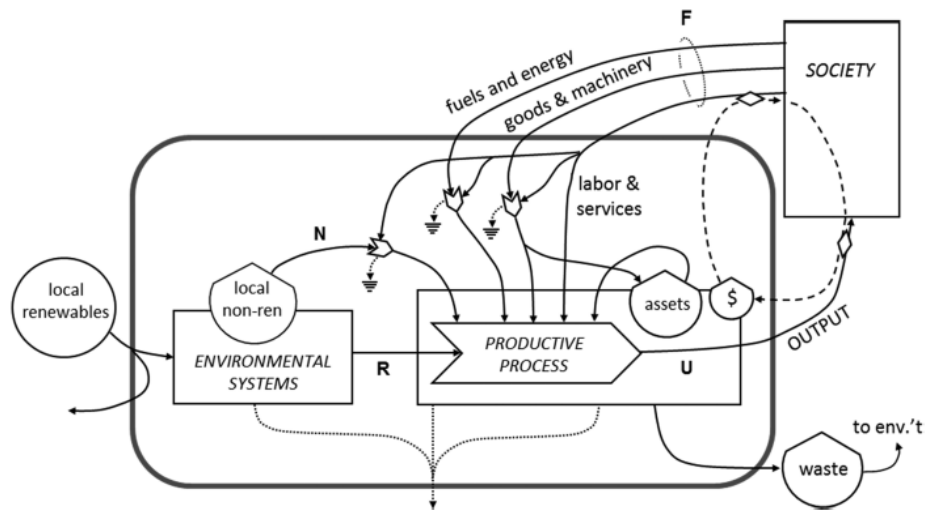
Figure 7: emergy diagram of a generic system, including environment and human activities (Perosa et al., 2019).

- *Transformity: emergy/unit product.* Whether we consider transformities (i.e. emergy per unit energy) or specific emergy (i.e. emergy per unit mass), the UEVs of the output(s) of a system are considered both a measure of product quality and of system efficiency. Defined as the solar emergy necessary to obtain a unit product (energy or mass), "the higher its value, the higher the complexity of the process and the quality of its product" (Bastianoni et al., 2009), so that when comparing different processes with different outputs, the output with higher UEV is assumed to be the one with higher complexity and quality. At the same time, when comparing different systems yielding the same output (same level of complexity), the one with the lower UEV is the one coming from the most efficient process. This can be explained by the fact that the lower the UEV, the lower the amount of emergy needed for the overall production.
- *Emergy Yield Ratio: EYR=Y/F.* Measure of the emergy purchased from the external economy (F) with respect to the total emergy output (Y). It is related to the extent to which the emergetic output of a system depends on resources purchased from outside. It indicates how efficient the system is in using environmental resources with a given input from the economy. It provides information about the local/nonlocal aspect of resources, without separating the renewable and non-renewable components of resources. Ranging from a minimum value of 1 (the output equals the purchased resources) to a potential value of infinity (high use of environmental resources with a small purchased input), the higher the value, the higher is the emergy output per unit purchased emergy, thus the more efficient the system is in using environmental resources.
- *Environmental Loading Ratio: ELR=(F+N)/R.* measure of the sum of the emergy received from the economy and the local non-renewable resources with respect to the emergy received from local renewables. It quantifies the renewable/non-renewable ratio without distinguishing between local or non-local resources. It is related to the environmental impact of the system, with a minimum value of 0 (system using only local renewables) to a potential value of infinity

(system using almost exclusively non-renewables). The smaller the value, the lower the impact of the system on the environment.

- *Emergy Sustainability Index: ESI=EYR/ELR*. Ratio of the previous two indicators, it represents an integrated measure of the economic yield and of the environmental performance of a system. It merges two indicators that quantify the spatial dependence (local-vs-nonlocal resources) and the renewability of the resources used, therefore constituting an integrated measure of the long-term sustainability of the system.
- *Emergy Investment Ratio: EIR=F/(R+N)*. Ratio between the emergy purchased from outside and the emergy provided from the local environment. It is a measure of how much the economy invests to exploit the environmental resources, thus it provides information about the local-vs-nonlocal nature of the resources used.

Beyond the most widespread indicators, several others can be calculated, or even designed ad hoc, to evaluate specific features of the system(s) depending on the system(s) under study. For the present work, a few indicators were selected from literature to evaluate the peculiarities of the lactic acid production systems.

- *Unit Emergy Investment (UEI)*. Some production systems fall in the category of 'integrated systems', where the byproduct(s) of a subsystem becomes raw material for a following subsystem. To evaluate the "advantage" of utilizing these byproducts to obtain further output, Patrizi et al. (2015) formulated the Unit Emergy Investment indicator: "We refer to emergy investment to indicate the quantity of inputs, expressed in emergy terms, that we add to an existing system or process, in order to obtain further output(s) or optimize the use of resources". It represents a measure of the required (additional) investment to obtain one unit of the "second" output. This output might also become a substitute for another product, perhaps derived from non-renewable resources: in the case study presented in the paper, a new plant for second generation bioethanol is proposed to take advantage of byproducts of local systems, to substitute part of the gasoline necessary for the local area. This indicator is useful to compare the same output produced by different systems when one output derives from raw matter and one from byproducts of a different system.
- *Pollutant Density Index: PDI = $10\log(\varepsilon\delta_{Total}/\varepsilon\delta_{Ref})$*. When dealing with chemical production systems, it is key to consider not only the resources used upfront, but also the potential environmental impact of the substances released in the surrounding environment. To quantify the effect of pollutants (e.g. nutrients, heavy metals, toxins) in terms of emergy, Brown (2009) proposes a Pollutant Density Index, which relates the emergy density of pollutants to the ones of the environment. The index stems from the idea that a pollutant creates a higher environmental impact the higher its emergy density is with respect to the emergy density of the background environment: as the UEV and concentration of a pollutant increases, the potential damage in ecosystems increases. From this premise, the index quantifies the potential impact of all pollutants released from a given system into a unit volume of environment (most commonly, freshwater) through the following formula:

$$PDI = 10\log(\varepsilon\delta_{Total}/\varepsilon\delta_{Ref})$$

where $\varepsilon\delta_{Total}$ is the total emergy density of the volume of environment, calculated as $\varepsilon\delta_{Ref} + \Sigma\varepsilon\delta_i$, sum of the emergy density of the background environment (reference, Ref) and the sum of the emergy density of each pollutant (sum of each $\varepsilon\delta_i$).

- *Unsustainability indices.* Sustainability, as it has been defined in the previous chapters, is more of an ideal state than a measurable quantity. Thus, some authors have proposed to shift the attention to the degree of unsustainability of systems, which is more clearly quantifiable as the distance between the current system and the ideal sustainable version of it. In emergy terms, different indices were proposed to achieve this goal. Artuzo et al. (2021) identifies the unsustainability of a system with the reciprocal of its sustainability:

$$EuSI=1/ESI=ELR/EYR$$

  where ESI is the Emergy Sustainability Index seen above. The EuSI remains related to the fraction of renewables-vs-nonrenewables and local-vs-nonlocal resources, but so presented it highlights the burden of the process on the environment. The more the burden, the higher the unsustainability. With the same aim, Bastianoni et al. (2009) propose a different approach. Starting from the idea of sustainability as an ideal state where no non-renewable resources are consumed, they elaborate a definition of unsustainability as the sum of local and non-local non-renewables (N+F). Furthermore, the authors claim that all the emergy indicators previously are not sufficient to quantitatively assess (un)sustainability. From EYR to EIR, these indicators are all expressed in form of a ratio, which makes them *intensive* quantities: they do not evaluate flows in absolute terms, but in relation to other flows. According to the authors, (un)sustainability is an extensive problem: since it is related to the quantity of non-renewables consumed, which should tend to zero, it is not possible to reduce the total use of non-renewables by improving intensive parameters only. As an example, to reduce the total amount of greenhouse gases emitted globally in one year, it is not enough to reduce the CO2eq per capita, if the population keeps increasing; it is necessary to add a decrease in total consumption, which is only measurable in extensive terms. For this reason, they propose the sum of N+F as an unsustainability indicator, to be coupled with other intensive indicators.

All emergy indicators are related to the sustainability of systems from a holistic view: they capture different facets of a system's structure and functioning without "breaking down" the system into its minor components. Emergy analysis include a thorough computation of the resources needed to generate something (whether goods, services, sectors, communities, or entire economies); this evaluation of the investment needed is also a quantification of the replacement cost of the "thing" produced, assessing its sustainability in terms of the renewability of its regeneration in space and time (Perosa et al., 2019).

If coherent with the scope of a study, calculating indicators for single subsystems or steps of a process is also possible. By comparing indicators of different steps, we can evaluate which phases have (for example) the higher efficiency or environmental load; this allows us to define the areas of improvement to enhance the overall sustainability of the system.

It is worth stressing that all the emergy indicators, regardless of their formulation, do not evaluate the sustainability of an *output* (or product, in common language), but of a *system* (or process). When dealing with systems that have a well-defined "target" output (such as industrial systems), indicators do not aim at answering the question "Is this product more sustainable than this other?", but rather "Which is the most sustainable system that produces this output?". It is still possible to compare systems with different outputs with emergy analysis, but careful consideration is needed to avoid erroneous interpretation of results.

5. But we already have LCA...

Life Cycle Assessment (LCA) is a widely established method to evaluate the environmental impacts of human-dominated systems. It is standardized at international level through the 14040's ISO norms, which define LCA as the "compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle" (ISO, 2006a, 2006b). It aims at assessing systems from their resource consumption to their potential environmental burden ("from cradle to grave"). LCA studies follow a four-step procedure:

1. *Definition of scope and objective of the study*. It answers the question "What do I want to study and why?";
2. *Creation of the Lice Cycle Inventory (LCI)*. Through a spreadsheet table or a software, a table with all the relevant matter and energy flows involved in the process are listed and quantified.
3. *Life Cycle Impact Assessment (LCIA)*. Several indicators are calculated from the process flows, to evaluate resource requirements and/or environmental impacts. Among the most used indicators there are the Global Warming Potential (GWP) associated with greenhouse gas emissions, the Cumulative Energy Demand (CED) related to energy consumption and the ReCiPe 2016 (which includes the previous Ecoindicator99) that encompasses several impacts, e.g. land use and human toxicity.
4. *Interpretation of results*. The resulting indicators are commented on and potential improvements of the system are proposed.

Several commercially available LCA softwares (e.g.OpenLCA and SimaPro) and databases (e.g. Ecoinvent and AGRIBALYSE) provide referenced data for a considerable number of matter and energy flows; these tools drastically reduce the time-consuming task of retrieving or creating data for specific flows, thus making LCA more widely accessible.

So - if this LCA tool is so widespread and powerful, why would we need emergy analysis? Despite the many similarities, three key points make LCA and emergy perspectives different. First, LCA adopts a pragmatic user-side perspective like other environmental assessment methods, evaluating flows of matter and energy "depending on what human technologies are able to extract from them" (Brown and Ulgiati, 2004). It does not consider the environment in all its complexity, but as "a source of the used materials and energy and a sink for the waste emissions and heat" (Raugei et al., 2014). On the contrary, emergy analysis stems from a donor-side perspective, where all flows are accounted for depending on how much the geobiosphere invests to produce them. As expressed by Perosa et al. (2019), unlike LCA, "emergy analysis is not established to address an environmental impact, but rather to evaluate the upstream impact on the geo-biosphere in terms of "investment", in turn measured in terms of emergy."

Besides the systemic perspective, the LCA procedure involves the evaluation of processes as a purely linear cause-effect chain of steps (Perosa et al., 2019), without including neither the concept of energy quality nor feedbacks from latter to previous phases. This hinders the possibility of evaluating the systems dynamics and the way higher-quality flows exert a control function on lower-quality flows, which instead a focus of emergy.

Last, but most impactful, the two methods have a divergent approach when it comes to the types of emergy and matter flows considered: while LCA focuses on human-controlled systems and most often includes only non-renewable resources, emergy analysis can also assess ecological systems, and it accounts for the inputs provided by the environment (e.g.

solar energy, rain, soil organic matter), by the action of human labor and services and flows of information. These ecosystem and societal services are often discounted and "taken for granted" in environmental assessment, but they are essential for any human system to operate. By excluding these crucial inputs, LCA assesses resources consumption and potential environmental impacts from a purely human-centered perspective, precluding the study of how the effects of the system interact with the surrounding environment.

Perosa et al. (2019) also propose a more nuanced observation about emergy analysis in human-dominated systems: applying this assessment method, instead of a user-centered like LCA, aims to "prevent a "shifting of the burden", typical of strategies that increase the global environmental load upon addressing the change in a single "local" specific factor of production". This "shifting of the burden" refers to business economic strategies that generate a false improvement in their environmental performance: by changing one process step or process feature inside their local system to appear "greener", they create a higher environmental impact in a different location. A non-environmental example is the business practice of delocalization, with which factories are moved to countries where the cost of labor is lower (and the environmental regulations often laxer) to avoid the costs of labor force or environmental compliance. This type of practice creates externalities, which are costs (economic or environmental) incurred by third parties who have no control over the creation of these costs. In the context of human-dominated systems, the use of emergy analysis instead of LCA aims at decreasing the risk of greenwashing related to creation of these externalities by adopting a systemic instead of a reductionist approach.

However, there are not only divergences between LCA and emergy analysis: several authors have highlighted their complementarity and advocate a joint use of both methods. A bright example is the work of Raugei et al. (2014), which not only provides a more in-depth vision of the differences and similarities of emergy analysis and LCA, but it suggests a way to capitalize on their distinct perspectives to obtain an integrated assessment tool. By taking advantage of emergy's broader system boundaries which include the natural ecosystems, the boundaries and scope of LCA can be expanded "providing a donor-side perspective, a unified measure of the provision of environmental support, and an indication of the work of the environment that would be needed to replace what is consumed" (ibidem). After highlighting a few methodological issues to be addressed before being able to integrate emergy into LCA, the authors propose a roadmap to achieve this objective. We also argue that a careful application of emergy algebra would also solve (or at least, simplify) the problem of allocation in LCA, which can create problematic interpretation in systems that present coproducts, since allocation rules in emergy algebra remove the need of choosing a criterion to allocate flows to coproducts.

If integrating emergy into LCA can be considered a long-term goal for emergy and LCA analysts, the opposite process can also bring benefit to environmental assessments: when performing emergy analysis, Life Cycle Inventory data from recognized databases "offer a valuable source of data and technological network knowledge to advance the calculation of UEVs" (Raugei et al., 2017). These can be used to quantify energy and matter flows in emergy tables. After being complemented with labor, services and information data, the LCA flows can be multiplied for the appropriate UEVs to calculate emergy flows and, from these, the emergy indicators of a system can be obtained as in a purely emergetic analysis. This can be remarkably useful to obviate the lack of available emergy data for novel or specific systems, for which instead LCA studies might already be published. This approach was adopted also in this work, to calculate several UEVs of inputs that lack emergy literature.

Chapter 4 - Case study

1. Where we start from

This work starts from a paper from Morales et al. (2015), which proposes a new production process for lactic acid based on a novel catalyst. Through an environmental and economic assessment, the authors claim that this alternative pathway is more sustainable than the current production route. Our work aims at analyzing the same two production processes from two different points of view (eMergy analysis and green chemistry) to prove or reject this hypothesis.

First, Morales et al. (2015) presents the state of art of racemic lactic acid production via fermentation of organic matter. The conventional pathway is based on the anaerobic fermentation of glucose syrup: the raw material is extracted from crops, such as cane or beet, and is converted into calcium lactate by *lactobacillus* bacteria in controlled-pH environment using calcium hydroxide ($Ca(OH)_2$). This lactate is later hydrolyzed to lactic acid using sulfuric acid (H_2SO_4), yielding lactic acid and calcium sulfate ($CaSO_4$, gypsum) as a byproduct. The main drawback of this route is the quantity of gypsum produced: for every kg of LA, approximately 0,95 kg of $CaSO_4$ are obtained. This product must be disposed of in landfills, hence it represents an environmental concern.

As a lower-impact alternative, the paper presents a novel production process based on glycerol, a byproduct of the biodiesel industry. In this process, glycerol undergoes fermentation with *gluconobacter oxydans* bacteria and is converted to dihydroxyacetone (DHA), which is subsequently isomerized to racemic lactic acid with a zeolite catalyst. Several variations of the same process are proposed, setting the reaction with catalysts with different treatments, varying the number of runs with the same catalyst or changing the solvent. This alternative process is claimed to have a double upside: it both recycles the main byproduct of another production chain (for every kg of biodiesel synthesized, about 10 wt% glycerol is discarded) and it avoids the formation of considerable amounts of unused gypsum.

To prove that the alternative path is "advantageous [...] in terms of sustainability and operation costs" (ibidem) the authors performed LCA and economic assessment of the two processes. In the first method, three indicators used in previous chemical processes assessments were calculated: the global warming potential (GWP-100a), the ecoindicator 99 (EI99) and the cumulative energy demand (CED), accounting only for the non-renewable fraction of energy. As for the economic assessment, the paper reports the calculation of operating costs of the process excluding the investment costs related to the construction of the plant.

We chose to start from this paper because it provides comprehensive information for making further comparisons of the two processes presented, starting from the LCA metrics already presented, allowing us to analyze their sustainability and greenness from a broader perspective. Overall, the synthetic pathway proposed seems promising, but the assessments performed in the work are not sufficient to prove that the alternative is "more sustainable" than the conventional. This is due to both intrinsic limitations of the methodologies chosen and to choices of the authors on how to carry out the assessment. First, LCAs focus on

calculating environmental impact indicators, not on evaluating the energy and material demand on the donor side. LCIs do not include information about electricity consumption, machinery used, maintenance costs, labor force and services required, which are instead essential in eMergy analysis to estimate the major contributions to the total emergy demand (e.g. if a process is mainly based on renewable or non-renewable resources). Similarly, taking into account only the non-renewable fraction of the cumulative energy demand (CED) can indeed highlight the depletion of resources, but it also provides incomplete information regarding the sustainability of the system as a whole. Having both renewable and non-renewable CED would allow to (i) have an estimate of the order of magnitude of the total energy expenditure and (ii) compare the renewable and non-renewable energy requirements and evaluate what fraction of the total demand creates a burden on the environment. Another difficulty in performing a comprehensive sustainability assessment of these processes is that the alternative path proposed is only a theoretical study: there are no literature references to derive electricity consumption, labor force or services needed, thus estimates have to be made.

2. Methodology

Starting from the data provided in Morales et a., 2015, we selected one process route among the "alternative" proposed (the one reported as "LA.3" in the paper, based on crude glycerol) and compared it to the conventional process. Our methodology is divided into five steps:

1. diagramming. From the processes flowsheet, a flowchart and a system diagram were drawn, including all the sources and components. A condensed version of this diagram was drawn and compared to a condensed version of the conv-LA system, then the extended systems of both production methods were compared;
2. emergy inventory and transformities calculation. The transformities of all sources were either found in literature or calculated from literature data, then the transformity of the output (LA) was calculated using the rules of emergy algebra;
3. EMA indicators calculation. The main indicators used in emergy analysis (EYR, ELR, ESI) and a few additional ones specific for the present case study, mentioned in the previous chapter, were estimated;
4. green chemistry metrics calculation. The most used green metrics were determined in different scenarios to explore how their values change depending on the judgment of the operator who performs the analysis. Values of yield, atom economy, reaction mass efficiency, mass index and E-factor were evaluated;
5. EMA-GC comparison. The calculated emergy indicators and green metrics were confronted to explore whether the two languages provide overlapping or contrasting information.

3. Diagramming

Before understanding whether a system is "sustainable", it must be clear what its structure is and how it operates. To do so, we followed the standard eMergy procedure described below, starting from three key questions, then listing the sources and components of the systems and last drawing the diagram.

For both the alternative lactic acid process (from here on: alt-LA) and the conventional process (conv-LA), the analysis started by answering the three key questions for any eMergy model:

    A. What is the main scope of the system?
    B. What is the main output of the system?
    C. What is the main process of the system?

Note that what is called "system" in eMergetic jargon is what is called "production process" in chemistry studies. Unless specified, from here on they will be used interchangeably.

The following answers were identified:

Conv-LA

    A. The main scope is making profit.
    B. The main output is lactic acid (LA).
    C. The main process is a series of chemical reactions, mainly glucose fermentation to LA.

Alt-LA

    A. The main scope is making profit by producing LA in a "sustainable" way.
    B. The main output is lactic acid (LA).
    C. The main process is a series of chemical reactions, mainly glycerol fermentation and DHA isomerization.

A few aspects to highlight:

i. the main output of the two processes is the same, but the main process is different, hence the structure of the systems will be different;

ii. scope and output are almost never the same. (clarify the definition of scope) In the human economy, the prerequisite for a business or an industry to sustain itself is making profit. The type of product or service produced is less relevant;

iii. the definition of the scope of a system is subjected to interpretation. Here we chose to see the two systems under a slightly different light: in the alt-LA system, the scope could have been "making profit" as well, since this is the general pattern for business models. Nevertheless, we chose to include in the scope the idea that this production process must be more sustainable than the main one available on the market. This double-main scope resembles the structure of Benefit Corporations, which add the commitment to generate public benefits beside making profit.

After defining the key aspects of the systems, the flowsheets presented in Morales et al. 2015 were analyzed to derive the verbal description of the model and the corresponding flowcharts. Flowsheets (figures 8, 9 and 10) represent the structure of the systems and the interconnections between the components. Flowcharts (figures 11 and 12) are schemes that describe each phase of the process showing inputs and outputs.
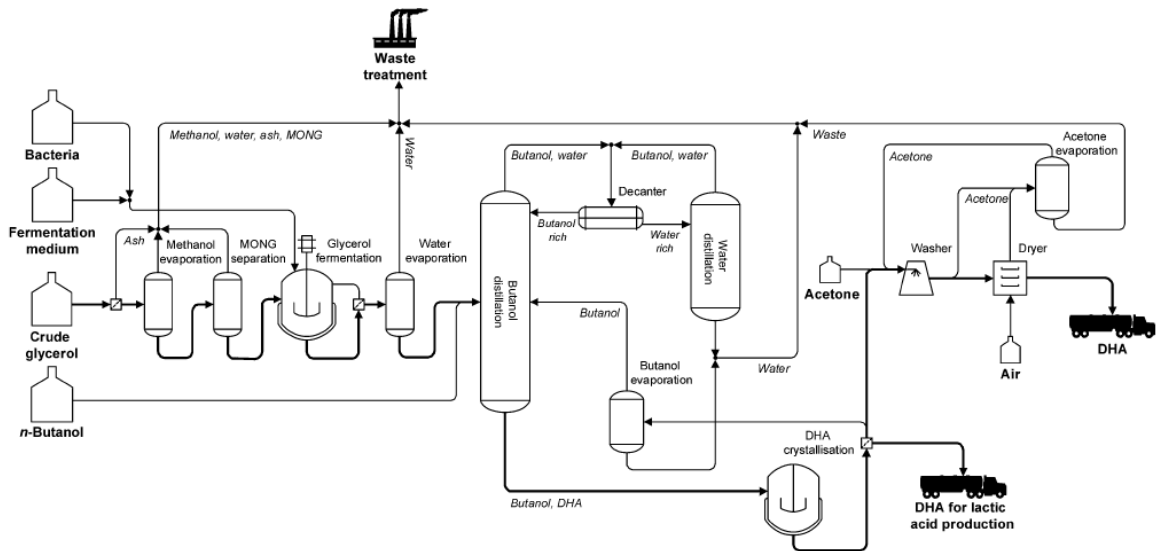
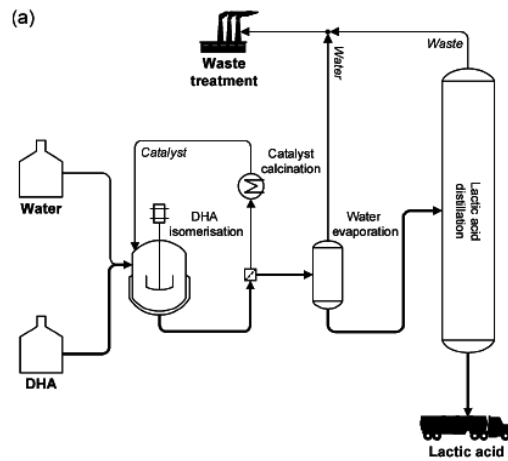*Figure 8: flowsheet of alt-LA system from crude glycerol to DHA (Morales et al., 2015)*

Figure 9: flowsheet of alt-LA system from DHA to lactic acid (Morales et al., 2015)
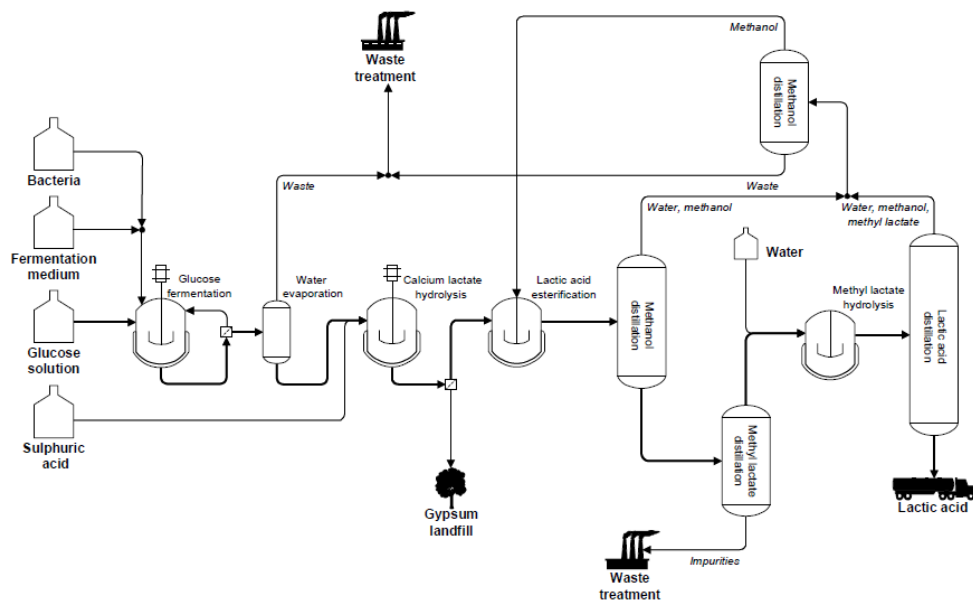

Figure 10: flowsheet of conv-LA, full system (Morales et al., 2015)

From the flowsheets reported, the verbal models (i.e. the descriptions of the systems structure and functioning) are derived as a summary of the main features of the processes, and reported in the following paragraphs.

Alt-LA. The system uses crude glycerol, main byproduct of the biodiesel industry, as a raw material to produce lactic acid through a series of consequent chemical reactions. Glycerol enters the system and undergoes a series of reactions to be purified from ash, methanol and organic matter. The impurities are disposed of as waste, whereas purified glycerol is fed to a batch reactor with water, nutrients and bacteria where it undergoes fermentation, yielding dihydroxyacetone (DHA). This intermediate is concentrated by water evaporation and crystallized using butanol as a solvent. From this step, a stream of DHA in butanol is sent to the next phase of the process and a flux of butanol-water mixture exits towards the recycling subsystem. In this step butanol is recovered from the aqueous mixture and fed back to the DHA concentration step, whereas water is disposed of as waste. The crystallized DHA is split in two fluxes to different processes. A fraction is further washed with acetone to obtain a product of higher purity that exits the system as a coproduct to be sold on the market. The acetone used in this step is recovered and reused, whereas impurities exit the system as waste. The main fraction remains in the system and reaches the following step, where it is isomerized to lactic acid in a batch with water and the catalyst. After the reaction, the catalyst is recovered from the mixture and calcined in order to be reused. The recycled catalyst is then fed back to the DHA isomerization step. Last, the mixture with lactic acid is concentrated via water evaporation and distillation obtaining pure lactic acid, that is the main output of the system. The water remaining from this step is disposed of as waste.

Conv-LA. The system uses glucose syrup as a raw matter to produce lactic acid through a series of consequent chemical reactions. The syrup enters the system in a batch with water, nutrients, calcium hydroxide and bacteria and undergoes fermentation yielding calcium lactate. This resulting broth is condensed to remove part of the water, which is sent to wastewater disposal. The condensed calcium lactate is hydrolyzed with sulfuric acid to obtain crude lactic acid, producing calcium sulfate (gypsum) as a byproduct. This gypsum exits the system as waste to landfill. To purify the product, lactic acid undergoes an esterification using methanol both as a methylating agent and solvent, yielding methyl lactate. The solvent is separated from the lactate via distillation and reaches the recycling subsystem, while the remaining methyl lactate undergoes distillation to remove impurities. These impurities exit the system to waste disposal. The purified methyl lactate is hydrolyzed with water to yield lactic acid, which is subsequently condensed via distillation. The mixture of methanol and water obtained from the distillation step reaches the recycling subsystem, whereas lactic acid is the main output of the system. In the recycling subsystem, two fluxes of methanol and water reach a distillation column and are separated to recover methanol, which is then reintroduced into the main system at the lactic acid distillation step. The remaining water is disposed of as waste. All steps of the synthesis use electricity, machinery, labor and services as inputs for their operations.

From the flowsheets and the verbal models, the flowcharts for both processes were drawn (figures 11 and 12). These schemes summarize the main steps of the processes, reporting inputs and outputs for each step. The division of the process in steps follows the description provided in Morales et al., 2015, for the most part.
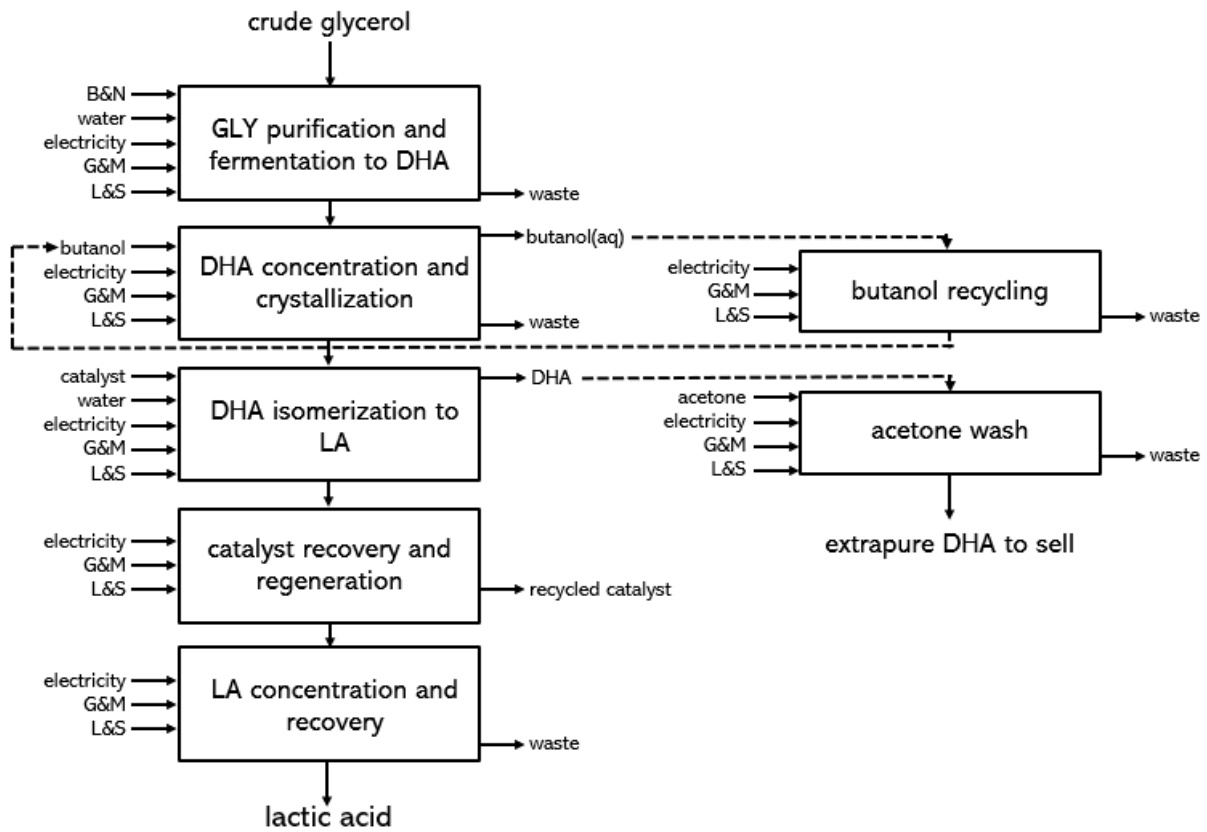
Figure 11: flowchart of the alt-LA production process. GLY=crude glycerol, B&N=bacteria and nutrients, G&M=goods and machinery, L&S=labor and services, butanol(aq)=aqueous butanol.
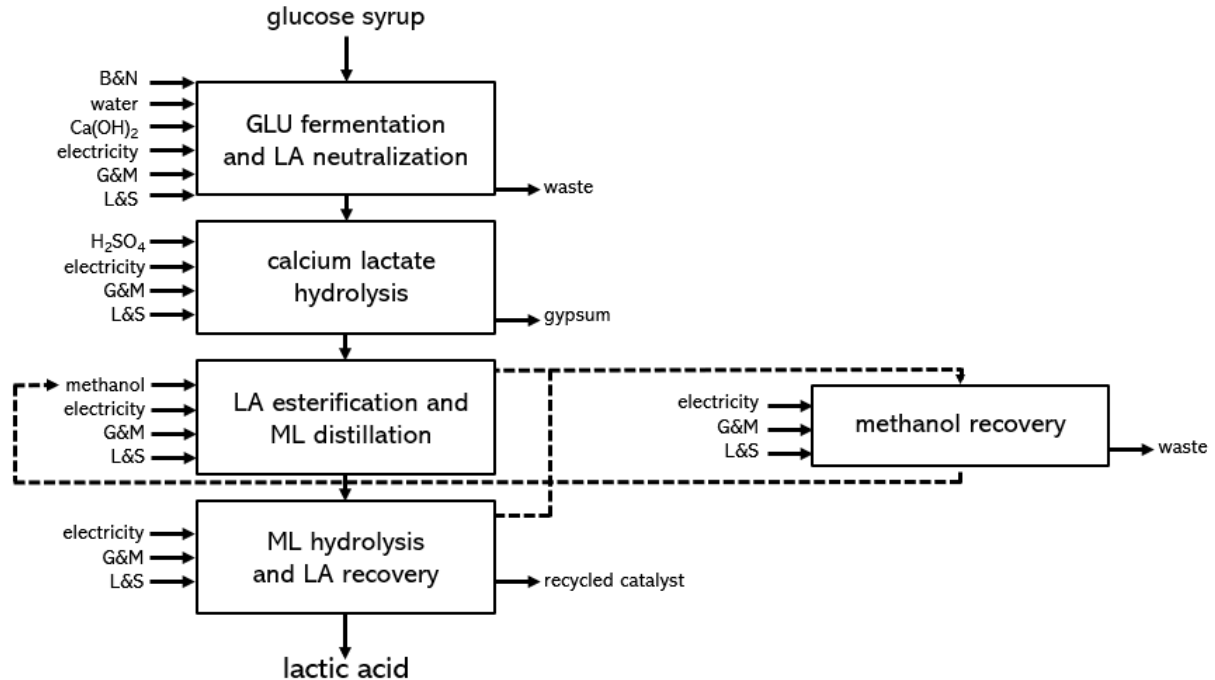

Figure 12: flowchart of the conv-LA production process. GLU=glucose syrup, B&N=bacteria and nutrients, Ca(OH)₂=calcium hydroxide, G&M=goods and machinery, L&S=labor and services, ML=methyl lactate.

As visible from the flowcharts, both processes are characterized by a linear chain of reactions. This linear sequence of steps is typical of human-designed systems compared to natural systems.

In the case of alt-LA, five main steps were identified. The first is the fermentation of glycerol to DHA, that includes the previous purification, obtaining an aqueous solution that contains the intermediate, residual nutrients and bacteria. In the second step this broth is condensed via water evaporation and DHA is extracted and crystallized with butanol. The third step is the isomerization of DHA to lactic acid using a catalyst, which is recovered from the reaction mixture and calcined in the fourth step, in order to be reused. In the final step lactic acid is condensed and recovered purified via distillation. To increase the economic feasibility of the process, butanol is separated from water and recycled back into the process in a separate step, and in a last collateral step part of the DHA produced as an intermediate is washed with acetone to be purified and sold as extrapure DHA.

For conv-LA, four main steps were identified. In the first, the glucose syrup undergoes fermentation to lactic acid and neutralization to calcium lactate, then it is condensed through water evaporation. In the second step the calcium lactate is hydrolyzed with sulfuric acid to yield lactic acid. The third step is the esterification of LA with methanol to obtain methyl lactate and its distillation to remove impurities and solvent, which is recycled in a separate step. In the fourth step methyl lactate is hydrolyzed to yield purified LA, which is condensed into the final product.

Besides these linear chains of processes, in both cases an internal feedback for solvent recycling can be recognized. In alt-LA, the butanol used in the crystallization step is recovered by collecting the water-butanol mixture and distilling it to separate the components, so that butanol can be fed back to the same step. For conv-LA, the water-methanol mixture used in the LA esterification is separated in the fourth step and fed to the recycling process; in the same way, the solvent used in the last step is recovered, and both flows undergo distillation to separate methanol from water, to reuse the former in the esterification reaction. These two recycling processes present some differences but have the same function: in alt-LA the solvent is recovered and reused as one flux in the same step, whereas in conv-LA two fluxes of solvent arrive at recycling and are fed back to a different reaction step, but both have the goal of reusing an internal flow of matter to minimize the need of the corresponding purchased flow from outside the system (the more solvent is recycled, the less is bought). This is also in contrast to natural systems functioning, where self-catalytic feedbacks allow the use of more internal matter flows to increase the amount of energy and matter used from the outside.

Last, in the alt-LA production process a second "nonlinear" element is present: after the second step, the DHA flow is split in two and one fraction undergoes a separate step, washed with acetone, to obtain purified DHA to sell. This step does not directly contribute to the LA production, but in the paper it is said to be crucial for the economic sustainability of the production plant, since the market price of DHA (4500 USD per ton) is significantly higher than that of LA (1700−2100 USD per ton) (Morales et al., 2015).

Having established detailed knowledge of the systems, it is now possible to draw their emergy diagrams. In this diagramming phase, only the alt-LA process was analyzed, since it is the main focus of the reference paper (Morales et al. 2015). Money and information flows are excluded in this phase of analysis, to focus on the material and energy flows involved. Before drawing the diagram of the entire system, the diagrams of the main steps of the production process were outlined following the flowchart, to highlight the interconnections

between stocks and flows. Due to the high linearity of the reactions involved, steps 3, 4 and 5 of the flowchart were merged in one diagram. The steps diagrams were later merged into a single diagram for the entire alt-LA production process. In the following paragraphs, all the steps diagrams are presented and explained, before reporting and describing the system diagram. The sources that enter the system are listed according to the Life Cycle Inventory reported in the reference paper. Due to the lack of a detailed description, all the processes are assumed to involve the use of air, steam and cooling water in equal parts. In all the following diagrams, the lightning symbol stands for "electricity".
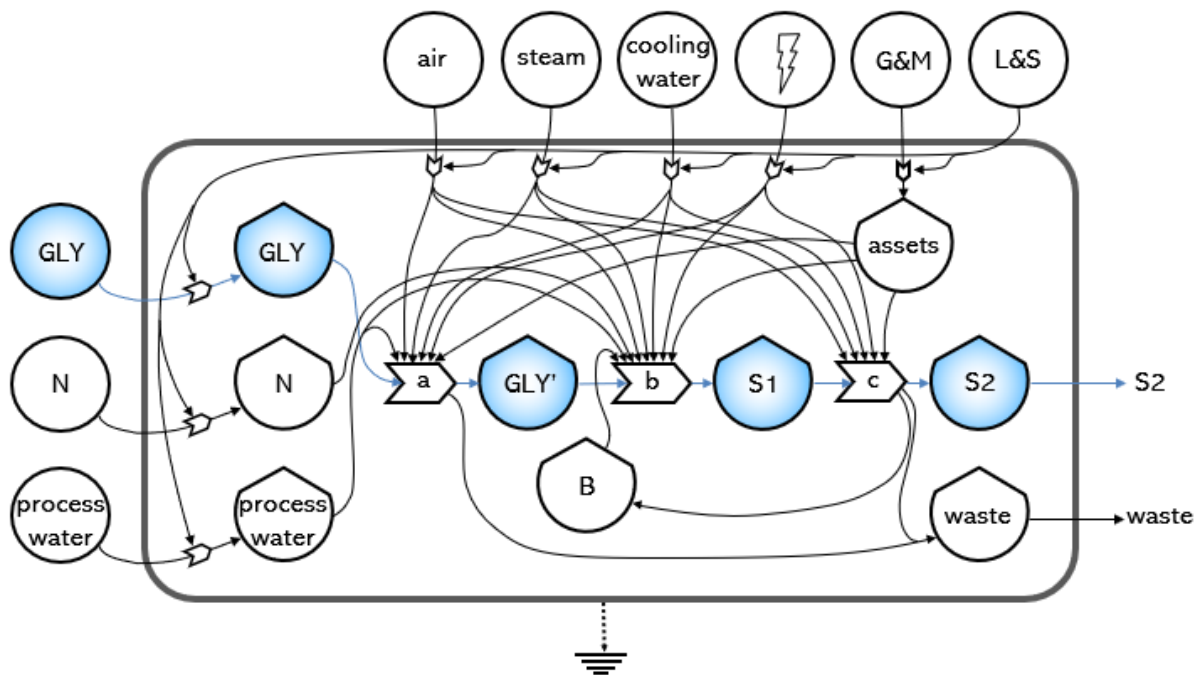
Figure 13: alt-LA step 1 - glycerol purification, fermentation and water evaporation. GLY=crude glycerol, N=nutrients, G&M=goods and machinery, L&S=labor and services, GLY'=purified glycerol, B=bacteria, S1=aqueous solution of DHA with bacteria, S2=purified aqueous solution of DHA; a=glycerol purification, b=glycerol fermentation to DHA, c=bacteria recycling.

Alt-LA, step 1 (Figure 13). The first diagram represents the first step of the process. On the left side the local renewable resources (i.e. the reagents of the reactions, crude glycerol, "GLY", nutrients, "N" and process water) are reported, whereas on the top side the imported-non renewable resources are represented (air, steam, cooling water, electricity, goods & machinery, "G&M" and labor and services "L&S"). The reagents are transported inside the system through services and generate a stock of each material. The glycerol stock enters the process "a", "impurities removal", that represents the purification from ash, methanol and organic matter which yields a stock of purified glycerol (GLY') together with a flow of waste as a byproduct. This storage GLY' undergoes the process "b", "fermentation", together with nutrients, bacteria (in the stock "B") and water, yielding a stock of aqueous solution of DHA and bacteria ("S1"). This solution is used in the process "c", "bacteria filtration and recycling", that produces a stock of aqueous DHA ("S2"), which exits the system towards step 2. All the waste flows reach a waste stock, which exits the system to disposal. In all stocks and processes inside the system, some energy is dissipated in heat, which is represented by the flows to the heat sink; since this is in common to all the other diagrams, it will not be mentioned in the following descriptions.
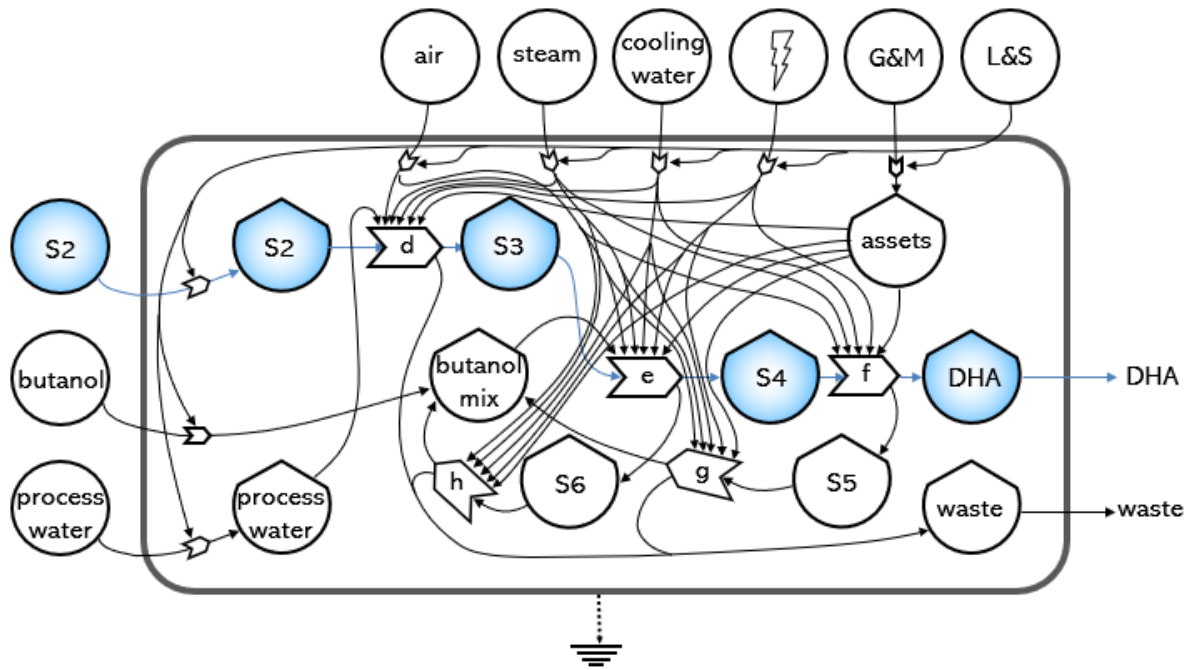
Figure 14: alt-LA step 2 - DHA condensation and crystallization. S2=purified aqueous solution of DHA, G&M=goods and machinery, L&S=labor and services, S3=concentrated aqueous solution of DHA, S4=solution of DHA in butanol, S5=aqueous solution of butanol with impurities, S6=aqueous solution of butanol, butanol mix=butanol-water mix; d=solvent evaporation for DHA recovery, e=DHA distillation with butanol, f=DHA crystallization, g=evaporation for butanol recovery, h=butanol recycling.

Alt-LA, step 2 (Figure 14). This system uses the product of the previous step (aqueous DHA, "S2" source) together with butanol and water to yield crystallized DHA as main output. The source of butanol enters the system and is fed to the "butanol mix" stock, a storage that contains both purchased and recycled butanol fractions. The DHA solution S2 enters the system and undergoes process "d", "evaporation for DHA recovery", obtaining a stock of concentrated aqueous DHA ("S3") and a flow of wastewater, that exits the system to disposal. This is fed to process "e", "distillation with butanol", together with a flow from the "butanol mix" stock; in this process DHA is extracted from water and distilled in butanol, yielding a solution of DHA in butanol ("S4") and a mixture of butanol and water ("S6"), which is recovered through process "h", "butanol recycle". In this process the diluted butanol mixture is concentrated to eliminate the water and then fed back in the "butanol mix" stock. S4 stock is the input of process "f", "DHA crystallization and filtration", which yields a stock of crystallized DHA ("DHA"), which exits the system and splits towards steps 3 and 4. This process als yields a coproduct, "S5" ("butanol and impurities from DHA"), a solution of butanol and dissolved impurities derived from distillation; this stock undergoes process "g", "evaporation for butanol recovery", where impurities are removed and exit the system as waste, whereas the flow of butanol reaches the "butanol mix" stock where all the solvent is stored.
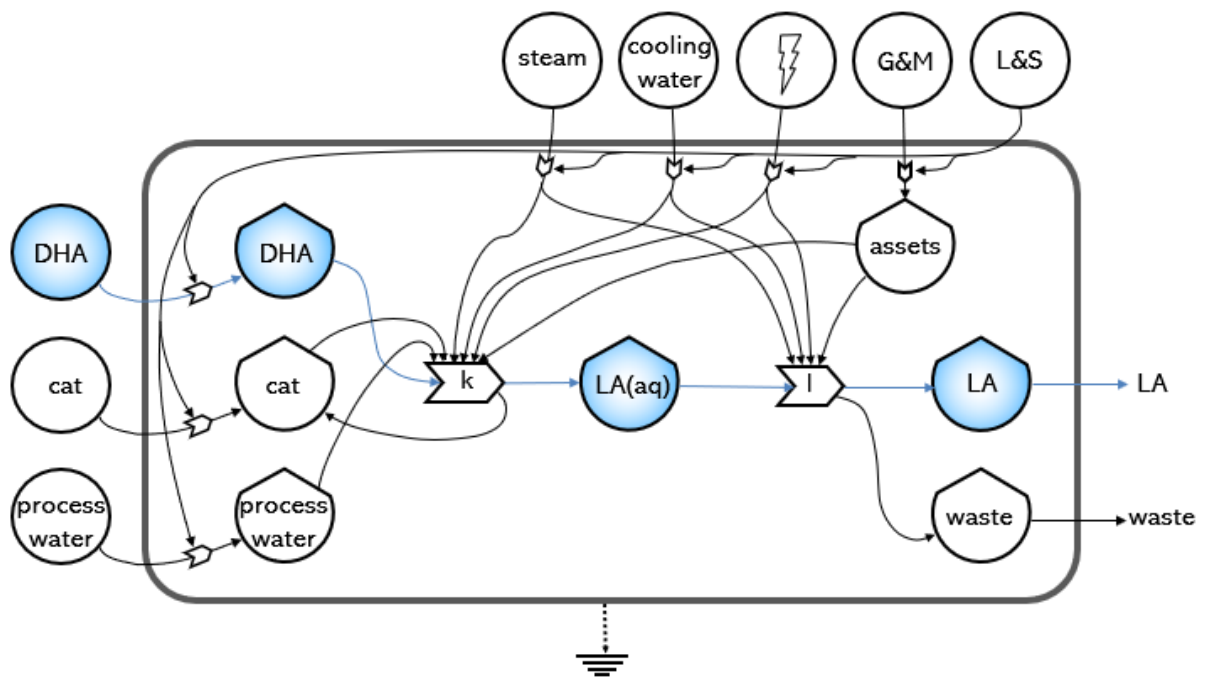
Figure 15: alt-LA step 3 - DHA isomerization and LA distillation. cat=catalyst, G&M=goods and machinery, L&S=labor and services, LA(aq)=lactic acid aqueous solution, LA= pure lactic acid to sell; k=DHA isomerization to lactic acid, l=catalyst recovery and recycling.

Alt-LA, step 3 (Figure 15). This step represents the processes of DHA isomerization to LA and the distillation of the final product. The zeolite catalyst needed for the isomerization ("cat") enters the system as a stock and becomes an input for process "k", "DHA isomerization and catalyst recovery", together with DHA and water. In this process, aqueous DHA is isomerized to lactic acid due to the catalysis of the zeolite, which is later separated by filtration and regenerated via calcination. This catalyst flow is recycled back to the catalyst stock, whereas the product, aqueous lactic acid (stock "LA(aq)") is fed into process "l", "lactic acid distillation", where lactic acid is distilled to remove water and produce the stock of the final product, solid lactic acid ("LA"), which exits the system to be sold on market. Process "l" also generates waste, which exits the system to disposal.
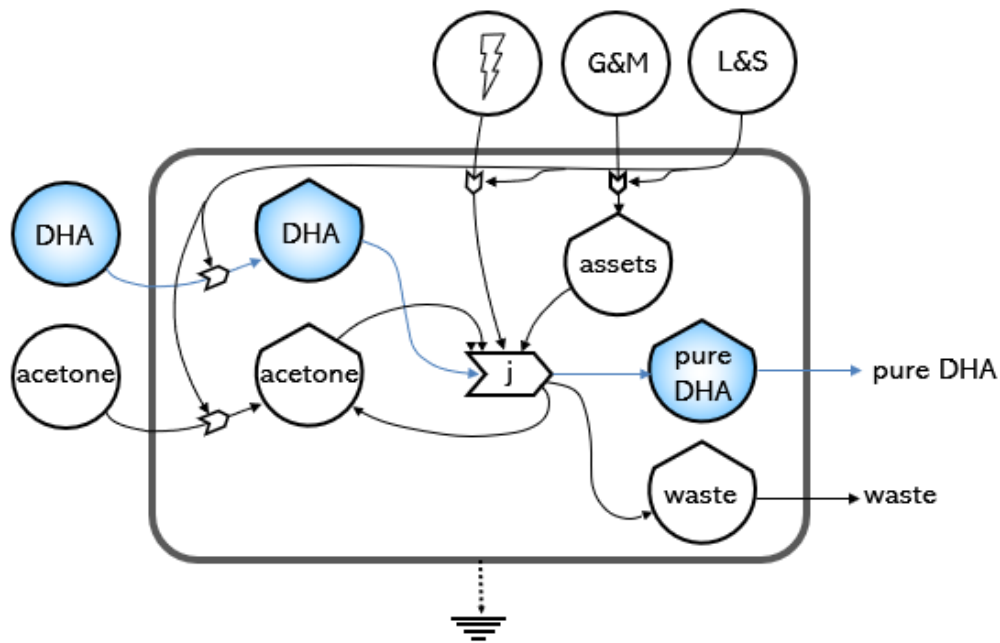
Figure 16: alt-LA step 2.2 - acetone wash. G&M=goods and machinery, L&S=labor and services; j=DHA purification.

Alt-LA, step 2.2 (Figure 16). In this step the intermediate ("DHA") is washed with acetone to be sold as high-purity DHA. Acetone enters the system as a stock, aided by services (mainly transport) and enters the process "j", "DHA wash, dry and acetone recycling", where DHA is washed with the solvent, dried and it generates a stock of "pure DHA", while the solvent is recycled back into the "acetone" stock. The purified DHA exits the system as the second main output, whereas process "j" also produces waste, which exits the system to disposal. Due to lack of quantitative information regarding the fraction of DHA dedicated to this used with respect to the quantity of DHA isomerized, this step is neglected in the diagram of the total process. This choice is also justified by the fact that the acetone wash step is included purely for economic purposes, since DHA market price is higher than lactic acid price.
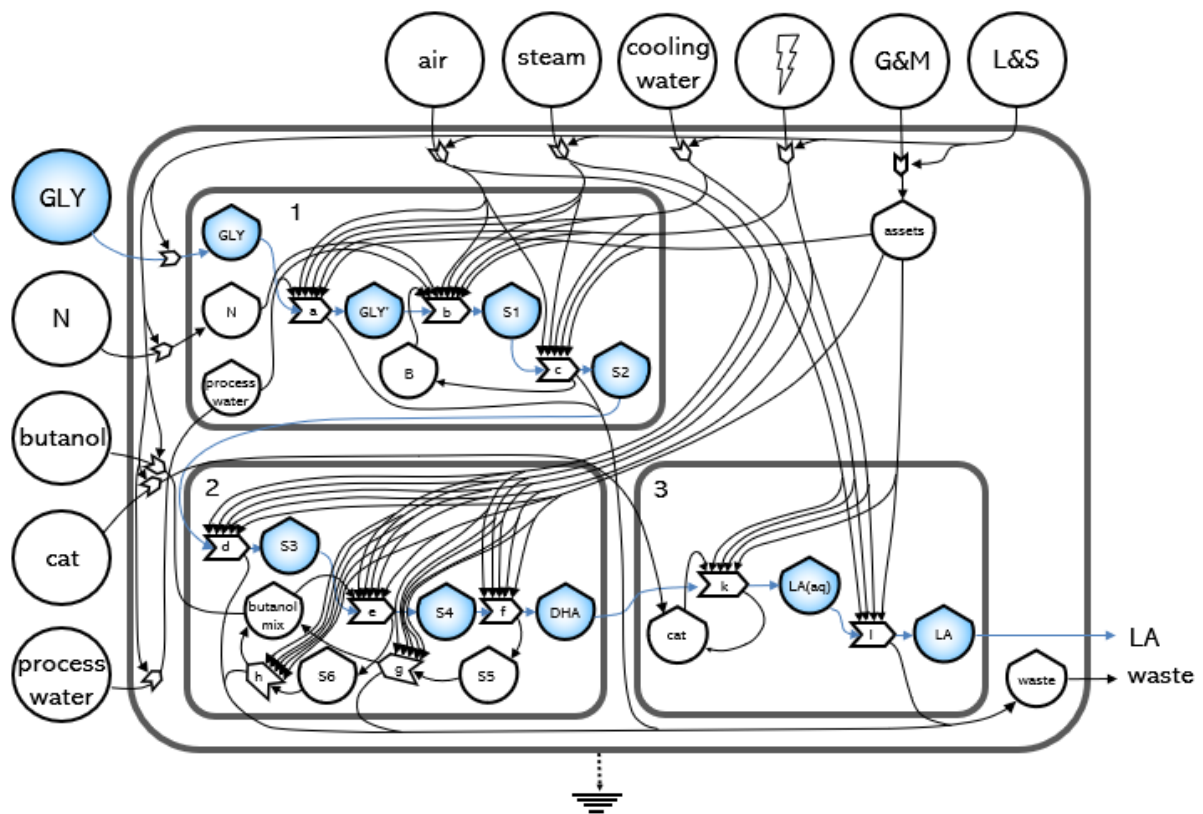
Figure 17: alternative LA production system diagram.

Alt-LA, full process (Figure 17). This diagram is the union of all the previous steps, seen as one complete system. On the left, all the local renewable sources needed are visible (glycerol, nutrients, butanol, catalyst, water), and on the top side, the imported non-renewable inputs (air, steam, cooling water, electricity, goods and machinery, "G&M" and labor and services, "L&S") are reported. On the right side the two outputs are shown: lactic acid (to the market) and waste (to disposal). This figure shows the connections between the series of steps: the aqueous solution of DHA (stock "S2") exits the first step and becomes an input for step 2. From here, the "DHA" stock is fed into step 3 to be isomerized to lactic acid ("LA"). All the waste flows converge in one stock, "waste", outside the subsystems, which is sent to disposal. steam, cooling water, electricity, G&M (through "assets") and L&S reach all the processes of the system, whereas air is used in steps 1 and 2.

A similar procedure was adopted for the conv-LA process, drawing a diagram of the entire system without decomposing the steps (figure 18).
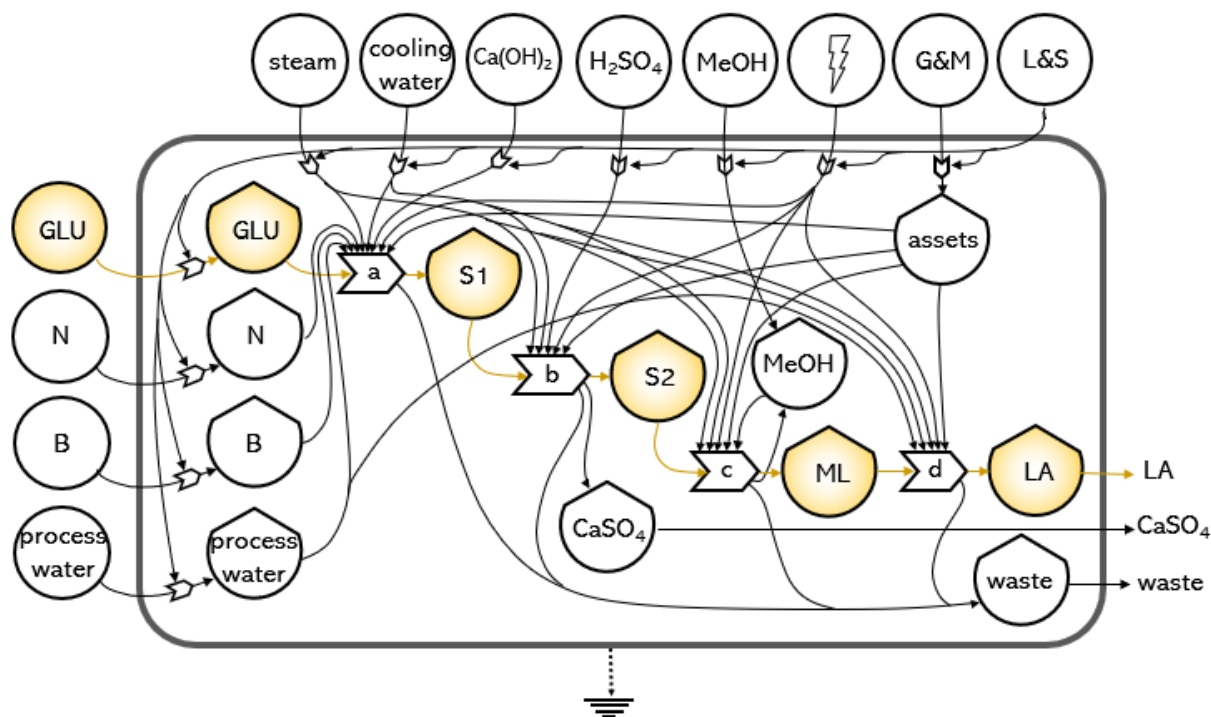
Figure 18: conventional LA production system diagram. GLU=glucose syrup, N=nutrients, B=bacteria, Ca(OH)$_2$=calcium hydroxide, H$_2$SO$_4$=sulfuric acid, MeOH=methanol, G&M=goods and machinery, L&S=labor and services, S1=aqueous solution of calcium lactate with impurities, S2=aqueous solution of lactic acid with impurities, ML=methyl lactate, LA=lactic acid, CaSO$_4$=calcium sulfate (gypsum, to landfill); a=glucose fermentation, b=calcium lactate hydrolysis, c=lactic acid esterification, d=methyl lactate hydrolysis to lactic acid.

Conv-LA, full process (Figure 18). The diagram summarizes the conventional production system. On the left side, all the inputs derived from local renewable sources are reported (glucose syrup, nutrients, bacteria, process water); on the top side imported non-renewable (steam, cooling water, calcium hydroxide, sulfuric acid, methanol, electricity, goods and machinery and labor and services) are visible, whereas on the right side the three outputs are shown: lactic acid (only product to the market), gypsum (to landfill) and waste (to disposal). Glucose, nutrients and bacteria enter the system as stocks, aided by services (transport), and are fed into process "a", "glucose fermentation", where also calcium hydroxide is fed, to yield an aqueous solution of calcium lactate (stock "S1"). This is fed into process "b", "calcium lactate hydrolysis" together with sulfuric acid, where the intermediate, calcium lactate, is hydrolyzed by sulfuric acid to yield an aqueous solution of lactic acid with impurities (stock "S2"). The hydrolysis process also produces the major byproduct, calcium sulfate (gypsum), which accumulates in a stock ("CaSO$_4$") which exits the system to landfill. Stock "S2" becomes an input for process "c", "esterification and methyl lactate recovery", together with methanol, which enters the system as a stock ("MeOH") and is fed into the process through this stock. In this step lactic acid undergoes esterification with methanol yielding methyl lactate, which is recovered through distillation to remove impurities and accumulates in the stock "ML", whereas methanol is recycled back to the "MeOH" stock. Purified methyl lactate undergoes process "d", "methyl lactate hydrolysis to lactic acid", where the ester is hydrolyzed to lactic acid with process water, that also enters the process from the corresponding stock, and is purified by distillation. The output is a flow of purified lactic acid, which gathers in the "LA" stock and exits the system to be sold on the market.

Beside the main outputs, processes "b", "c" and "d" also produce a stream of waste, which is collected in the "waste" stock and exits the system to disposal. Electricity, G&M and L&S are used in all processes. Due to lack of information in the reference paper, it is assumed that also steam and cooling water are utilized in equal parts in every process.

After drawing the diagram of the complete systems for both alt-LA and conv-LA, the same were condensed in a simplified version (figures 19 and 20). These diagrams are compared in order to highlight similarities and differences between the two processes. Note that in the alternative LA diagram, step 2.2 (DHA acetone wash) is reported for the sake of complete comparison between the two production processes.
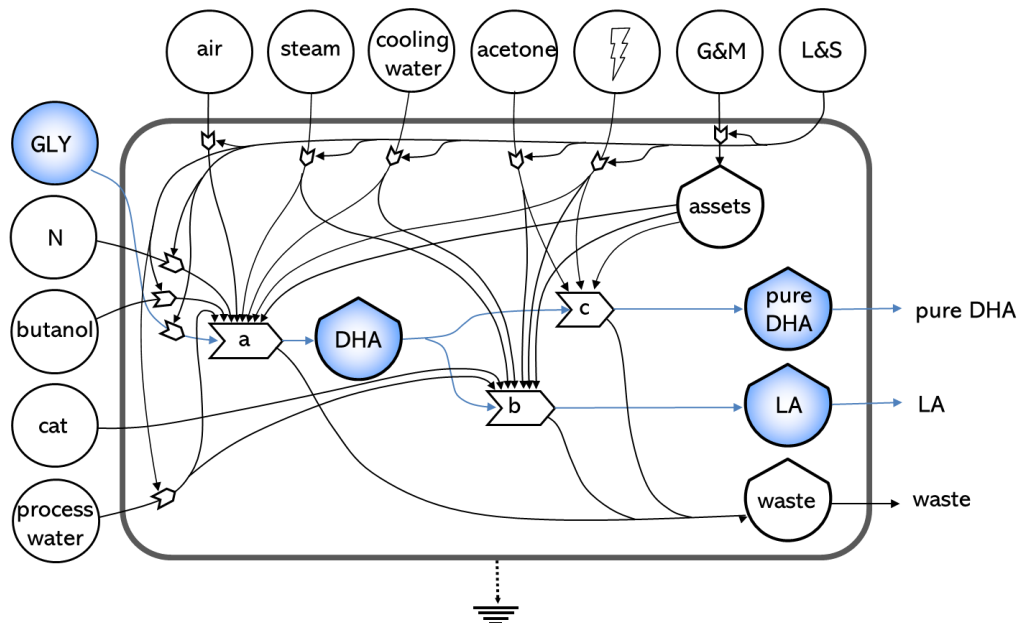
Figure 19: alt-LA condensed diagram. GLY=crude glycerol, N=nutrients, cat=catalyst, G&M=goods and machinery, L&S=labor and services; a=glycerol fermentation to DHA, b=DHA isomerization to LA, c=DHA purification.
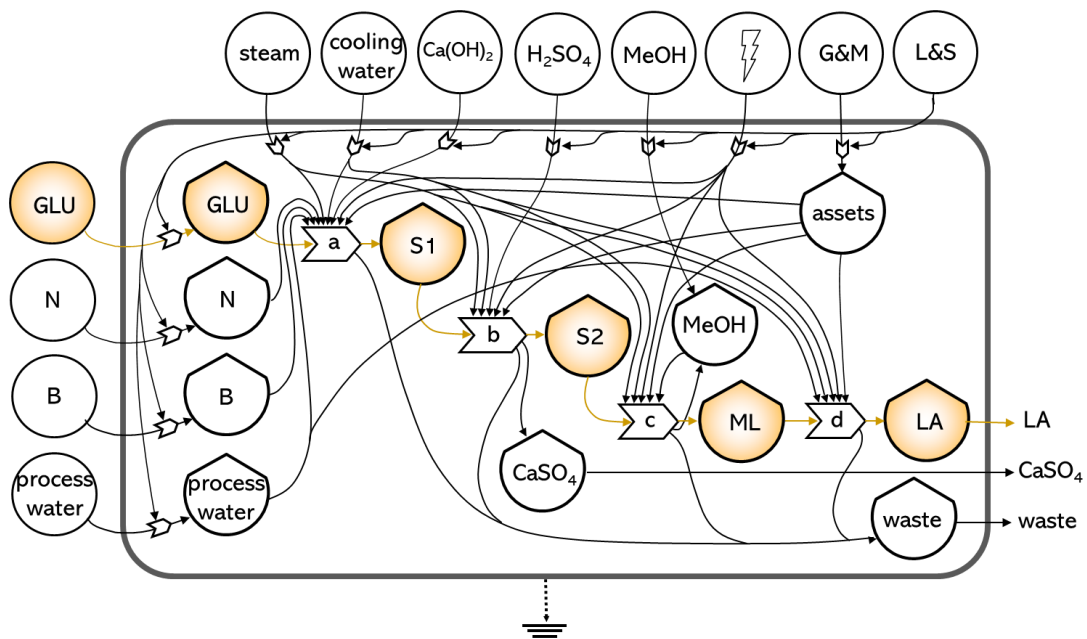
Figure 20: conv-LA condensed diagram. GLU=glucose syrup, B=bacteria, S1=aqueous solution of calcium lactate with impurities, CaSO$_4$=calcium sulfate (gypsum, to landfill); a=glucose fermentation and neutralization to calcium lactate, b=lactate purification and conversion to lactic acid.

The two systems share evident similarities: both start from a raw matter which appears as a source (glycerol and glucose) and enters the system to undergo a fermentation process, together with nutrients and bacteria (these latter are not reported in the alt-LA due to the low amount imported). The product of this first process is a stock of intermediate ("DHA" or calcium lactate in "S2") which is fed into a second process ("b") to be converted into the final product and purified. This process includes a feedback for solvent recycling (butanol for alt-LA, methanol for conv-LA). Both systems produce one main output (lactic acid) and a stream of waste.

The main differences between alt-LA and conv-LA, besides the different sources, are seen in the main flow and in the byproducts. While conv-LA has only one flow of matter related to the final product, and there is only one main output, alt-LA presents a split in the matter flow after the DHA production, one fraction undergoing isomerization to LA and the other being washed to be sold as such. Regarding byproducts, both systems produce a stream of waste not specifically characterized (because not of interest), but in the conv-LA a flow of gypsum is highlighted and separated from the rest of the waste stream because it represents the primary drawback of this conventional production process. Note that representing these gypsum flow and stock is a deliberate choice in the model design, to highlight one main concern about the broad sustainability of the processes. Overall, the former system produces two coproducts (LA and pure DHA) and one byproduct (waste), whereas the latter produces one product (LA) and two streams of byproducts (waste and gypsum).

In the field of sustainability assessments, a system might appear sustainable at first glance only because it relies on externalities that impact other parts of society.

To explore whether these systems can sustain themselves in the long run without impacting the surroundings, the extended systems of both alt-LA and conv-LA processes are diagrammed. These extended systems include both the reference system (the lactic acid production plant) and the part of the environment that supports the reference system. In the case of both alt-LA and conv-LA, the supporting environment is mainly composed of the cultivation and manufacture of the crops from which glucose and glycerol are derived. Since the analysis of the entire extended systems is beyond the scope of the study, these diagrams were drawn based on literature data. To the best of our knowledge, there are no emergy studies or sustainability assessments focusing on lactic acid production from biomass, hence systems with similar features were selected. For alt-LA, four emergetic case studies about biodiesel production from different feedstocks (sunflower oil, soybean oil, jatropha oil, palm oil) were considered. From the diagrams of the four case studies, the common features were selected and condensed in a "model" diagram of a generic extended system. For conv-LA, four emergetic case studies about first-generation bioethanol production were selected, and the same process was carried out. Figures 21 and 22 show the emergetic diagrams of the extended systems for alt-LA and conv-LA, respectively, which are described and commented on in the following paragraph.

Figure 21: alt-LA extended system. geolog.proc.=geological processes, CO_2&N=carbon dioxide and nutrients, B=bacteria, G&M=goods and machinery, L&S=labor and services, GLY=crude glycerol.

The alt-LA extended diagram (figure 21) portrays the three main phases of lactic acid production from glycerol: agriculture, biorefinery and lactic acid production. On the left side, the local renewable resources are reported: sun, wind, deep heat, carbon dioxide (CO_2) and nutrients (N), geological processes, rain and surface water. On the top side, the purchased non-renewable resources are listed: fuels, chemicals, bacteria, electricity (lightning symbol), goods and machinery ("G&M") and labor and services ("L&S"), whereas on the right side the outputs of the system are shown. All the non-renewables (except L&S) enter the system mediated by L&S (mainly transport). The internal processes begin with the agricultural phase ("agriculture and harvesting"), which uses solar energy, wind, deep heat, CO_2 and nutrients, together with stocks of "water" and "soil" which are generated by rain, surface water and geological processes. Agriculture also uses fuels, chemicals, assets (derived from G&M) and L&S to produce and harvest the crop, which flow reaches the manufacturing phase where it is processed ("transport and biorefinery"). This step also produces wastewater which is collected in the corresponding stock and fed back into the water stock, aided by labor and service (mainly for sewage treatment). In this second phase, water (which flow splits in liquid water and steam), fuels, chemicals, bacteria, assets, electricity and L&S are used to transport the crop to the biorefinery, process it and produce biodiesel, obtaining glycerol as a byproduct. The subsystem produces two main outputs: the biodiesel, which exits the system to be sold on the market, and the glycerol, which enters the third phase ("lactic acid production"). This corresponds to the reference system for alt-LA, where glycerol is fermented and isomerized to lactic acid. This constitutes the second main output of the extended system, which exists to be sold on the market. All processes produce solid waste, which exits the system for disposal or recycling.
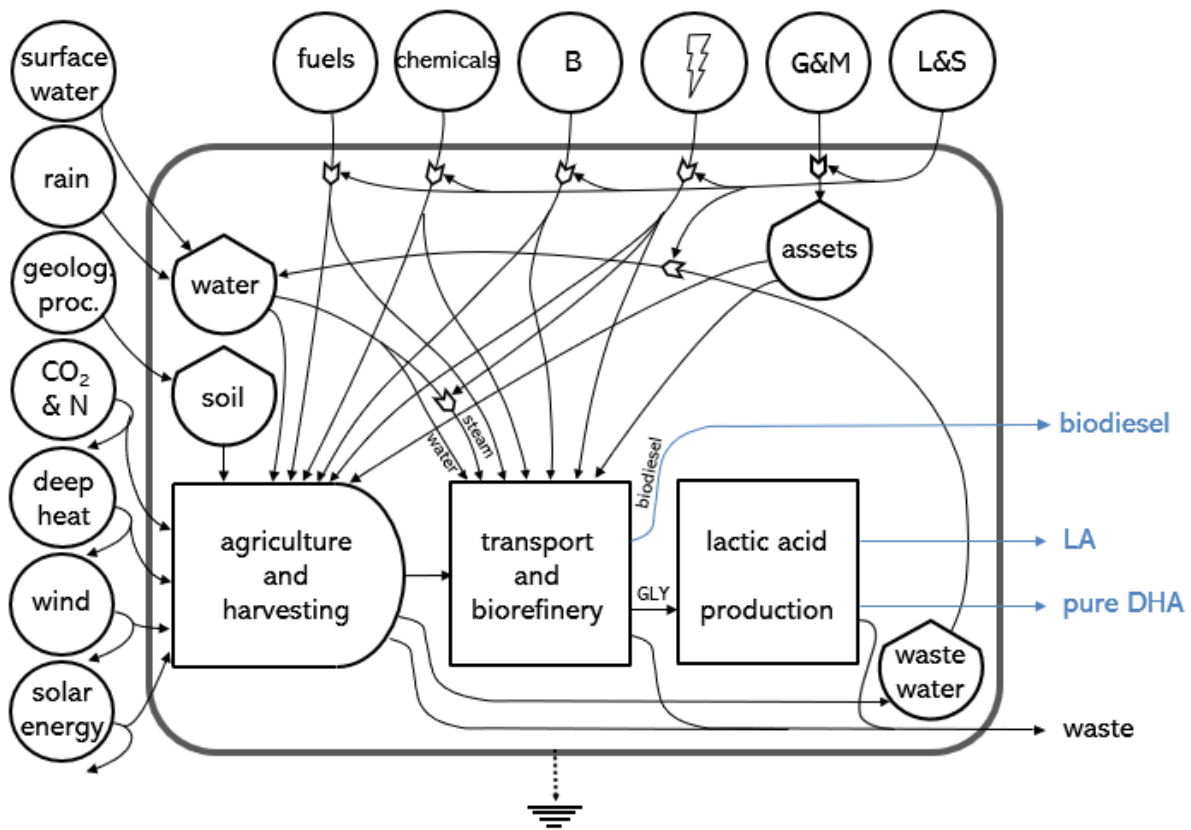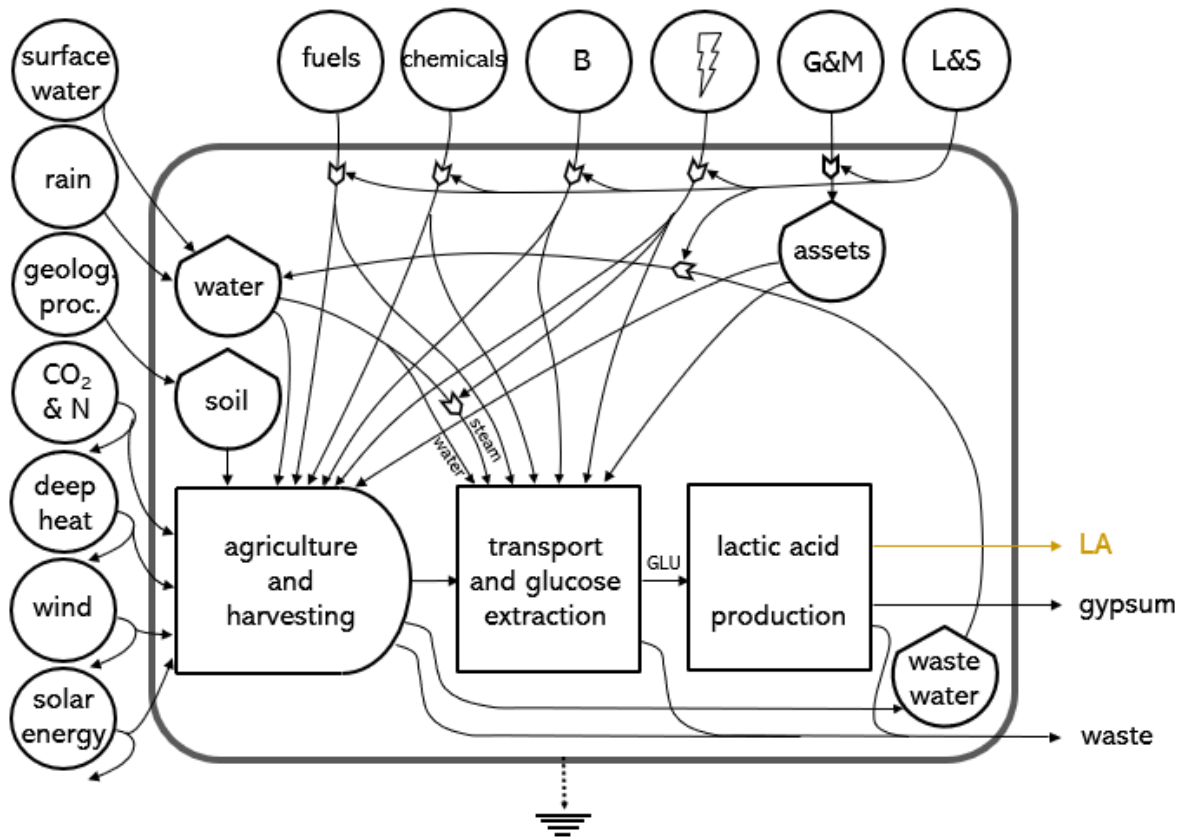
Figure 22: conv-LA extended system. geolog.proc.=geological processes, CO₂&N=carbon dioxide and nutrients, B=bacteria, G&M=goods and machinery, L&S=labor and services, GLU=glucose syrup.

The conv-LA extended diagram (figure 22) presents the same sources and structure of the alt-LA case. The first subsystem, "agriculture and harvesting", produces the crop used in the following manufacturing phase ("transport and glucose extraction") and wastewater, which is fed back into the agricultural phase aided by L&S. In the second step the glucose syrup is extracted from the crop and fed into the third phase, "lactic acid production", which corresponds to the reference system for conv-LA. From this subsystem, lactic acid is produced and exits the system as the main output. Similarly to the previous diagram, all processes produce solid waste, sent to disposal or recycling.

The two extended systems share the same sources, a similar structure and common features. Both are divided into three subsystems, one agricultural and two industrial, and present the same flow scheme. However, two relevant differences can be pointed out in terms of main processes and main outputs. Regarding the nature of the subsystems containing the main processes, in the case of alt-LA the first industrial phase, the biorefinery, is an already existing and self-sufficient system, which produces an autonomous output (biodiesel) and can sustain itself economically regardless of the following step. On the other hand, the conv-LA first industrial phase ("transport and glucose extraction") produces only one product (glucose syrup) which is an intermediate here used exclusively for LA production. This output could also be used for other types of industrial processes, but its flow would be split in two or more flows, hence in emergy accounting it would be treated as a split, not as two coproducts. As for the main outputs, while the conv-LA extended system uses all the crop cultivated to generate one main output (lactic acid), the alt-LA extended

system uses the same crop to yield two coproducts (in emergy language), biodiesel and lactic acid. From a commercial point of view though, the main output is biodiesel, which has been gaining momentum as a possibly sustainable alternative to fossil fuels, hence the production of lactic acid from glycerol can rightfully be considered a recovery of a byproduct. This makes the alt-LA reference system intuitively more "sustainable" than the conv-LA reference system, because it uses a byproduct of an existing process in the extended system (biodiesel production) to generate an output with higher value added (lactic acid instead of glycerol). In the conv-LA extended system, a new production chain is created only to produce lactic acid from glucose, whereas in the alt-LA extended system the byproduct of an existing production chain is used to generate a more commercially valuable product. The question yet to be answered is whether this existing biofuel production chain can be considered sustainable or not, but this is beyond the scope of this study.

4. Transformities calculation

After diagramming the two production processes, an emergy table containing all the inputs and main outputs was created for each of them (tables 2 and 3). All inputs and outputs correspond to the sources and outputs of the emergy diagram. Knowing that the reference paper does not provide data about acetone use, nor the fraction of DHA which is sold as such, the contribution of step 2.2 of the diagram is here neglected. Since the number of inputs and outputs involved in minimal quantities is often high, a cutoff threshold of 1% w/w with respect to the main output (lactic acid) was applied, except where explicitly stated. The input amounts were taken from the Life Cycle Inventories (LCI) provided by the reference paper and its supplemental materials, adding electricity consumption, goods and machinery (G&M) and labor and services (L&S) as indicated in the emergy diagrams. Due to lack of literature data, the electricity consumption for both processes was assumed equal to that of another existing process of lactic acid production based on lactonitrile, taking the amount of kWh used from LCA data (Ecoinvent v3.1). For goods and machinery, the reference paper does not provide specific costs for each piece of equipment used in the production processes, and to the best of our knowledge it is not possible to estimate this quantity from literature data; for this reason, we have considered the cost of production of both processes from the reference paper (Morales et al., 2015) as a proxy for the value of G&M. As for L&S, the price per kilogram of commercial lactic acid (Merck, SigmaAldrich) was considered a measure of the labor and services embodied in the product.

For every input, a corresponding transformity was either found in literature or calculated. The solar emergy related to each specific input was calculated as the product of the amount of input used and its transformity, then these emergies were summed to yield the total emergy related to the system. From this total emergy, calculated both including and excluding labor and services, the transformities of the outputs were calculated. All transformities are reported in reference to the 12,00E+24 global emergy baseline.

In the following section, the methodology for choosing or calculating the transformities of the inputs are described.

# (ref.)	item	amount	unit/yr	transformity (sej/unit)	solar emergy (sej)
center	alternative LA with no DHA-to-sell (unit/kg LA) - with petro butanol				
GLY fermentation to DHA					
1 (-)	crude GLY	1,8	kg	8,21E+13	1,48E+14
2 (a)	nutrients	0,06	kg	4,86E+11	2,92E+10
3 (b)	process water	18,04	kg	1,00E+08	1,80E+09
DHA isomerization to LA					
5 (-)	butanol	0,072	kg	9,41E+13	6,78E+12
6 (-)	catalyst	0,1	kg	5,65E+14	5,65E+13
7 (b)	water for steam generation	67,34	kg	1,00E+08	6,73E+09
8 (-)	electricity for steam generation	4,16E+07	J	3,35E+05	1,39E+13
9 (b)	cooling water	1252,6	kg	1,00E+08	1,25E+11
10 (c)	air	3,72	kg	6,56E+10	2,44E+11
both steps					
11 (-)	electricity	581,39	J	3,35E+05	1,95E+08
12 (d)	G&M	1,1	€	1,02E+12	1,12E+12
13 (d)	L&S	63,3	€	1,02E+12	6,46E+13
output					
	total emergy (with L&S)				2,84E+14
	total emergy (without L&S)				2,20E+14
O1	LA (with L&S)	1	kg		2,84E+14
O1	LA (without L&S)	1	kg		2,20E+14
W1	waste	19,3	kg		1,14E+13

Table 2: emergy table for alt-LA without DHA-to-sell. (-)=calculated transformity; (a)=Agostinho et al., 2015; (b)=Lyu et al., 2021; (c)=Zhang and Long, 2010; (d)=emergy-money ratio from Morandi et al., 2014.

# (ref.)	item	amount	unit/yr	transformity (sej/unit)	solar emergy (sej)
conventional LA
*GLU fermentation + LA neutralization*
1 (-)	glucose	1,52	kg	2,63E+12	4,00E+12
2 (b)	process water	14,8	kg	1,00E+08	1,48E+09
3 (-)	Ca(OH)$_2$	0,76	kg	7,88E+13	5,99E+13
4 (a)	nutrients	0,07	kg	4,86E+11	3,40E+10
*hydrolysis of Ca lactate*
5 (e)	H$_2$SO$_4$	1,48	kg	6,72E+11	9,95E+11
6 (b)	cooling water	107	kg	1,00E+08	1,07E+10
*esterification to ML and ML recovery*
7 (b)	methanol	0,02	kg	8,82E+12	1,76E+11
8 (b)	water for steam generation	52,1	kg	1,00E+08	5,21E+09
9 (-)	electricity for steam generation	3,22E+07	J	3,35E+05	1,08E+13
*both steps*
10 (-)	electricity	581,39	J	3,35E+05	1,95E+08
11 (d)	G&M	1,56	€	1,02E+12	1,59E+12
12 (d)	L&S	63,3	€	1,02E+12	6,46E+13
*output*
	total emergy (with L&S)				1,42E+14
	total emergy (without L&S)				7,75E+13
O1	LA	1	kg		1,42E+14
O2	LA	1	kg		7,75E+13
W1	waste	16,7	kg		8,51E+12
W2	gypsum	0,95	kg		1,50E+14

Table 3: emergy table for conv-LA. (-)=calculated transformity; (a)=Agostinho et al., 2015; (b)=Lyu et al., 2021; (d)=emergy-money ratio from Morandi et al., 2014; (e)=Fahd et al., 2012.

Transformities from literature
Most transformities are derived from previous studies, indicated in the first column of each table. Since several references for the same data can be found in literature, a few common criteria were adopted in choosing which transformities to use:
1. similarity. Different processes yielding the same output will lead to different transformity for the same product. Thus, transformities related to processes which were most similar to the ones analyzed in this work were chosen;
2. primary sources. Some papers also cite transformities from other sources; to the best of our possibilities, we tried to find the original source of those data, i.e. the paper where the transformity was calculated. In some cases this was not possible due to unavailability of the source; in these cases the source which is nearest to the primary is cited.

3. recent works. Since production processes and related technologies evolve in time becoming more efficient, we can expect transformities to change as well. To take this into account, the most recent references were selected;

4. absolute value. When finding two different transformities related to apparently equivalent processes, the one with highest value was chosen to obtain a conservative estimate of the product transformity. This avoids overestimation of the sustainability of the processes;

5. geographical location. Wherever possible, data was collected from locations which can be considered most similar to Italy, as a reference point;

6. authors. When finding papers with different transformities for the same product, the one related to a paper written by subject expert authors was chosen (HT Odum, MT Brown, S Ulgiati among others).

7. L&S. As a measure of emergy of labor and services, where not available from literature, the price per kg of the output was considered, multiplied by the most recent emergy-money ratio of Italy available.

Calculated transformities
The transformities not found in literature were calculated following various procedures, to ensure the most accurate estimate possible. The methodologies followed for each input are described below, first for raw matters and then for other inputs.

1. *crude glycerol*
Despite the lack of literature data about glycerol transformities, several emergy studies dealing with biodiesel production from various feedstocks were found. The same four case-studies examined for the extended system were taken as a reference (Bastianoni et al., 2008; Cavalett and Ortega, 2010; Goh and Lee, 2010; Ju and Chen, 2011) and, from the data provided in the papers, UEV and specific emergy of glycerol with and without L&S were calculated. Most articles provided data about biodiesel raw data (in joule and/or grams), biodiesel UEV (in sej/J) and total emergy of the system including L&S. From the emergy table provided, the total emergy without L&S was calculated subtracting the value of labor and services inputs from the total emergy. The raw amount of glycerol in grams was derived knowing that, for every unit of biodiesel produced, approximately 10% w/w of glycerol with respect to biodiesel is generated, hence multiplying the raw data of biodiesel (in grams) for 0,1. The amount of energy contained in the glycerol produced was calculated multiplying the raw data in grams for the energy equivalent of glycerol (i.e. the amount of energy per gram, in J/g, (Dorado et al., 2006), considering the average of low heating value and high heating value reported in the paper). Once these values were obtained, the UEVs and specific emergy glycerol and biodiesel, wherever missing, were calculated as the ratio between total emergy and raw data, either in joules or grams; this was repeated both with and without L&S. The specific emergy of glycerol used in this work was then obtained as the average of the four results. Data from literature is assumed to all refer to the 15,83E+24 global emergy baseline (Odum, 2000), whereas the final transformity is converted to the 12,00E+24 baseline (Brown and Ulgiati, 2016). Literature data and calculations results are reported in Table 4 (calculated values in green).

feedstock	biodiesel raw data (J)	biodiesel raw data (g)	biodiesel UEV (sej/J)	biodiesel UEV (sej/J)	biodiesel Sp (sej/g)	biodiesel Sp (sej/g)	total emergy (sej)	total emergy (sej)
for 1 ha, 1 yr	-	-	with L&S	w/o L&S	with L&S	w/o L&S	with L&S	w/o L&S
sunflower oil	1,76E+10	5,25E+05	2,78E+05	2,77E+05	9,31E+09	9,28E+09	4,89E+15	4,87E+15
jatropha	3,86E+10	4,75E+06	3,95E+05	2,77E+05	1,61E+10	1,13E+10	1,53E+16	1,07E+16
soybean	1,92E+10	5,99E+05	3,89E+05	3,80E+05	1,25E+10	1,22E+10	7,46E+15	7,30E+15
palm oil	1,56E+11	3,91E+06	4,92E+05	1,17E+05	1,76E+10	4,19E+09	1,01E+17	2,42E+16

feedstock	glycerol raw data (J)	glycerol raw data (g)	glycerol UEV (sej/J)	glycerol UEV (sej/J)	glycerol Sp (sej/g)	glycerol Sp (sej/g)	reference
for 1 ha, 1 yr	-	-	with L&S	w/o L&S	with L&S	w/o L&S	
sunflower oil	1,32E+09	5,25E+04	3,72E+06	3,70E+06	9,31E+10	9,28E+10	Bastianoni et al., 2008
jatropha	1,38E+10	5,50E+05	1,11E+06	7,76E+05	2,78E+10	1,95E+10	Ju & Chen, 2010
soybean	1,11E+09	4,42E+04	6,73E+06	6,59E+06	1,69E+11	1,65E+11	Cavalett & Ortega, 2009
palm oil	1,76E+10	7,04E+05	5,72E+06	1,37E+06	1,43E+11	3,44E+10	Goh & Lee, 2010
average Tr., 15,83E+24 baseline			4,32E+06	3,11E+06	1,08E+11	7,80E+10	Odum, 2000
average Tr., 12,00E+24 baseline			3,28E+06	2,36E+06	8,21E+10	5,91E+10	Brown & Ulgiati, 2016

Table 4: calculation of glycerol transformity from literature data.

 2. *glucose*

To the best of our knowledge, there are no emergy studies for glucose production from sugar beet, thus emergy studies of sugarcane cultivation were taken as reference, with the goal of finding glucose specific emergy from the specific emergy of cane. Three papers about bioethanol production from sugarcane were examined (Da Vitoria and Rodriguez, 2016; Pereira and Ortega, 2010; EPA Handbook of Emergy Evaluation Folio 4, 2000). Unfortunately, these studies do not calculate the transformities for glucose, which is only an intermediate in the biofuel production, but they do provide data to calculate the transformities for sugarcane. Thus from these papers the specific emergies of sugarcane were obtained, with the same procedure described for glycerol, and their average was calculated. This average was used to calculate the transformity of glucose based on a LCA study of sugar production (Renouf et al., 2008), assuming the monosaccharide described in the study was equivalent to glucose. To verify that sugarcane can be used as a "proxy" for beet, crop yield and sugar content of the two crops were compared. Due to lack of data for glucose content and given the low % of glucose in raw juices (~1%) (Ullman's Encyclopedia of Industrial Chemistry, 2007), sucrose content was evaluated instead of glucose content, assuming sucrose as an equally suitable input for the conv-LA process (as reported in the reference paper, Morales et al., 2015). Various data were collected from independent sources. Crop yield (in tons of crop per hectare) was obtained from the FAOSTAT database, calculating a global average from 2010 to 2019 (the average from Italy could not be used because Italy does not produce relevant amounts of sugarcane). Average sugar yield (in tons of sucrose per hectare) for sugarcane was taken from Aguilar-Rivera et al., 2012, and for sugar beet was calculated as the product of crop yield and the average sugar concentration in beet (16,5% w/w) (Ullman's Encyclopedia of Industrial Chemistry, 2007). From Renouf et

al. (2008), another estimate of crop yield and sugar content were taken from two case studies of sugarcane (Australia) and sugar beet (UK) cultivation. The collected data and respective references are presented in table 5.

for 1 ha, 1 yr	crop yield (t/ha)	sugar yield (t sucrose/ha)	sugar yield (t monosaccharide/ha)	reference
sugarcane	57,48547	-	-	FAOSTAT
	-	7,9879	-	Aguilar-Rivera 2012
	85	-	12,1	Renouf et al., 2008
sugar beet	48,0988	-	-	FAOSTAT
	-	7,936302	-	Ullman's encyclopedia
	49,6	-	7,6	Renouf et al., 2008

Table 5: sugar beet and sugarcane compared; crop yield and sugar yield data.

Given that both crop yield and sugar yield of cane and beet are in the same order of magnitude, cane is therefore assumed to be a "proxy" for beet where no data for beet are available. As for the transformity of beet crop, a value of its specific emergy was later found in literature in Yang et al. (2018), drawing from Odum (1996). In the original source, the authors consider transformities for beet and cane to be the same, hence the newly calculated value for cane was considered in the following calculations. From this premise, the transformity of cane was calculated as the average of the values obtained from literature as described above. The results are presented in Table 6 (calculated values in green).

cane raw data (J)	cane raw data (g)	cane UEV (sej/J)	cane UEV (sej/J)	cane Sp (sej/g)	cane Sp (sej/g)	total emergy (sej)	total emergy (sej)	reference
		with L&S	w/o L&S	with L&S	w/o L&S	with L&S	w/o L&S	for 1 ha, 1 yr
-	9,89E+07	-	-	1,78E+08	1,78E+08	1,76E+16	1,76E+16	(f)
2,14E+11	8,00E+07	2,80E+04	2,80E+04	7,50E+07	7,50E+07	6,00E+15	6,00E+15	(g)
4,12E+11	2,27E+07	2,10E+04	2,11E+04	3,81E+08	3,83E+08	8,70E+15	8,70E+15	(h)
				2,11E+08	2,12E+08			average

Table 6: sugarcane transformities calculated from literature. (f)=da Vitoria and Rodrigues, 2016; (g)=Pereira and Ortega, 2010; (h)=EPA Handbook of Emergy Evaluation folio 4, 2000.

To find the transformity of glucose, LCA data were retrieved from literature, starting from the LCI for cane and beet processing published in Renouf et al. (2008). The paper examines the process for a more generic "monosaccharide production", but given that other sugars can be utilized in fermentations to obtain lactic acid, this monosaccharide process is considered to be a sufficient proxy for glucose. Given that several inputs were used in amounts below the 1% w/w cut off, only the input falling above this threshold were considered. From the three crops examined in the case study, the data about beet processing were taken and the corresponding transformities were found in literature - except for beet itself, for which the cane transformity previously calculated is used as a proxy. The amounts of inputs in the LCI were given per ton of monosaccharide produced, hence the amounts of inputs per hectare of

crop were calculated by multiplying the LCI entries for the sugar yield (in tons of monosaccharide per hectare) to obtain the LCI expressed per hectare of crop. To this modified LCI, the values for labor and services were added, taking amounts and transformities from a sugarcane the EPA Handbook of Emergy Evaluation (Folio 4, 2000) as a proxy for beet. The solar emergy related to each input was calculated as the product of the amount of input used and its transformity, then all the entries were summed to calculate the total solar emergy associated with monosaccharide production. From this, the specific emergy of the monosaccharide was calculated dividing the total emergy for the amount of monosaccharide produced per hectare, both with and without L&S. This specific emergy is used as an equivalent for glucose specific emergy. The results are shown in Table 7.

LCI for monosaccharide production (for 1 t product)				(for 1 ha crop)	
input	*amount/t*	*amount/ha*	*unit*	*amount/ha*	*new unit*
agricultural phase - crop cultivation					
beet	6,5	49,4	t	4,94E+04	kg
manufacturing phase - crop processing					
electricity	740	5624	MJ	5,62E+09	J
natural gas	2186	16613,6	MJ	1,66E+10	J
coke	334	2538,4	MJ	2,54E+09	J
limestone	150,5	1143,8	kg	1,14E+03	kg
emergy table for monosaccharide production (for 1 ha crop)					
# (ref.)	item	amount	unit	transformity (sej/unit)	solar emergy (sej)
agricultural phase - crop cultivation					
1 (-)	beet	4,94E+04	kg	2,11E+11	1,04E+16
manufacturing phase - crop processing					
2 (-)	electricity	5,62E+09	J	3,35E+05	1,88E+15
3 (i)	natural gas	1,66E+10	J	1,35E+05	2,24E+15
4 (j)	coke	2,54E+09	J	6,52E+04	1,66E+14
5 (k)	limestone	1,14E+03	kg	1,27E+12	1,45E+15
6 (h)	labor	1,37E+07	J	4,38E+06	6,00E+13
7 (d)	services	1,18E+03	€	1,02E+12	1,21E+15
output					
	total emergy (with L&S)				1,74E+16
	total emergy (without L&S)				1,62E+16
O1	monosaccharide/ha (with L&S)	7600	kg	2,30E+12	
O1	monosaccharide/ha (without L&S)	7600	kg	2,13E+12	

Table 7: LCI and emergy table of monosaccharide production. (-)=calculated; (b)=Lyu et al., 2021; (d)=emergy-money ratio from Morandi et al., 2014; (h)=EPA Handbook of Emergy Evaluation folio 4, 2000; (i)=Brown et al., 2011; (j)=Bastianoni et al., 2009; (k)=Wang et al., 2006.

3. *bacteria*

In the reference paper, data about bacteria use for alt-LA are not reported, whereas for conv-LA the amount falls under the 1% cut off. For this reason, endorsed in literature (Agostinho et al., 2015), the contribution of bacteria to the emergy table was neglected.

4. *electricity*

Where the source of energy (fossil, wind, solar, etc) was not specified, an average transformity for the Italian energy mix was used. This was calculated as a weighted average of transformities provided in Lyu et al. (2021) and Corcelli et al. (2017), using the fraction of sources in the Italian energy mix reported by the International Energy Agency (IEA) in 2020 as weights (reported in Table 8).

percentages of energy sources in Italy electricity energy mix 2020 (IEA) (%)			
coal	4,64	hydro	17,3
oil	3,47	geothermal	2,14
natural gas	48,9	solar photovoltaic	8,86
biofuels	6,15	wind	6,64
waste	1,71	other	0,19

Table 8: Italian energy mix (International Energy Agency).

5. *goods and machinery*

For lactic acid production, the same transformity used for labor and services is applied. For the inputs to lactic acid production, the emergy contribution due to goods and machinery was considered included in that of labor and services, considering it related to the price.

6. *steam*

In more than one LCI, steam is reported as one of the inputs. From an emergetic point of view, steam is not a purchased good, but it is generated inside the system to aid processes, hence it is not treated like the purchased resources. Instead of finding a transformity in literature, the mass of water needed and the amount of energy to produce steam are calculated, assuming electrical energy is used and steam is always obtained at 6 bar as reported in lactic acid LCIs. The mass of water is equal to the mass of steam reported in the LCIs, whereas the amount of energy was calculated as the sum of the energy needed to heat water to boiling temperature, the latent heat of vaporization and the energy needed to heat the steam to usage temperature and pressure. All the transformations were assumed isochoric, since it is assumed they occur inside the production plant components. Water was assumed to be heated from room temperature (20 °C) and steam to be used at 300 °C (slightly above the equilibrium temperature at 6 bar). The mass of water used and the energy required were multiplied for the same transformities used for water and electricity. Data, calculations and results are reported in table 9.

LCI	m(steam) = m(water)		ΔU water (J) m*Cv*(T2-T1)	heat of vap. (J) m*Hvap	ΔU steam (J) m*Cv*(T2-T1)	tot energy (J) ΔU + heat of vap. + ΔU	
alt-LA	67,34	kg	22394590,4	168350	19000654	41563595	4,16E+07
conv-LA	52,1	kg	17326376	130250	14700536	32157162	3,22E+07
bio-butanol	11,43	kg	3801467,105	28577,30263	3225349	7055393	7,06E+06
isochoric specific heat capacities (Cv) and latent heat of vaporization							
water Cv			4,157	J/(g*K)	Engineering ToolBox (2004)		
steam Cv			1,4108	kJ/(kg*K) = J/(g*K)	Kyle, B. G., Chemical and Process Thermod.		
latent heat of vaporization			2500	kJ/kg = J/g	Ullman's Encyclopedia of Industrial Chemistry		

Table 9: calculation of the energy needed for water vaporization to obtain steam according to LCIs.

7. butanol

For reagents such as butanol, several synthetic routes exist for their production, which might result in different transformities. To gain a wider perspective on this reagent, two production processes were considered: a "worst case scenario", in which butanol is synthesized from petrochemical derivatives, and a "best case scenario", where it is obtained from biomass. These two routes were also analyzed starting from LCI data. Since the resulting transformities are in the same order of magnitude, only the worst case scenario result is reported in the previous emergy table for alt-LA (table 2).

Worst case scenario: petrochemical butanol. Among the possible synthetic pathways, hydroformylation of propylene was chosen, with propylene derived from steam cracking of petroleum. The LCI of the process was retrieved from Ecoinvent 3.1 (referring to 1 kg output), adding the contribution of L&S. A transformity was assigned to each input and the transformity of petrochemical butanol was calculated dividing the total emergy for the amount of output. Since transformities for liquefied gases (hydrogen and nitrogen) were not found in literature, they were calculated from the specific emergies of their gaseous form adding the emergy invested to liquefy them. This latter was obtained from the energy necessary to liquefy a kg of gas (US Dep.t of energy, 2009; Knowlen et al., 1998) multiplied for the amount of gas used as reported in table 10 (in green the calculated values). The transformity of carbon monoxide, not found in literature, was obtained from Bargigli et al. (2004) from that of syngas. Knowing the fraction of CO, hydrogen and other gases in the syngas, hydrogen and syngas UEVs, and assuming that the UEV of the unspecified fraction of syngas was the same of the entire mixture, the UEV of carbon dioxide was calculated with an equation; from the UEV, the heat of combustion and the molecular weight, the specific emergy was derived. In the same way, from hydrogen UEV and high heating value (to have a conservative estimate) the specific emergy was obtained. The calculations and related data and emergy table for butanol transformity are summarized in tables 11 and 12, respectively.

gas	energy used		mass of gas		total energy			consumption reference
H_2	13,00	kWh/kg	0,057233	kg	0,744029	kWh	2678504,4 J	US Department of Energy
N_2	0,50	kWh/kg	0,0074701	kg	0,00373505	kWh	13446,18 J	Knowlen et al 1998

Table 10: energy to liquefy hydrogen and nitrogen to calculate transformities of gases

quantity	CO	H2	other	total	unit
w% in syngas	50	30	20	100	%
MW	28	2	N/A	N/A	g/mol
heat of combustion	282,98	N/A	N/A	N/A	kJ/mol
LHV	N/A	119,93	N/A	N/A	kJ/g
HHV	N/A	141,8	N/A	N/A	kJ/g
UEV	2,60E+04	9,66E+04	5,25E+04	5,25E+04	sej/J
equation: $0{,}5*UEV(CO)+0{,}3*UEV(H_2)+0{,}2*UEV(other)=1*UEV(syngas)$					
specific emergy	UEV*hoc*1000/MW	UEV*HHV*1000	N/A	N/A	sej/g
specific emergy	2,63E+08	1,37E+10	N/A	N/A	sej/g

Table 11: calculation of carbon monoxide specific emergy.

petrochemical butanol production					
# (ref.)	item	amount	unit/yr	transformity (sej/unit)	solar emergy (sej)
liquefaction of gases					
1 (-)	electricity for hydrogen liquefaction	2678504,4	J	3,35E+05	8,97E+11
2 (-)	electricity for nitrogen liquefaction	13446,18	J	3,35E+05	4,50E+09
hydroformylation of propylene					
3 (l)	propylene	0,59761	kg	2,60E+13	1,55E+13
4 (-)	carbon monoxide	0,39779	kg	2,63E+11	1,05E+11
5 (-)	electricity, medium voltage	665.496,00	J	3,35E+05	2,23E+11
6 (b)	heat, district or industrial, natural gas	5,6773	MJ	1,33E+11	7,55E+11
7 (b)	heat, district or industrial, other than natural gas	5,1401	MJ	1,03E+11	5,29E+11
8 (-)	hydrogen, gas	0,057233	kg	1,37E+13	7,84E+11
9 (c)	nitrogen, gas	0,0074701	kg	4,19E+12	3,13E+10
10 (b)	Water, cooling, unspecified natural origin	91,315	kg	1,00E+08	9,13E+09
11 (b)	water, deionised, from tap water, at user	0,83002	kg	1,00E+08	8,30E+07
12 (d)	L&S	74,96	€/kg	1,02E+12	7,65E+13
outputs					
	total emergy (with L&S)				9,44E+13
	total emergy (without L&S)				1,80E+13
O1	butanol (with L&S)	1,00000	kg	9,44E+13	
	butanol (without L&S)	1,00000	kg	1,80E+13	

Table 12: emergy table and transformity calculation for petrochemical butanol. (-)=calculated; (b)=Lyu et al., 2021; (c)=Zhang and Long, 2010; (d)=emergy-money ratio from Morandi et al., 2014; (l)=Sha et al., 2015.

Best case scenario: butanol from biomass. One of the most widespread synthesis of butanol from biomasses used to be ABE fermentation (acetone-butanol-ethanol), which was progressively abandoned when petrochemical routes became more economically convenient (Gabriel, 1928). Now the need to rediscover refinery processes based on biomass is increasing, and ABE fermentation is gaining new momentum. This process uses crop biomass to produce acetone, butanol and ethanol (in a ratio of approximately 3:6:1) via fermentation with Clostridium bacteria. By using engineered bacteria strains, several studies are focusing on how to improve the yields of one or more of the products, of which Veza et al. (2021) provide a review. Data about ABE fermentation were gathered from an LCA case study that uses corn (Brito and Martins, 2017) which provides the LCI of inputs and outputs of the process. These data were normalized for 1 kg butanol, considering it as the main output, and the contribution of L&S was added. Transformities of inputs were found in literature and the total emergy was calculated, so as to obtain the transformities of all main outputs. Normalized results are summarized in table 13.

bio butanol production					
# (ref.)	item	amount	unit/yr	transformity (sej/unit)	solar emergy (sej)
fermentation					
1 (m)	corn	4,22697	kg	1,45E+12	6,13E+12
2 (b)	water	10,37668	kg	1,00E+08	1,04E+09
3 (-)	electricity	3,64E+06	J	3,35E+05	1,22E+12
4 (b)	water for steam	11,4309	kg	1,00E+08	1,14E+09
5 (-)	electricity for steam generation	7,06E+07	J	3,35E+05	2,37E+13
6 (d)	L&S	73,20	€/L	1,02E+12	7,47E+13
outputs					
	total emergy (with L&S)				1,06E+14
	total emergy (without L&S)				7,35E+12
O1	butanol	1	kg	1,06E+14	
O2	butanol	1	kg	7,35E+09	
O2	acetone	0,22747	kg	4,65E+14	
O3	acetone	0,22747	kg	3,23E+10	
O3	ethanol	0,026753	kg	3,95E+15	
O4	ethanol	0,026753	kg	2,75E+11	

Table 13: energy table and transformity calculation for butanol produced from biomass. (b)=Lyu et al., 2021; (d)=emergy-money ratio from Morandi et al., 2014; (m)=Dong et al., 2008.

8. catalyst

Since the catalyst in the reference paper was newly synthesized, no transformity is available in literature and the data about electricity, labor and services could not be retrieved from the article. With this in mind, and assuming that the contribution of the catalyst to the total emergy is not extremely high, the production process for a standard commercial zeolite was considered in lieu of the specific catalyst. The LCI of a commercial zeolite was taken from Ecoinvent 3.1 with the 1% cut off for inputs, whereas the estimate of L&S was obtained from

its market price. A few assumptions were made while assigning transformities to inputs, for those that could not be found in literature. For clay, bauxite, gravel, iron ore and sodium chloride the specific emergy of the average crust was used. For CO_2 and oxygen the air specific emergy was used. For natural gas, its amount in MJ was calculated from m^3 assuming the gas is 100% methane, hence using methane calorific value. For electricity generated from biomass, some studies report a transformity of 0 considering biomass use an internal recycling, while others use a calculated transformity assuming biomass is imported in the system. For a conservative estimate, this second assumption was made and the average transformity of electricity production for the Italian energy mix was used. The emergy table from the LCI is reported in Table 14.

# (ref.)	item	amount	unit	transformity (sej/unit)	solar emergy (sej)
zeolite catalyst production					
inputs					
1 (n)	Aluminium	0,89063	kg	9,53E+12	8,49E+12
2 (h)	Calcium carbonate, in ground	0,19847	kg	1,27E+12	2,53E+11
3 (o)	Clay, unspecified, in ground	0,08569	kg	1,33E+12	1,14E+11
4 (o)	Gangue, bauxite, in ground	9,5814	kg	1,33E+12	1,27E+13
5 (o)	Gravel, in ground	2,8544	kg	1,33E+12	3,80E+12
6 (o)	Iron, 46% in ore, 25% in crude ore, in ground	0,047663	kg	1,33E+12	6,34E+10
7 (o)	Sodium chloride, in ground	0,92491	kg	1,33E+12	1,23E+12
8 (c)	Carbon dioxide, in air	0,14407	kg	6,56E+10	9,45E+09
9 (c)	Oxygen, in air	0,040285	kg	6,56E+10	2,64E+09
10 (i)	Coal, brown, in ground	4,19935	MJ	5,03E+10	2,11E+11
11 (i)	Coal, hard, in ground	26,14543	MJ	7,36E+10	1,92E+12
12 (i)	Oil, crude, in ground	16,39780	MJ	1,12E+11	1,84E+12
13 (i)	Gas, natural, in ground	23,36409	MJ	1,30E+11	3,04E+12
14 (p)	Energy, geothermal, converted	0,24165	MJ	1,11E+11	2,68E+10
15 (b)	Energy, gross calorific value, in biomass	1,5932	MJ	3,35E+11	5,34E+11
16 (b)	Energy, kinetic (in wind), converted	0,16600	MJ	3,41E+10	5,66E+09
17 (b)	Energy, potential (hydropower), converted	2,0913	MJ	2,47E+11	5,17E+11
18 (q)	Energy, solar, converted	0,00027461	MJ	3,19E+11	8,77E+07
19 (d)	Water, turbine use, unspecified natural origin	13,797	m^3	1,00E+11	1,38E+12
20 (d)	L&S	518	€/kg	1,02E+12	5,28E+14
outputs					
	total emergy (with L&S)				5,65E+14
	total emergy (without L&S)				3,62E+13
O1	catalyst (with L&S)	1,00000	kg	5,65E+14	
O1	catalyst (without L&S)	1,00000	kg	3,62E+13	

Table 14: emergy table and transformity calculation for a generic zeolite catalyst. (b)=Lyu et al., 2021; (c)=Zhang and Long, 2010; (d)=emergy-money ratio from Morandi et al., 2014; (h)=EPA Handbook of

Emergy Evaluation folio 4, 2000; (i)=Brown et al., 2011; (n)=Brown and Buranakarn, 2003; (o)=De Vilbiss and Brown, 2015; (p)= Brown and Ulgiati, 2002; (q)=Corcelli et al. 2017.

9. *calcium hydroxide*

The LCI of Ca(OH)$_2$ production was retrieved from Ecoinvent 3.1, using the weighted average of electricity transformity both for high and medium voltage, and adding L&S contribution from its market price. Data and results are presented in table 15.

# (ref.)	item	amount	unit/yr	transformity (sej/unit)	solar emergy (sej)
calcium hydroxide production					
hydration of lime					
1 (b)	quicklime, in pieces, loose	0,77556	kg	1,72E+10	1,33E+10
2 (-)	electricity, high voltage	2,32E+04	J	3,35E+05	7,77E+09
3 (-)	electricity, medium voltage	2,25E+04	J	3,35E+05	7,53E+09
4 (b)	heat, other than natural gas	0,00141	MJ	1,03E+11	1,45E+08
5 (b)	Water, well, in ground	0,00084781	m^3	1,00E+11	8,48E+07
6 (d)	L&S	77,10	€/kg	1,02E+12	7,86E+13
outputs					
	total emergy (with L&S)				7,87E+13
	total emergy (without L&S)				2,89E+10
O1	calcium hydroxide	1	kg	7,87E+13	
	calcium hydroxide	1	kg	2,89E+10	

Table 15: emergy table and transformity calculation for calcium hydroxide. (b)=Lyu et al., 2021; (d)=emergy-money ratio from Morandi et al., 2014.

5. Calculation of emergy indicators

After calculating the transformity of each input and of the output, the emergy indicator listed in the previous chapter can be estimated. In most emergy analyses, especially the ones dealing with systems at the border between ecosystems and human intervention (e.g. agriculture), it is sufficiently easy to recognise which inputs are renewable and which are not, or which are local and which are purchased. In the present case though, none of the starting materials can be considered purely renewable in the conventional sense, since they do not derive directly from the geobiosphere but they are always produced by human transformations. Thus, to be able to calculate the main indicators, a distinction between the nature of the inputs was made, hypothesizing two limit scenarios:

1. fermentation materials (glycerol, glucose, nutrients, bacteria) are considered renewable, since they are the closest to the investment of the geobiosphere, and all the nonrenewable inputs are considered local except electricity, G&M and L&S;
2. all inputs are considered nonrenewable and nonlocal.

The two scenarios lead to different values of the indicators, as reported in table 16.

indicator	description	alt-LA (1)	alt-LA (2)	conv-LA (1)	conv-LA (2)
Tr	emergy/unit product (sej/kg)	2,84E+14	2,84E+14	1,42E+14	1,42E+14
EYR	Y/F	1,98E+00	1	3,52E+01	1
ELR	(F+N)/R	9,69E-01	N/A	3,42E+01	N/A
ESI	EYR/ELR	2,05E+00	N/A	1,03E+00	N/A
EIR	F/(N+R)	3,77E-01	N/A	8,72E-01	N/A
UEI	Em to add for another process	N/A	N/A	N/A	N/A
PDI	$10\log(\varepsilon\delta Total/\varepsilon\delta Ref)$	N/A	N/A	N/A	N/A
EuSI	1/ESI	4,88E-01	N/A	9,72E-01	N/A

Table 16: emergy indicators for alt-LA and conv-LA.

6. Calculation of green metrics

From the same LCIs used for emergy analysis, some of the most widespread green metrics were estimated, namely chemical yield (%Y), atom economy (AE), Reaction Mass Efficiency (RME), Mass Index (MI) and E-factor (E). Some of them are calculated more than once varying the types of inputs included or excluded to explore how these metrics can change for the same process. Results for alt-LA and conv-LA are reported in tables 17 and 18, respectively.

metric	description	value	notes
%Y	% yield: actual yield/theoretical yield*100 here: (yield step 1* yield step 2)/100	83,70	DHA yield = 90%, LA yield = 93%. It is impossible to calculate it from the mass of reagents because glycerol is crude, hence the net mass of GLY is not known.
AE	atom economy: MW product/MW reagents*100	96,74	MW LA = 89, MW GLY = 92, GLY:LA=1:1. Excluding catalysts and solvents.
RME	reaction mass efficiency: mass(product)/mass(reagents)*100	0,01368	Excluding cooling water.
		51,02	Excluding cooling water, solvents, steam and air.
		55,56	Including only GLY, since nutrients are for bacteria and bacteria and zeolite are catalysts.
MI	mass index: mass all inputs/mass product	91,13	Excluding cooling water.
		20,07	Excluding cooling water, steam and air.
		2,032	Excluding process and cooling water, steam and air.
E	E-factor: kg waste/kg product here: MI-1	90,13	Excluding cooling water.
		19,07	Excluding cooling water, steam and air.
		1,032	Excluding process and cooling water, steam and air.
		19,3	Calculated from LCI waste output.

Table 17: green metrics calculated for alt-LA.

metric	description	value	notes
%Y	% yield: actual yield/theoretical yield*100 here: %yield CaL*%yield ML* %yield LA/10000	75,24	CaL yield = 90%, ML yield = 88%, LA yield = 95%. Impossible to calculate from the mass of reagents because glucose is crude, hence the net mass of pure glucose is not known.
AE	atom economy: MW product/MW reagents *100	30,27	MW LA=89, MW GLU=180, GLU:LA=2:1, MW Ca(OH)$_2$=74, MW methanol=32, MW H$_2$SO$_4$=98. Excluding catalysts and solvents.
RME	reaction mass efficiency: mass(product)/mass(reagents)*100	0,05362	Excluding cooling water.
		0,2611	Excluding water and methanol (solvents).
		0,2660	Only GLU, Ca(OH)$_2$, H$_2$SO$_4$ are included, because nutrients are for bacteria and bacteria are catalysts.
MI	mass index: mass all inputs/mass product	70,75	Excluding cooling water.
		18,65	Excluding cooling and steam generation water.
		3,85	Excluding process, cooling and steam generation water.
E	E-factor kg waste/kg product here: MI-1	69,75	Excluding cooling water.
		17,65	Excluding cooling and steam generation water.
		2,85	Excluding process, cooling and steam generation water.
		17,65	Calculated from LCI waste output.

Table 18: green metrics calculated for conv-LA.

As an example of comprehensive assessment, the values of EcoScale for the two processes were calculated. Since the method is semiquantitative and involves some discretionality in the attribution of the penalty points, for alt-LA the score was evaluated in four different scenarios, to test how the judgment of the operator can vary the result:

1. assuming the catalyst is classified as inexpensive because it is not purchased from an external source, and assuming all the glassware used is classified as "common";
2. assuming the catalyst is classified as expensive due to the costs related to the synthesis, and assuming all the glassware used is classified as "common";
3. assuming the catalyst is classified as inexpensive because it is not purchased from an external source, and assuming all the glassware used is classified as "special";
4. assuming the catalyst is classified as expensive due to the costs related to the synthesis, and assuming all the glassware used is classified as "special"

Results for both processes are presented in table 19.

Table 19: EcoScale calculation for alt-LA in the four scenarios and for conv-LA (continues).

Parameter	Penalty points	(1) feat.	(1) score	(2) feat.	(2) score	(3) feat.	(3) score	(4) feat.	(4) score	conv-LA feat.	conv-LA score
1. Yield (100 − %yield)/2	-	83,7	8,15	83,7	8,15	83,7	8,15	83,7	8,15	75,2	12,4
2. Price of components (for 10 mmol of end product)											
Inexpensive (< $10)	0	all	0	0	0	all	0	0	0	all	0
Expensive ($10<price<$50)	3	0	0	0	0	0	0	0	0	0	0
Very expensive (> $50)	5	0	0	cat.	5	0	0	cat.	5	0	0

3. Safety											
N (dangerous for env.t)	5	0	0	0	0	0	0	0	0	0	0
T (toxic)	5	1	5	1	5	1	5	1	5	1	5
F (highly flammable)	5	1	5	1	5	1	5	1	5	1	5
E (explosive)	10	0	0	0	0	0	0	0	0	0	0
F+ (extremely flammable)	10	0	0	0	0	0	0	0	0	0	0
T+ (extremely toxic)	10	0	0	0	0	0	0	0	0	0	0
4. Technical setup											
Common setup	0	all	0	all	0	0	0	0	0	most	0
Controlled addition of chem.	1	0	0	0	0	0	0	0	0	0	0
Unconv. activation	2	0	0	0	0	0	0	0	0	0	0
Pressure equipment, >1 atm	3	1	3	1	3	1	3	1	3	0	0
Special glassware	1	0	0	0	0	11	11	11	11	3	3
(Inert) gas atmosphere	1	0	0	0	0	0	0	0	0	0	0
Glove box	3	0	0	0	0	0	0	0	0	0	0
5. Temperature/time											
Room temperature, < 1 h	0	most	0	most	0	most	0	most	0	most	0
Room temperature, < 24 h	1	0	0	0	0	0	0	0	0	0	0
Heating, < 1 h	2	2	4	2	4	2	4	2	4	1	2
Heating, > 1 h	3	6	18	6	18	6	18	6	18	7	21
Cooling to 0°C	4	0	0	0	0	0	0	0	0	0	0
Cooling, < 0°C	5	0	0	0	0	0	0	0	0	0	0
6. Workup and purification											
None	0	0	0	0	0	0	0	0	0	0	0
Cooling to r.t.	0	most	0	most	0	most	0	most	0	most	0
Adding solvent	0	most	0	most	0	most	0	most	0	most	0
Simple filtration	0	most	0	most	0	most	0	most	0	most	0
Solvent removal bp<150°C	0	most	0	most	0	most	0	most	0	most	0
Crystallization and filtration	1	1	1	1	1	1	1	1	1	0	0
Solvent removal bp>150°C	2	0	0	0	0	0	0	0	0	0	0
Solid phase extraction	2	0	0	0	0	0	0	0	0	0	0
Distillation	3	3	9	3	9	3	9	3	9	4	12
Sublimation	3	0	0	0	0	0	0	0	0	0	0
Liquid-liquid extraction	3	0	0	0	0	0	0	0	0	0	0
Classical chromatography	10	0	0	0	0	0	0	0	0	0	0
sum of penalty points	-	-	53,15	-	58,15	-	64,15	-	69,15	-	60,4
EcoScale score	-	-	46,85	-	41,85	-	35,85	-	30,85	-	39,6

Table 19: EcoScale calculation for alt-LA in the four scenarios and for conv-LA.

7. Results

The first aspect to notice is that not all indicators can be calculated in both scenarios: in particular, ELR, ESI, EIR and EuSI cannot be estimated for the second scenario, because in a system with no renewable sources the denominator of ELR becomes zero,hence all the other indicators are indeterminate. Secondly, the PDI cannot be calculated without knowing the emergy density of the background environment and without further information regarding the toxicological effect of the inputs of the systems studied. These two aspects highlight two shortcomings of emergy analysis: on one side, it cannot effectively deal with purely human systems, unless a much more extensive retrospective study is performed. To correctly estimate the renewable and non renewable fractions, in fact, we should quantitatively assess also the inputs of the extended systems that include agricultural inputs, where the distinction between renewables and non renewables is clear. For this reason we will compare only the results of scenario 1. The second shortcoming is the considerable amount of highly specific data required for some indicators: the PDI, for example, would require a more extensive analysis of the potential impacts of the inputs and outputs involved in the system, analysis which is difficult to perform at a first stage of assessment. As for the UEI, this indicator is conceived to be calculated exclusively for alt-LA, because this system is conceived as part of an integrated industrial production system that encompasses a previous biorefinery, thus quantifying the additional investment needed to create the lactic acid production system represents a more reliable estimate of the emergy investment with respect to the transformity of the output. However, it is not possible to perform the calculation without further information about the extended system that supports this production.

Looking at the numerical result, it is evident that the two processes do not appear so different from an emergetic point of view: the transformities of the two types of lactic acid are in the same order of magnitude (that of alt-LA being actually slightly higher), and so are the other indicators. A slightly higher EYR for conv-LA would make this process appear more efficient, but a higher ELR makes it also have a higher impact on the local environment. The ESI, which is a measure of the overall sustainability of the systems, indicates that alt-LA is still preferable with respect to conv-LA, but the difference between the two values is not particularly wide, hence the two processes can be deemed similar from the point of view of their sustainability.

As visible from the emergy tables (tables 2 and 3), for both processes the highest investment inputs in terms of total emergy are electricity production and labor and services; what differs is that for conv-LA the other most emergy-intensive input is calcium hydroxide, whereas for alt-LA they are glycerol and the catalyst. This can be explained by the high cost of extraction and processing of the hydroxide, from the multi-step, finely tuned synthesis of the zeolite catalyst, and from the fact that glycerol "carries" the emergy investment of all the previous biorefinery production chain, being a byproduct of biodiesel production. It is worth noting that part of the similarities between the systems in terms of emergy inputs is due to the fact that the same data was used as a proxy in both cases, when more precise estimates were not available: it is the case of electricity usage and labor and services, for which the reference paper did not report information. This lack of data is easily explained by the fact that the newly proposed process, alt-LA, has been exclusively modeled in silico and not realized in laboratory experiments, even less at industrial scale. From this observation, a

further difficulty in approaching emergy analysis can be noted, since modeled systems can hardly be studied in satisfactory detail due to the lack of experimental data.

At first sight, the clear difference between the two processes is visible: alt-LA has a higher yield, also due to less purification steps, considerably higher atom economy, due to the absence of stoichiometric reagents such as calcium hydroxide and sulfuric acid, and higher RME when water is not considered. However, some potential interpretation issues arise when looking at RME, MI and E-factor, because depending on which inputs are included or excluded from the calculation the results showed marked differences. The RME appears similar for both processes when calculated excluding only the cooling water, but lies in favor of alt-LA as a more efficient process when calculated also solvents, steam and air. This is due to the heavy contribution of calcium hydroxide and sulfuric acid in lowering the RME of conv-LA, since they are stoichiometric and not catalytic reagents. On the contrary, mass index and E-factor follow a different pattern: when estimated including all the inputs, their values are much higher in the alt-LA process, indicating that it is less convenient regarding the production of waste, but when evaluated excluding cooling water (and further also steam and air) the values for the two process become comparable. In general, these seemingly contradictory results show that the calculation of green metrics, and the subsequent evaluation of the greenness of processes, strongly depend on what we consider to be a "reagent".

A similar situation results from the application of EcoScale: the four scenarios for alt-LA demonstrate that the final score on the same scale can vary greatly depending on the opinion of the operator. This is because, to the best of our knowledge, there are no detailed lists or data regarding what to consider, for example, "common setup", "special glassware" or "unconventional activation techniques", thus leaving room to interpretation when performing an evaluation. It is certainly to be noticed that this tool is designed for an application in education, where developing critical thinking skills is more important than performing a correct evaluation; nevertheless, it is key to underline that this tool, like other semi-quantitative measures, can lead to unclear results due to personal interpretation. Overall, the calculation of green metrics and the application of simple assessment tools have the strong advantage of being extremely quick to estimate and not data-intensive, but they might leave room for uncertainty in their interpretation, providing less sound results than other methods.

After calculating both green metrics and emergy indicators, it is evident that the two languages provide different information on the same system, sometimes even with apparently contradictory results. However, both points of view are a valid aid in evaluating the overall sustainability of a process and, even though they might be hard to integrate with each other, they still can be used jointly to widen our understanding of chemical systems, as we will see in the next chapter.

Chapter 5 - Comparison

After a winding journey inside the lactic acid world, we are now approaching the core of our reflection. With the introduction and the case study explored in the previous chapters, this work aims to scratch the surface of the emergy and green chemistry languages, drawing a comparison between their philosophy and approach. Do they stem from the same concepts? Do they follow the same mindset? Do they offer different perspectives? Do they overlap, and provide the same information, or does each of them enlighten us on diverse aspects of the world? How do they intertwine with each other, and with our broader view of sustainability? And beyond their theoretical value, how can we use them? How can we exploit their potential to unlock the path to our overall goal, which is sustainability?
We are going to try to answer some of these questions in this chapter.

1. epistemologies

First of all, they are born in a similar way for two distant causes: brainchildren of two fathers (Howard T. Odum for emergy, Paul T. Anastas for green chemistry), the former stems from the curiosity of a man and his *thirst for understanding* the dynamics of nature; the latter originates as a *reaction to an existing problem*. And even though both are probably the fruit of the same love for nature, they might have been guided by different emotions: while Odum was encouraged to explore the natural mysteries and rely on curiosity and fascination, Anastas felt a call to action when he saw the wetlands behind his home bulldozed away to make room for "development" (Greenwire, New York Times, 2011).
Given the almost antithetic circumstances they were born in, it does not surprise us that the two disciplines developed a contrasting approach to knowledge and science. Green chemistry draws its premises from the 'current' (1990s) development and mindset of chemistry, where little attention was paid to the potential harm of chemicals in their design stage, and it starts from a practical issue to build a solution. It fits into an already established theoretical framework of chemistry -one that uses words like 'yield', 'waste', 'reagents' and 'products'- to try to revolutionize -not the framework itself but- how this is put into practice. It adopts the same *reductionist* approach that has been typical of most scientific research since the formalization of the scientific method itself: by breaking down a system into its constituent pieces and studying each one by one, it aims at "simplifying" the understanding of the system in its entirety. It starts from 12 pragmatic principles, with no whims of axiomatization, to change the way "chemists do chemistry" both in terms of efficiency (e.g. consuming less resources, generating less waste) and in terms of ethics, as a more "environmentally-friendly" chemistry. In a way, it almost appeals to "common sense" in the way it suggests a more deliberate, but cautious, use of resources. On the other hand, emergy was born in and grew its own *conceptual framework*, which created its own algebra and vision. Not only it tells us 'how to do science', but it explores "three epistemological levels: Modell (model), Weltbild (image of the World), Weltanschauung (intuition of the World)" (Perosa et al., 2019) and it "talks us about deep aspects of the reality as a whole" (ibidem), aspiring at a "holistic framework of an integrated and "universal" culture" (ibidem). It leaves hints about how to look at the world: "You cannot understand a system without understanding the next larger and next smaller systems" (King, 2004). It tells us "what can and cannot be done", which is "determined by the simple laws that govern the system"

(Odum, 1971). With its novel framework, it detaches from the traditional reductionism of science, adopting instead a *holistic* view of systems. In this framework, systems are not broken down into their constituents anymore, but they are studied as a whole which is "bigger than the sum of its parts"; each part in fact contributes to generate *systemic* properties that cannot be explained by looking at the single pieces, but can be understood only by examining the system in its entirety.

The concept of emergy itself even defines the *value* of a thing, "measured as the quantity and quality of the energy required to replace it, or bring it into being and sustain it" (King, 2004). The process of defining the value of things is not typical of science, which often leaves the valuation process to other disciplines or to market dynamics. Laying the foundation of concepts for then passing to their implication and implementation is rather customary of epistemology, which makes emergy theory a discipline on the blurry border of these two branches of knowledge. Furthermore, in this valuation process emergy takes the opposite side of most disciplines: while the most common way of thinking is rooted in a *'user-side' point of view*, in which the value of goods and services are established by their perceived utility for the market (market which is composed by humans), emergy disrupts this paradigm by adopting a *'donor-side' perspective*, in which the value of a product is determined by the investment that the overall geobiosphere -human labor included- must perform to maintain the system production and sustenance.
It is evident that the scope of emergy goes well beyond suggesting how to operate in the Earth system; it envisages a whole new perception of Earth itself. If green chemistry changes the way we *do* the world, emergy changes the way we *view* the world.
Despite the profound divergence between the context from which these two languages emerged, there is a mutual understanding that this gap must be bridged in order to maximize the transformative potential of these tools. Paul Anastas and following researchers (see for example Ribeiro and Machado, 2013) recognised that "traditional" chemistry is based on reductionism, which disclosed groundbreaking benefits and innovations for humanity, but also caused unexpected drawbacks due to lack of systemic understanding. His idea of green chemistry aims at going further: "By thinking in terms of systems, Green Chemistry can pursue significant innovations while avoiding unintended results" (Anastas and Eghbali, 2010). For this reason, he remarks how the 12 principles are not meant to represent 12 independent goals, but "rather an integrated cohesive system of design". Real sustainability can be achieved only by applying all principles together. And with a forward-thinking mindset, he states: "By seeking out the mutually reinforcing aspects of the principles, systemic sustainable design is possible and can facilitate transformative innovation rather than incremental improvement" (ibidem). This reinforces the idea that green chemistry must overcome the perspective that created it, by adopting the same holistic approach on which emergy analysis is founded.

The two disciplines use different language to describe the same concepts from two distinct points of view: while green chemistry talks about '(production) processes' as the entire system for the production of a substance and of 'reactions' as the single steps of these processes, emergy refers to 'systems' instead of processes and 'processes' as components of a system, precisely where two or more flows converge and are transformed to different flows. Also, green chemistry stresses the relevance of the concept of 'waste', and encourages to pursue ways to minimize their production, without often evaluating its effects

in the surrounding ecosystems, whereas the emergy mindset comes from the knowledge that 'waste' is an exclusively human concept, a product of which we can study the costs of disposal and the effects on ecosystems if not treated appropriately. In green chemistry, we aim at an ideal "zero-waste" concept; in emergy, it is well known that the concept of "zero-waste" is not achievable due to thermodynamics constraints, so human systems should instead aim at reducing their waste production under a threshold determined by how much the environment can absorb and process.

These parallel vocabularies and concepts, which stem from the divergences in background discussed above, might confuse a reader who approaches both at the same time; nevertheless, the *scope is common*: evaluating the environmental implications of the "part" of the world we are studying. What this *'environmental implication'* is, is expressed by two deceitfully similar, though distinct in their hues: *'greenness'* and *'sustainability'*. Although several studies report 'greenness evaluations', it is still hard to find a common and "official" definition of 'greenness'. To create a common background, here we consider it as "the property of a process of adhering to the core essence and ethics of the 12 principles of green chemistry". Consider this definition, and the one of 'sustainability' built in the first chapter, we can see that they do not refer to exactly the same concepts - hence we can hypothesize some divergences in their implications. If 'greenness' is linked to green chemistry, we can reasonably expect that it embraces its paradigm too; this means that the reductionist, anthropocentric and user-side perspective also applies. Since the idea stems from the 12 principles, it refers exclusively to the concepts encompassed by the principles, and nothing outside of them. Overall, but not to be taken for granted, 'greenness' is a word that refers to chemistry, and tangentially to the related subjects such as chemical engineering, industrial chemical production and molecular design. On the other hand, 'sustainability' is a much broader term. The concept condenses the idea of "something that can indefinitely sustain itself over time", so in its core it does not have specific principles, or a particular area of application. It can encompass every branch of knowledge and any area of action of humankind, including the famous 'social' and 'economic' aspects of systems. The "basic" question "Will this system be able to sustain itself indefinitely over time?" can include questions like "Will the production system be optimized enough to guarantee the lowest possible environmental impact?", but also "Will the work environment favor employees' well-being and realization of their potential?" and "Will the business model benefit the surrounding community and the overall society?". If we compare the two terms, we will notice that while 'greenness' was born in a specific discipline (chemistry) and has now acquired a broader connotation in the non-scientific audience, 'sustainability' derives from an extremely generic principle that can be subsequently applied to any area or topic. From an epistemological point of view, 'greenness' is an inductive concept, whereas 'sustainability' is deductive. As Gonzales and Smith from EPA noted (2003), "The essence of Green Chemistry and Engineering is a focus on environmental effects. However, a larger focus is needed for chemistries and technologies to be used - namely, they must be sustainable".

In terms of methodological approach, both disciplines introduce a radical novelty in the field of environmental assessments: not only they take into account the downstream impacts of a system, derived from its action in the surrounding environment, but also the upstream requirements to make that system function. This is not as new in some human-dominated

fields as it is in chemistry: a recent work from Perosa et al. (2019) exploring the potential of integrated emergy and green chemistry use suggests that "The idea that the environmental impact evaluation of chemicals requires not only the downstream but also the upstream impact is relatively new, and it has much to do with the transgenerational character of the very concept of sustainability" (ibidem). This 'transgenerational' refers to a vision of sustainability closer to the sustainable development of the Brundtland report, seen as meeting "the needs of the present without compromising the ability of future generations to meet their own needs": the use of resources is as key to this goal as the environmental impacts, because both have direct consequences on future generations. In this sense, both green chemistry and emergy embrace the same ethics of environmental preservation with a forward-thinking perspective, not only accounting for the immediate impacts of systems, but also the future outcomes.

In conceiving the temporal and spatial dimensions though, the two disciplines adopt two distinct perspectives and operate at different scales. The goal of green chemistry is to "clean" chemistry, which means its concerns are focused on the aspects of systems that revolve around chemistry: type and quantity of reagents used, process efficiency, waste produced, energy consumption and nature of raw materials (whether fossil or from biomass) are the main aspects considered. How reagents are produced, where the energy used comes from (whether fossil or renewable) or the quantification of environmental impacts of a process are usually beyond the scope of green chemistry studies. On the contrary, the boundaries of systems in emergy analysis are not necessarily drawn around a "subject", but they are chosen depending on the scope of a study. Temporal and spatial limits can be as restricted as one reaction on a single lab bench, or as wide as the entire global production of a good - in both cases, emergy is usually not interested in the specifics of process efficiency, but aims at gaining the "bigger picture" of a system's overall sustainability. Emergy analysis usually takes into account all the aspects of a process mentioned above. One could say green chemistry has a "molecular" and "process-efficiency-based" approach, "dealing with the intrinsic rather than the circumstantial properties of a product or process" (Anastas and Lankey, 2000), whereas emergy adopts a macroscopic and "system-view-based" perspective, that does not aim at quantifying any property 'intrinsic' of a product, but of the route (hence, system) that produces it. Furthermore, green chemistry usually evaluates the 'greenness' of a process based on parameters which are specific and constant to each reaction; in emergy analyses, on the other hand, the sustainability of a system can drastically change by changing the system's boundaries. Thus the two disciplines deal with the same topic from separate temporal and spatial scales, so they can differ in results but provide complementary perspectives, aspect that will become more clear when dealing with green chemistry and emergy metrics. Meanwhile, the main features of the two languages are summarized in table 20.

	green chemistry	emergy analysis
	born from a 'father' and his relationship with nature	
	"problem-solving-oriented": born to solve an existing issue	"concept-oriented"/"learning-oriented": born for a thirst of knowledge
	currently reductionist, aims at holism	holistic
	starts from the current framework of chemistry	proposes a new theoretical approach
	founded on 12 principles	founded on a new corpus of knowledge
	focuses on chemistry	can be applied to virtually any system
	evaluates greenness	evaluates sustainability
	user-side perspective, anthropocentric	donor-side perspective, ecocentric
	talks about 'processes' and 'reactions'	talks about 'systems' and 'processes'
	evaluate both upstream and downstream impacts of systems	
	focuses on a molecular temporal scale	focuses on long-term temporal scale
	"process-efficiency-based"	"system-view-based"
	uses mostly mass-based metrics	uses emergy-based indicators
	"self-sustaining": metrics can be calculated solely from data of the present study	not "self-sustaining": analyses can often be performed only relying with previously gathered data
	easy-to-use and not data-intensive metrics	not easy-to-use and data-intensive indicators
	does not account for geobiosphere contribution	accounts for geobiosphere contribution

Table 20: main green chemistry and emergy analysis features - similarities and contrasts.

2. metrics: do they overlap?

In both disciplines, the results of the analyses are condensed in "simple" numbers. Green chemistry calls them 'metrics', emergy calls them 'indicators', but they have a similar scope: quantifying the level of greenness or sustainability of the system under study, respectively. However, the metrics adopted present some methodological and epistemological differences.

In a chemical reaction described in green chemistry terms, several variables are involved: green metrics are mass-based quantities, but the masses of reagents, products and waste cannot be summarized in one single flow or quantity, because they are compared *between* each other in metrics such as yield, E-factor, mass intensity, etc., and because their ratio can change by changing the reaction setup, thus making the metrics vary. In the field of emergy analysis, instead, there is only one main type of flow involved (emergy, expressed in sej), which is compared to "traditional" unit measures such as mass, energy or currency. From these comparisons, the main indicators previously described and many others are obtained, usually in the form of a ratio. If we do distinguish between different flows of emergy, we define them in terms of "renewable" versus "non renewable" and "local" versus "purchased", and not from one reagent to another. On one side, green metrics are highly "specific" to some

aspects of the process examined (eg atom economy for atom-use efficiency, E-factor for waste production) and they aim at quantifying the *process efficiency* of a reaction; conversely, emergy has more "generic" indicators that do not refer to flows of any particular chemical reagent or product, but that distinguish only emergy of 'inputs' and 'outputs' to quantify the overall sustainability of a system. Emergy indicators are still plenty and highly diversified, but they convey information on the same entire system, emphasizing its various facets (e.g. different spatial or temporal scales, upstream or downstream impacts, shortcomings from environmental, social or economic point of view).

A strong point in favor of green metrics is that they are specifically designed to evaluate chemical processes. Even though it might seem redundant, these tools can capture aspects of chemical processes that are not well understood with other assessment tools and help chemists redesign processes towards environmental amelioration. Emergy, instead, provides an evident example of this difficulty: since it was not born to analyze chemistry, it can provide suggestions for improving the functioning of a system through its leverage points, but it cannot evaluate whether a new process is "chemically more convenient" than a previous one. Furthermore, some EMA indicators cannot be calculated for exclusively human-dominated systems due to the lack of "immediate" renewable sources used on the level of the analysis. To correctly perform an emergy assessment, we need to adopt a "retrosynthetic" approach and analyze the wider system that embeds the one under study, to understand how the geobiosphere supports its functioning. If this retroanalysis cannot be performed, there is the risk of relying on subjective attribution to discern which inputs are renewable and which are not (as it was done in the estimation of the indicators for this case study). The same is true for the local-vs-nonlocal aspect of sources in emergy: without a thorough knowledge of the system, it is impossible to correctly attribute the sources to its geographical location with respect to the system. When dealing with modeled systems, as in this study, there is again the risk of relying on subjectivity when dealing with allocation uncertainties. The problem of attribution is then reflected on indicators calculations, whose values vary greatly depending on the ratio between renewables and nonrenewables, or local and nonlocal resources. This exposes emergy analysis to potential "greenwashing", if the calculation of indicators is not performed with the necessary transparency.

Another striking advantage of green metrics is that they are "simple to use and give instant feedback to a change to the process or the reaction pathway and can therefore easily be used for modelling or what-if analysis" (Tufvesson et al., 2013). They usually do not require prohibitive amounts of data and they are both immediate to calculate and to interpret. This is not the case for emergy analysis and indicators: performing this type of assessment implies relying on transformities obtained from previous studies, whose reliability and similarity to the system under study cannot be empirically verified. On several occasions, compromises need to be made due to the lack of data that describe precisely the conditions of a case study, surrendering to use the transformity of the "closest neighbor" or our process.

However, it must be noted that the most common green metrics, summarized in chapter 2, do not take into account all the 12 principles, but they can measure only the adherence of a system to some of them. In particular, principles 1 and 2 are well-captured by the E-factor, atom economy and (process) mass efficiency; the fifth is partially considered in the choice of solvents, which is still a qualitative parameter; the sixth is quantified by energy consumption metrics, but it does not express concern regarding the source of that energy (whether renewable or not); and the 9th is partly covered by the turnover number, that refers to the "useful life" of a catalyst. The others, unfortunately, do not have corresponding metrics

that can quantify whether a process respects those principles or not. In particular, one issue that has been raised is that the E-factor and waste-related metrics do not distinguish between different types of waste in terms of environmental impacts; a kg of sodium chloride "counts" the same as a kg of dioxins emitted. A proposed solution to this is the introduction of the environmental quotient but, relying on subjective ranking of the "hazard" of substances, cannot be considered an objective metric. Molecular design, risk assessment and toxicological studies can aid the evaluation of the greenness of a system from the "missing principles" perspective, but these methods are considerably more data-intensive, they require dedicated software and expertise and they are not immediately interpretable. For this reason, the main shortcoming of green metrics as a whole is the inability to capture the broad picture of the system and to provide one univocal answer to the core question: "Is this process sustainable?". By applying only 'some' of the 12 principles, as if they were independent goals and not a united framework, green metrics do not respect the underlying idea of the principles as an "integrated system of design" (Anastas and Eghbali, 2010). Emergy indicators, by contrast, descend from a different perspective, thus have somewhat opposite features: they are always the result of a complete emergy analysis, hence they are highly data-intensive and time consuming to calculate, but they provide a systemic view of the "state of art" sustainability. While green metrics originate from a reductionist approach, emergy indicators fully embody the holistic perspective of emergy. Some authors have highlighted an apparent inconsistency between emergy indicators and other metrics, but they attribute this to a contrasting underlying ethics, which sees emergy being ecocentric and other disciplines (green chemistry included) being still anthropocentric (Liu et al., 2016; Perosa et al., 2019). The reason for not calling green metrics 'holistic' is that they examine one facet at a time; the single metrics can be "summed" or aggregated together, but each of them still represents a single aspect of a process. In emergy analysis, indicators are the summary of the analysis of the entire system altogether, examined in its complexity. This is why we can define emergy as 'holistic' and green metrics as still 'reductionistic'. In this interpretation, green metrics at a molecular level are not comprehensive enough to adhere to the broader idea of green chemistry, which proposes to overcome the reductionist mindset. Some authors have recognized that greenness is a complex concept and needs holistic metrics, but this has not been extensively explored yet, due to a persisting reductionist mindset in chemistry research and education (Ribeiro and Machado, 2013).

Another lasting defectiveness of green chemistry evaluations is that calculations often overlook the mathematical and chemical relationships between metrics. One example is the determination of E-factor and Mass Index as two separate indicators. They are sometimes reported together as a presumed source of more information, but their mathematical relationship (E-factor=MI-1) shows that they are not independent, thus no further information is obtained by calculating both. Similarly, some metrics are not directly related to each other, but give rise to conflicting results that do not provide clear information on how to improve the system. One example is described in Ribeiro and Machado (2013), which studies the greenness of reactions with known stoichiometry through green metrics. The study notices that inconsistencies may occur between effects of different reaction parameters on the calculation of E-factor, Mass Index and Reaction Mass Efficiency: when the yield of a reaction increases, the first two metrics decrease and the third increases, with an improvement in the "greenness" according to these, but if a stoichiometric reagent excess is used to increase the conversion to products (common practice in chemistry), the first two metrics increase while the third decreases, with an overall decrease in "greenness". However,

with a stoichiometric reagent excess, the yield of the reaction might increase, which would make the three metrics increasing and decreasing in opposite directions. This case shows how some mass metrics can fail to provide univocal indications regarding improvement of "greenness", leaving the poor chemist alone to find a compromise between yield and reagent excess. As a further challenge, these results are not generalized, but must be verified for every case study, hence the metrics give no general indication on how to improve the efficiency of a process. The mathematical relationship between some green metrics and their inability to provide clear direction for improvements make these tools not optimal in the holistic evaluation of the overall performance of a chemical reaction. As the authors note, "rather than showing complexity, some of the relationships between indicators seem to highlight an interdependence between some indicators through simple algebra" (ibidem), dependence that is made explicit in their paper. And this is the best case scenario - when stoichiometry is known. For several reactions involving catalysts, such as fermentations or enzymatic reactions, stoichiometry is unknown or challenging to estimate. In these cases, conventional mass metrics simply cannot be applied, and the issue of how to quantify the greenness or sustainability of those systems remains.

To obviate the shortcomings of single green metrics, simple models and more nuanced "sustainability assessment" tools in the field of chemistry were developed, often consisting of a combination of the previously mentioned metrics. EcoScale, for instance, assesses the "quality of organic preparation" (Van Aken et al., 2006) through a score which depends on reaction components cost, safety, setup and methodologies. GREENSCOPE by EPA, instead, defines a process for its "current or potential level of sustainability" (Gonzales and Smith, 2003) by evaluating its performance in four areas (Efficiency, Energy, Environment, Economics), each of them quantified by a list of indicators and/or metrics. Green Star (Ribeiro et al., 2010) goes even further, using the power of visualization and proposing an assessment method which stems from the 12 principles of green chemistry, defining qualitative scores for each of them and representing these scores in a twelve-cornered star-shaped graph. Without going further with the number of examples (refreshing the methods seen in chapter two will suffice), we can note some similarities between these proposals. Although they start from different premises (EcoScale and Green Star as semi quantitative approaches, GREENSCOPE as a combination of existing metrics), they all adhere to the reductionist idea of studying a whole as a sum of several parts. The act of dividing a system's sustainability into several areas and/or indicators is a clear signal of this framework. A holistic approach, by contrast, consists of studying the same system in its entirety and investigating how the interactions between the parts shape its functioning. Thus, if we know that a (complex) system is not the sum of its parts, we can agree that its sustainability cannot be the sum of a few (or myriads) indicators.

It is also worth mentioning that these "integrated" assessments can create ambiguity in terms of information management and communication: the more these evaluations are "made complicated", trying to synthesize information in them to convey a higher level of complexity, the more they detach from the idea of transparency that should be considered essential in environmental assessment methods. Taking EcoScale as an example, a chemical process with a score of, say, 75, could have excellent workup and purification procedures but highly expensive and hazardous reagents, or the opposite - or it could have mediocre performance in all these areas. By looking at the mere score, nothing is said about the practical features of a process. A non-transparent indicator is a useless indicator, because it does not convey the information that it claims to provide, since that information is

not accessible to the reader. Conversely, emergy indicators are usually easier to interpret. Since they are usually not the combination of other indicators, their value immediately conveys information about a system. If a system presents a high Environmental Loading Ratio, we know its impact on the environment is non negligible, and vice versa. Of course, as all the ratios, the main emergy indicators (ELR, EYR, ESI) do not provide information regarding the absolute value of the quantities involved (a system with a certain ELR might have high impacts and high total emergy flow, or low impacts and low total emergy flow), but they clearly display accessible information to answer the overall question: "Is this process sustainable?". The drawback of these indicators is that they cannot provide precise direction regarding where to act to improve process efficiency. If by looking at green metrics finding ameliorations is sufficiently intuitive (e.g. reducing E-factor, increasing Reaction Mass Efficiency), identifying leverage points in emergy requires looking at the system as a whole. As a first step, we can examine the UEVs of inputs and outputs as a rough measure of the efficiency of the system, but in-depth understanding can be gained only by exploring the relationship between flows and processes inside the system. This introduces a further differentiation between green chemistry and emergy analysis: while green metrics are attributes of systems (as well as most emergy indicators), UEVs are values that refer to each specific substance, good or service: they summarize the emergy that the geobiosphere invested to produce them, hence they are assigned to and specific to each item. Even a chemical reaction with a unique equation on paper and same products can lead to different UEVs in emergy terms, because emergy depends on the process route followed, hence even just a change in the quantity of one reagent, or a variation of temperature, will change the UEV of the product.

As a last point of divergence of the two disciplines, the temporal and spatial scales at which they operate are fundamentally different. Recalling what was mentioned for their epistemologies, green chemistry is a 'molecular' and 'process-based' approach, whereas emergy has a 'macroscopic' and 'system-based' perspective. The first examines exclusively the system of chemical production, the latter also explores the levels immediately above and immediately below the system under study, investigating how it interacts with the macrosystem in which it is embedded. Furthermore, in most of the literature taken into consideration for the present work, green metrics are calculated for laboratory experiments, not yet for industrial scale productions, for which have specifically tailored reaction setups. Emergy analyses, by contrast, have been performed on a variety of scales, from a single animal shelter (Gonella et al., 2019) to entire agricultural systems (Agostinho and Ortega, 2012), societal sectors or even nations (Ulgiati et al., 1994). In this field, the sustainability of a system can drastically vary with the boundaries we set (Spagnolo et al., 2020). For green metrics instead, this is true for some instances and not for others: on one side, metrics like atom economy, yield and carbon efficiency are constant for a fixed reaction; on the other, quantities such as E-factor and solvent intensity may strongly depend on the boundaries of the system we consider, for instance whether we account for emissions and wastewater or not, or whether we include solvents to pre-purification of reagents or not. It is worth reminding that green metrics cannot account for the non-material investments that sustain the system, such as human labor and environmental services, which instead are accounted for in emergy analysis. In that sense, green chemistry evaluations remain defective regarding the geobiosphere contribution. In both disciplines, all green metrics and emergy indicators can be calculated both for the overall process and for single steps, to better identify potential areas of improvement to increase greenness or sustainability.

Numerically speaking, this case study shows that green metrics and emergy indicators can at times appear to provide conflicting results in terms of sustainability of a system. While green metrics favor the alternative route for lactic acid production, emergy indicators do not present striking differences between the two processes, in fact indicating that this alternative route is slightly more emergy-intensive. This does not necessarily mean that the route is less sustainable or not viable for implementation, since the higher transformity of the resulting output might also be linked to a higher efficiency in the use of resources, but the result invites a more careful interpretation before expressing a net conclusion.

In virtue of these differences, emergy indicators and green chemistry metrics can be used concurrently to provide different but complementary information to the field of environmental assessment. In so doing, they both constitute an invaluable tool to provide advice and direct future long-term development of sustainable systems.

In recent years, researchers have tried to "merge" several evaluation tools to create integrated assessment methods, dealing with several opportunities and challenges - but we will see this in a few paragraphs.

3. in scientific research

Several academic works have dealt with the improvement of the two techniques towards a widespread adoption in institutions and business but, to the best of our knowledge, there have been no successful attempts to standardize and adopt green chemistry or emergy analysis in the national institutions frameworks. But if these languages are so promising and revolutionary, why haven't we yet adopted both?

Generally, humans seem to be "naturally" averse to change, especially if it involves the re-discussion of their entire theoretical framework, habits or way of doing things. In this regard, the application of both disciplines demand a profound revision of our current paradigm, thus requiring a collective self-analysis that we are not necessarily willing to accept. After this challenging change of mindset, performing both analyses as greenness and sustainability assessments requires a considerable amount of information, hence research work and data collection. In emergy, the process of calculating UEVs is often lengthy and expensive in terms of time and data; in green chemistry, going beyond the calculation of the simplest metrics and adhering to the 12 principles as an 'integrated system of design', the evaluation of the eco- and human toxicity of chemicals is needed. This latter is performed through toxicological analysis, which also requires substantial information and tools, and deals with the study of complex systems of which we do not have perfect knowledge, hence it is still not "exact science". Another common critique moved to green chemistry and emergy analysis is that both lack a degree of soundness and standardization typical of more widely established assessment methods. For green chemistry, this is due to the fact that by excluding or including some inputs the calculation of the same metric can change, as seen in the previous chapter. For emergy analysis, some methodological issues include low accuracy, reproducibility and completeness (Rugani and Benedetto, 2012; Raugei et al., 2014). In both cases, the lack of data and soundness can be overcome by integrating other measurements and tools in their practice, such as in silico toxicology tests for green chemistry (Maertens and Plugge, 2017) and LCA databases and softwares for emergy analysis. More specifically, each discipline presents its own challenges, both from a theoretical and a practical point of view, hence it deserves a separate discussion.

In the field of emergy analysis, some of the theoretical assumptions of discipline create skepticism among reductionists scientists: some reject the validity of the maximum empower principle as a fourth law of thermodynamics (Sciubba, 2011); some objections have been made to the concept of energy quality that involves a "difference" in the value of different forms of energy: "The idea that a calorie of sunlight is not equivalent to a calorie of fossil fuel, or electricity strikes many as preposterous, since a calorie is a calorie is a calorie" (Brown and Ulgiati, 2004); some ostracize the theory as a whole because it "does not appear to conform to first law accounting principles" (ibidem) or because they believe "it is impossible to quantify the amount of sunlight that is required to produce a quantity of oil" (ibidem). Last but not least, a methodological objection is about how emergy deals with uncertainty of data, pointing at the lack of statistical analysis. To this last dissent, emergy analysts respond with the same sensitivity analysis used in the previous chapter, that evaluates how results change by varying each input of a certain quantity. The other doubts, theoretical rather than practical, seem to stem from a misconception or misunderstanding of emergy principles, and they appear to be possible to bridge only with further dialogue between emergy practitioners and skeptics. Overall, it is worth reminding that, to the best of our knowledge, emergy analysis is the only environmental assessment method that can account for the energy invested by the geobiosphere, which provides the ecosystem services which are essential for human life and development; thus, having a method that account for both natural and anthropogenic contributions to systems with some uncertainty seems still better than having none at all, or having statistically sound methods that leave out an essential component of resource investment. To resolve some of these objections, more dialogue needs to be fostered between practitioners of different disciplines.

To obviate the lack of data and improve the soundness of the disciplines, it is common use to integrate these languages with LCA, a multicriteria assessment tool which is now standardized and widely accepted, both in research and business practice.

In the field of green chemistry, a few works have endorsed the synergistic use of these two approaches. Lankey and Anastas (2002) claim that "To meet the goals of sustainability and to enable industrial ecology, green chemistry and engineering *needs* to be studied from a life-cycle perspective." (italic added). Tufvesson et al. (2013) propose the application of LCA to potential green chemistry syntheses that lack a quantitative evaluation. A full-scale LCA is too time-consuming at the design stage, both for its comprehensive nature and for lack of inventory data, but adopting a few key life cycle principles can help quantifying potential benefits of an alternative route or product before the expenditure of testing syntheses and building facilities. The paper presents a review of several LCA studies on chemicals and chemical processes, and proposes some key parameters for an early-stage LCA application in chemistry. Reeb et al. (2013) propose an integration of green chemistry in combinatorial chemistry, a "parallel reaction assay methodology" to optimize reaction conditions, in a discipline called combinatorial green chemistry, to be merged with LCA and obtain a comprehensive assessment tool. In the same years, Kralisch et al. (2014) offer a compendium of LCA principles for green chemistry practitioners, to ease the integrated adoption of these two approaches, whereas Gustafsson and Börjesson (2006) provide an example of this joint assessment applied to a case study. Eckelman (2016) also highlights that the use of life cycle impacts assessments can also elucidate the toxicological aspect of chemical reactions that mass-based metrics cannot grasp. Not only LCA can be applied to green chemistry to provide more robustness, but the latter can also bring benefits to the life cycle philosophy: Anastas and Lankey (2000) specify that green chemistry brings "life cycle

innovation" in all the stages of a product life cycle, because by evaluating and modifying the intrinsic structure of the molecules we design we change their hazardousness over their all useful life.

In emergy analysis, meanwhile, several practitioners have been proposing the integration of emergy and LCA to obviate the shortcomings of the first. As mentioned above and in chapter three, emergy has been criticized both for a series of theoretical assumptions and for methodological weaknesses, among which its low accuracy and lack of standardization, that make it a less reliable tool for wide scale adoption. Wang et al. (2020) underlines how both approaches share "common attributes in the evaluation processes and research field" but that they "focus on different aspects of macrocosms and microcosms". With the possibility of accounting for geobiosphere inputs by emergy analysis and the environmental impacts assessment of LCA, an integrated tool would benefit from expanded systems boundaries, to include the contribution of the environment, and the standardization typical of LCA. The result that several scientists advocate for is the creation of a comprehensive assessment method that can account for the provision of environmental support, where emergy analysis is used as a "valuable complement, rather than an alternative, to existing life cycle impact assessment metrics" (Raugei et al., 2014; see also Rugani and Benedetto, 2012; Wang et al., 2020).

Overall, both emergy and green chemistry can bring benefit to every stage of the life cycle of products, analyzing their whole production system together with their single reaction steps. Starting from the calculation of metrics and indicators to identify the main areas of improvement, green chemistry explores the potential of different products and synthetic routes, whereas emergy mostly explores the overall impact of the system in space and time, addressing the leverage points and the weaknesses related to the general systemic performance. Both disciplines provide information and advice that stem from the same ethical principles, hence an integrated use of both languages can be proposed: the idea that "product that requires the largest input of resources should also be the most durable and the most easily reusable" (Anastas and Lankey, 2000) is both connected to green chemistry and how to design such a product, and to emergy, since the largest the input of resources, the largest the emergy involved the process. There are certainly relevant methodological differences and challenges to this integration, but the potential advantages are worth a try. To reach this goal, it is key to identify the common ground between the two approaches and adapt their features to foster collaboration. Perosa et al. (2019) claim that "Chemists are most of all interested in applying emergy-based approaches on large-scale production systems, or systems for which the use of chemicals is relevant, like for example in the tannery industry and in the agricultural sector". In the present case study, we have experienced some of the potential issues that green chemists and emergy practitioners might encounter when trying to collaborate with each other, but we have also highlighted how they can be overcome, relying on the fundamental alignment of the two theories in their ethical principles and goals. Green chemistry was not born from a holistic mindset but it aims at reaching this wide-range understanding; on the other side emergy analysis cannot effectively study systems which are far removed from ecosystems functioning yet, due to the difficulties in identifying renewable sources, but fostering closer cooperation between these two approaches is promising and desirable. We endorse the vision of green chemistry as a "multistakeholder community" (Iles and Mulvihill, 2012) and we claim emergy can aid building it.

4. in business practice

In the field of green chemistry, Tickner and Becker (2016) reports the results of a research of the Green Chemistry and Commerce Council (GC3), a "cross sectoral business to business network of firms working collaboratively to accelerate green chemistry", which has identified specific barriers to the mainstream adoption of green chemistry (Fennelly & Associates, 2015; Trucost, 2015): "(1) the complexity of global supply chains and their established infrastructures, (2) the costs and time to scale to adopt new technologies, (3) the incumbency of existing technologies that are cost-effective, high performing and familiar (but may be problematic environmentally), (4) concerns about the risks involved in moving to green chemistry solutions (performance, process changes, material incompatibility or costs of recertification and potential for substitutes to be later designated chemicals of concern); and (5) limited investment, incentives, education, and metrics" (Tickner and Becker, 2016). Coming from a business-oriented institution, these results refer to the adoption of green chemistry not only as an epistemological approach, but most importantly as a business practice. Several of these barriers are not concerning chemistry as such, but rather to the technology involved and its application in the wider context of the economy. Hence, the issue does not appear to be strictly scientific -also proven by the increasing interest in green chemistry research in the last decades-; it seems to be rather related to a reluctance of the productive sector to shift to new solutions. The same work (Tickner and Becker, 2016) also reports that the GC3 created an agenda to address these barriers, which "identifies five broad strategies to accelerate green chemistry innovation". These include (1) Enhance market dynamics, to facilitate a market shift towards widespread adoption of green chemistry; (2) Support smart policies, "designing and advocating for innovative state and federal policies that can effectively support the supply of and demand for green chemistry solutions", making the discipline part of the public institutions framework; (3) foster collaboration, creating partnerships among producers, suppliers and consumers; (4) Inform the marketplace, disseminating information and opportunities in the green chemistry area; and (5) track progress, designing more effective metrics and ensure periodic reports on progress achieved.

Another threat to the efficacy of green chemistry adoption is the distortion of its intent on the market: greenwashing. Sustainability is now a rapidly growing trend not only in science but also on the market, and this leads brands to "surf the green wave" trying to capitalize it. Since green metrics and environmental assessments are not so widespread in business practice yet, the risk of seeing claims of "greenness" referring to vague improvements in the production chain is very high. Moreover, the evaluation of production processes with "partial" indicators (e.g. evaluating only waste generation, or only energy consumption) and the adoption of comprehensive, but not explicitly specified, metrics can lead to opacity in firms evaluations. As seen with the case of Novartis, firms may feel encouraged to propose their own indices to evaluate their own performance to avoid comparisons with other brands, producing assessments that do not really favor the adoption of the most sustainable practices. In this context, mainstreaming green chemistry among researchers, businesses and institutions can present two further "emotional" challenges: the skepticism towards the idea of 'green' as "greenwashing", related to not-so-well specified sustainability claims, and the resistance towards systemic analises, where 'holistic' might still be seen as a vaguely-spiritual view from strictly reductionists chemists. In the process of comparing two languages, it is important to evaluate not only their syntax, but also the meaning and

implications of their words. Ideally, a scientific language should be free from ambiguities and allow to determine clear and objective results. The possibility of generating opacity, misunderstandings or, in the worst case, fraud, is an aspect that must be carefully examined when expressing considerations about a language. Generally speaking, it does not take much, alas, to turn a "deeper shade of green" into a "thicker layer of greenwashing".

Even though at this stage we see this risk only for green chemistry, this does not mean that emergy analysis is safe from it. The fact that there are no documented cases of "emergy-washing" is likely due to the fact that this discipline does not have any makir relevance on the market yet, since it is not widely adopted as a sustainability assessment method for firms. If emergy was as widespread in the business sector as green chemistry, two possible scenarios might unfold: in the most optimistic, this language would prove to be sound from "washing", since its basic indicators are used in virtually all emergy studies and are extremely transparent in their formulation; in the least naive picture, there could be the risk of seeing the same mis-representation of results that we see in green chemistry, by exploiting the uncertainty in "allocation" as mentioned in the previous section or creating new less transparent indicators or "branded" indicators with little correlation with each other, where both would hinder the possibility of comparisons between different brands.

Besides the formalization of principles or indicators, a lot of humans and human activities still do not follow the basic idea of respecting the environment that sustains our civilization, and there are plenty of possible reasons for this.

One possible explanation in the lack of widespread adoption of these two disciplines can be seeked in the current economic mindset, which is deficient in long-term planning: Tucker (2010) asserts that "In the short term, incentive for scientific superiority has been removed, potentially resulting in excess pollution, perpetuation of inferior methodology, and poor worker safety". In the last decades, especially in these "interesting times", humanity has struggled to face global challenges with a proactive approach, "reacting" to events rather than "acting" to shape the world we want. The comparison between climate change and the current pandemic is a hint in this direction: despite decades of warnings and data, our society has not been able to develop long-term solutions that ensure the well-being of the majority of the population; nevertheless, when an unforeseen emergency arises (unforeseen for most people, at least), humanity has been capable of reacting quickly to seek solutions. Perhaps the evolutionary traits of our brains that "keep us alive" are not meant to develop long-term plans. Whatever the intertwine of causes might be, humans often tend to prefer instant gratification to a sacrifice for a better future, and this is visible in realities that privilege profit over the sustainability of their activities. In the same paper, Tucker suggests that "The key component in a path to chemical business superiority, environmental responsibility, and long-term economic sustainability is leadership belief and support in the continual evolution toward scientific excellence" (ibidem). What we need, according to the author, are people who are capable of spreading a new vision and guiding people towards its development. And these people need to bring about ideas that the world of scientific research is already familiar with, such as industrial ecology, which aims at substituting production chains with production 'ecosystems' where the waste and residual heat of one plant becomes raw material and energy for another.

We must consider, though, that not everyone lives in the scientific community. Most people are simply not that acquainted with the world of science, thus, not even with its concepts. On the business side, it is not hard to see this, given that anyone can start a company regardless of their educational background. Tucker also highlights that "Corporate leaders are often

trained in disciplines of business, law, or economics, but rarely hail from scientific backgrounds. The result appears to be a leadership class that does not fully trust the scientific method" (ibidem). On the other hand, scientists might have underestimated the importance of dissemination and communication of their job. Even the most cutting-edge research will not make it out of the "ivory tower" if no one makes the effort of telling us. And given that even scientists are subjected to the competition for fundings, striving towards strictly academic excellence, it is understandable that no one "has time" for communication to non-specialists. However, the solution is embedded in the problem. The scientific community needs to increase their efforts to communicate to an audience that has little background in their sector, and the audience needs to make an effort to listen (and follow the advice given).

Last, but sadly not least, another major deterrent to the massive change we need in industrial production is due to one simple matter: cost. Fostering research and innovation, and subsequently deploying the newly obtained technology, requires substantial investment. When nations are led by forward-thinking leaders, public fundings can guarantee the possibility of innovating production sectors, but otherwise it is often difficult for private enterprises to sustain the initial cost and risk of adopting a new technology. And even in the case a company does succeed in implementing a new, greener production method, it is not to be taken for granted that it will be able to continue for a sufficiently long time to compensate for the initial investment (Sanderson, 2011). In the current economic paradigm, businesses are forced to compete in a challenge for "who is cheaper", and the ones that cannot guarantee an affordable price or a higher convenience with their products are rapidly cut off of the market. Tucker (2010) claims that globalization is "quickly eroding incentives for scientific evolution through the propagation of cost-cutting business models". To stop this vicious cycle, regulatory agencies can play a game-changing role: by adopting policies that favor the deployment of 'green' technology, more fundings can be available both for research and for more sustainable business practices to bridge the gap between the industry we have now and the industry that we want for our future. As for the previous issues, this is also a matter of leadership. We need forward-thinking individuals to start promoting the systemic change that is needed. To convince the skepticals, the same author leaves a point to reflect on: philosophically, "there is less risk of harm in pursuing positive scientific evolutionary paths through innovation than in propagation of paths that are ultimately unsustainable" (ibidem).

5. in communication

If we stopped somebody on a street and asked them "What is green chemistry?", we could reasonably expect that we would not get a precise definition, but that they would have a basic "grasp" of the concept. It is a "cleaner" chemistry, a more "eco-friendly" and less polluting way of producing. If someone says "emergy", instead, we can be sure that the same official and complete definition is reported in every book and paper on the topic, but statistically speaking no one will know what you are talking about. Considering the doom environmental circumstances we all live in, and the increasing collective awareness of this uncertainty, it is of no surprise that the notion of green chemistry appears intuitive to the wide audience. As stated in the first chapter, words like "green" or "greenness" are in our everyday vocabulary, even though not in a strictly scientific sense. On the other hand, it feels arduous that anyone other than Odum could have created the idea of emergy and designed a

framework of concepts that are so markedly far from the average human daily life. In simple terms, we might dare to say that emergy is "less popular" than green chemistry.

Why is this? The fact cannot be explained by looking at the "age" of the disciplines, since emergy analysis was born almost ten years before green chemistry. One first possible explanation is that the concept of emergy is less "intuitive" of that of green chemistry. If anyone has ever tried explaining it to a person with no scientific background, they will probably know the trouble: we have to mention "available energy", to clarify the concept of "work", to explain what expressing different quantities "in the same unit measure" and so on. Even the term "emergy" itself does not make explicit the basic meaning, let alone the deep implications and revolutionary potential of this language. The name 'green chemistry', instead, is much more "fortunate": all demographics have an intuitive idea of 'chemistry', and given the current marketing trends most people nowadays have a heuristic idea of 'green' (in an environmental/sustainability context); hence, the association between the two is a "ready made". The term 'green chemistry' is self explanatory, whereas 'emergy' is not.

But this marked difference in "popularity" cannot be reduced to this; in principle, no matter how obscure a concept can be, if someone explains it to you in sufficiently clear words, you will eventually understand it. Thus, if it is not for the "difficulty" of the concept, it might be due to the number of people who currently know or deal with the concepts. This, in turn, is likely to be impacted by the "attitude" of each discipline towards the non-scientific world. Being born as an attempt of solution to an existing pollution problem, green chemistry practitioners have probably always known that, in order to see their language adopted, they had to "advertise" or "sell" their perspective to potential users. In the attempt of convincing people of the potential of this approach, green chemistry has probably "spoken to" business and users more than emergy does. This is facilitated by its 'user-side' perspective, which is the same underlying framework adopted by economics and marketing in which the value of a product is still determined by the perceived utility on the market. Emergy's 'donor-side' perspective, instead, is hard to "sell", since it does not rely on an anthropocentric view in which human perception is the key to value creation. And we cannot even strip this perspective away from emergy, since it has been intrinsic in the theoretical framework of emergy since the beginning. User-side perspectives are more easily "marketizable", because they appeal to the same principles of "utility in the eyes of the beholder".

Green chemistry also has the advantage of requiring less "self-analysis": conceived as an operational tool, born to solve a problem, this approach is mostly concerned with being pragmatic and easily adoptable by industry and institutions. Emergy, on the other hand, conveys a different way to conceive and understand the world (and this seems to be also the position of many in literature), thus adopting this philosophy requires the rediscussion of our own principles. As in a little copernican revolution, every individual approaching emergy is forced to realize that they are not the center of the world, and that humans are just another of the millions of species that "evolved equal" on this planet. Without even exploring the clash that this paradigm has with most religions, undergoing such a profound change in our inner perception appears difficult.

Overall, in the way they "developed after" their creators, the two languages seem to have taken different paths: while green chemistry has "diffused" more towards industries, institutions, education and communication, emergy appears more focused on solving its own internal methodological issues, rather than proposing itself (or "selling itself"?) to the world. While emergy was going in depth towards the roots of the secrets of the existing nature and systems, green chemistry was "spreading out" on the surface - one was looking

inward whereas the other was looking outward. In an interview, Anastas said that the main avenue for propelling green chemistry is exposing more people to it (Greenwire, New York Times, 2011). Practitioners of this discipline have surely taken up his guidance, whereas emergy seems to still have in its Biennial its main locus of aggregation.

6. in education

No matter what the philosophy of a discipline is, it still needs to be taught and learnt in order to be preserved, widened and improved. In the current society, schools and universities are still the major custodian of knowledge and its dissemination. So, now that we have approached the basics of both disciplines, if we wanted to get more acquainted with them, what could we do?

A simple google research of the keywords "green chemistry university" shows several undergraduate and graduate programs that include courses in green chemistry, some of them being even centered around this concept. The American Chemical Society provides a list of academic programs that involve this subject (ACS). Emergy, instead, is much less widespread in education. With the same keywords ("emergy university"), no immediate results appear except the Centre of Environmental Policy at University of Florida, where the emergy theory was born. Searching "emergy courses" does not provide much more information - only a couple short courses held in the past appear, with no references or online content. Unfortunately, even the Emergy Society does not provide resources for practitioners or curious-minded people. This shows another reason for the wider "popularity" of green chemistry: there are more people learning it. There is only one trivial solution to this problem - teaching more. Not only providing undergraduate and graduate courses would benefit students' understanding of complex systems and their approach to other subjects, but creating a public body of knowledge on this topic would provide the community with an easily accessible "return on investment" for publicly funded research. Surely, emergy practitioners would have to face several confused expressions in a classroom, several apparently "dummy" questions and all the compromises between rigor and accessibility typical of science communication, but the effort is necessary to help the discipline grow and find applications. After all, Odum himself believed that information needs to circulate in a system through communication, teaching and discussion in order to be preserved from degradation in time.

Given this gap between the adoption of green chemistry and emergy in education, where again the former is more "popular" than the latter, how to bridge it? Emergy analysis is not a discipline useful only for its own sake. Its groundbreaking epistemological vision facilitates the understanding of many more disciplines and can open new paths of reasoning, learning and research. Perosa et al. (2019) suggest two possible ways to realize this potential: "Emergy analysis can be used in top-down educational approaches, for example, in teaching the environmental, toxicological, health, and sustainability issues that are at the basis of the green chemistry approach. On the other hand, emergy analysis is also well-suited for bottom-up paths, where one considers first the emergy of chemicals, and then the conceptual value and the use and outcomes of this determination". They propose two educational approaches for each type of institution, and we here advocate further consideration of these proposals to foster the diffusion of a holistic view in education.

7. sustainability framework

We have now reached the last mile of this comparative marathon. We have explored philosophies, potential, application and metrics of green chemistry and emergy, so only one main question is still left to answer: how do these languages relate to the overarching sustainability principles? In the first chapter, the concept of sustainability was restated, founded on two basic principles: the non-overexploitation of renewable resources (with consequent non-overproduction of waste) and the non-depletion of nonrenewables. Do green chemistry and emergy respect these imperatives?

In the world of green chemistry, we have highlighted how metrics cannot encompass all the complexity that lies inside the twelve principles. But what about the principles themselves? It was surely in Anastas and Warner's intention to design a set of rules that could guide the development of a sustainable version of chemistry, keeping in mind the complexity of sustainability. Their goal was to provide a corpus of principles to consider as a whole, thus the formulation of the twelve principles fully embraces the ideal of a holistic sustainability. On the other hand, if holism is rooted in the belief that the whole is not merely the sum of its parts, we cannot really imagine to "divide" sustainability in pieces and express for each one a rule - but the twelve principles achieve the best result possible. In trying to convey a systemic vision to a reductionist audience, they express each principle with clarity encompassing all the main aspects of environmental sustainability in chemistry. They do not dive into the social and economic aspects of it, since the human-nature relationship is too complex to be contained in twelve points, but their clear boundaries and concision contribute to make them an effective communication tool. They have made, and still are making, the difference in bringing about a change in paradigm in the field of chemistry.

Emergy, on its side, was born from different axioms but achieves similar results, being founded on the same holistic view that is key in our definition of sustainability. Not only its theoretical framework is based on this very principle, but also its indicators are the expression of this perspective: the act of unifying all the contributions acting on a system in one unit measure reflects the idea of unifying systems analysis, and all the main indicators stem from the difference between renewable and nonrenewable, local and nonlocal resources, and how each system utilizes them. This discipline also evaluates the environmental aspect of sustainability, but the study can be widened to explore how flows of information and money can influence the economic and social side of systems.

Being a molecular-scale assessment, green chemistry and its metrics can bring benefit "from the inside" of the chemistry of a process, by suggesting alternative synthetic routes or even alternative substances for the same scope. Emergy cannot propose alternative products, since it does not often enter into the details of chemistry or engineering, but it can evaluate whether a new process is more sustainable than a previous, and it suggests how to enhance the overall long-term sustainability of a system by acting on a system's leverage points. Green chemistry is much more rooted in the engineering of chemical processes, while emergy is more based on the two sustainability principles. A possible integrated application of the two disciplines is to use green chemistry to improve the engineering of a process, while keeping an eye on its emergy analysis for a systemic framework.

Our exploration of these two disciplines can now reach a conclusion: despite the differences in their birth and development, despite their divergence in the methods, both green chemistry and emergy analysis aim at the same overarching goal: aid the creation of a human world that is more respectful of and in harmony with the environment that supports it.

Chapter 6 - Conclusion

1. Steps

During our journey in the present work we touched several aspects of sustainability to bring a contribution to the field of sustainability assessment methods by comparing two of these languages: green chemistry and emergy analysis.

Setting off, we restated the fundamental challenge of climate change that humanity has created with its actions and we summarized its state of art, offering sustainability as the solution. In the first leg, we established the common ground needed to develop an operational solution: we refreshed our definition of sustainability as based on two key principles and we reversed the mainstream vision of the topic, highlighting the vital role of the environment to sustain our society and economy. We introduced the concept of greenness and the field of environmental assessment methodologies to provide some context to the present work.

After this warm up, we dived into the world of green chemistry to discover its birth, its principles and goals and how it is related to our life experience. Not a new branch of science, this discipline aims at changing the way chemistry is thought and enacted. We explored the most famous metrics and encountered some examples of more comprehensive green chemistry evaluation methods, together with some of the strategies that green chemistry practitioners adopted to spread them. Last, we examined potential and risks of using green metrics in business practice, key factor for "greening" firms but prone to be distorted into a marketing tool.

Then we devoted our attention to the emergy side of the journey. We flew over its history and investigated the mysteries behind its apparently obscure definition, to uncover its potential in widening our understanding of the world. We got acquainted with its symbols, algebra, objectives, methodology and indicators, highlighting the novelty of its holistic approach to sustainability, and we compared this theory to the more widespread LCA approach, to understand their similarities, differences and potential integration.

In the following chapter, we reached the core of this work. The case study that allows us to compare the two disciplines was introduced, starting from a paper that proposes a new lactic acid production route (alt-LA) that is presented as more sustainable than the conventional one (conv-LA). To confirm or reject this claim, we performed an emergy assessment on the two processes, starting from their diagrams, explaining their functioning, and ending with the calculation of the main emergy indicators for both cases. We found that the transformities of lactic acid produced with the alternative route and with the conventional route were 2,84E+14 sej/kg and 1,42E+14 sej/kg, respectively (with L&S). To arrive at this result we estimated the transformities (with L&S) of crude glycerol (8,21E+10 sej/kg and 2,36E+06 sej/J), glucose syrup (2,30E+12 sej/kg), butanol from petrochemical sources (9,44E+13 sej/kg) and from biomass (1,06E+14 sej/kg), calcium hydroxide (7,87E+13 sej/kg) and a generic zeolite catalyst (5,65E+14 sej/kg); we also described the procedure to calculate transformities of steam and electricity depending on a country's energy mix. Without quantitative information on the extended system supporting glycerol and glucose, we estimated a few emergy indicators treating fermentation materials (glycerol,

glucose, nutrients, bacteria) as renewable sources and treating all the nonrenewable inputs as local except electricity, G&M and L&S, obtaining EYR=1,98, ELR=0,969, ESI=2,05, EIR=0,377, EuSI=0,488 (for alt-LA) and EYR=3,52, ELR=3,42, ESI=1,03, EIR=0,872, EuSI=0,972 (for conv-LA). Both lactic acid specific emergies and indicators show that there is no marked difference between the two systems in terms of sustainability. Transformities highlight that, in case of alt-LA, the raw material (glycerol) is less 'expensive' emergy-wise, but the production process make the final product more 'expensive' than the conv-LA counterpart; on the contrary, glucose has a much higher specific emergy but the final product of the conv-LA route requires a slightly lower emergy investment. Indicators show that the alt-LA process has a lower emergy yield and a lower environmental load, resulting in a higher sustainability index; the opposite is true for the conv-LA route. The Emergy Unsustainability Index indicates that the conv-LA process is more unsustainable than the alt-LA, but overall further analysis is required to draw definitive conclusions. For the same two production routes we calculated the most widespread green metrics. For alt-LA we obtained Y%=83,70%, AE=96,74%, RME=51,02% (excluding cooling water, solvents, steam and air), MI=20,07 (excluding cooling water, steam and air) and E-factor=19,07 (excluding cooling water, steam and air) and E-factor=1,032 (excluding also process water); for conv-LA the results are Y%=75,24%, AE=30,27%, RME=0,2611% (excluding cooling water and solvents), MI=18,65 (excluding cooling water and water for steam generation), E-factor=17,65 (excluding cooling water and water for steam generation) and E-factor=2,85 (excluding also process water). We also evaluated the EcoScale score, obtaining 39,6 for conv-LA and values between 30,85 and 45,85 for alt-LA, whose score was estimated with different hypotheses. Although yield and atom economy clearly favor the alt-LA process in terms of greenness, the other metrics give less straightforward results; in particular, the values of RME, MI and E-factor greatly vary depending on what components are included or excluded from the calculation. The E-factors of the two processes are in the same order of magnitude, but this is largely due to the considerable amount of process water needed for the fermentation processes (14,8 kg for alt-LA and 18,04 kg for conv-LA), which makes the E-factors calculating excluding process water considerably lower. From these values, we notice that the alt-LA process is considerably less impactful in terms of waste generated (1,032 kg per kg alt-LA against 2,85 kg per kg conv-LA). Overall, the two processes are characterized by better performances in some areas and worse in others, thus these green metrics are not sufficient to provide a full picture to make a definitive decision about which of the routes is greener. We noted that the calculation of these metrics and indicators is not always smooth, and highlighted their promising and problematic sides.

The in-depth comparison between the two languages was kept for the last stage. After learning about their history, methods and goals we developed some reflections on their underlying philosophies, emphasizing both similarities and divergences. Green chemistry and emergy analysis are definitely coming from different backgrounds, but they are moving in the same direction. Their metrics and indicators are also markedly different, but they do not stem from opposite visions. We also explored their state of art in research, business practice, communication and education, scratching the surface of their progress and potential. Given the enrichment that they can both provide to the world of sustainability assessments, we hope to see an integrated application of the two disciplines to create a holistic environmental assessment method, deepen our understanding of chemical systems and facilitate their amelioration towards a truly sustainable chemistry.

2. Lesson learnt and further research

Goal of this chapter is to draw some conclusions. Hence, the question to answer is the following: What have we learnt from this experience?

The lactic acid case study teaches us that evaluating sustainability is not so simple or straightforward as someone might want us to think. It goes well beyond saving some material or energy, recycling outputs or improving the chemistry of a reaction - it encompasses this and more. Ideally, it means measuring quantitatively whether a process respects the two key sustainability principles or not, but building tools for this goal is still a work in progress. Examining the green metrics and emergy indicators obtained in this study, we came across some methodological ambiguities in the calculation of these quantities, that can be clarified by establishing a more transparent and standardized definition of green metrics and by broadening the boundaries of emergy analysis. On the other hand, we discovered that the two languages provide different information on the same system, since they stem from contrasting perspectives on the world. This shall not discourage us from adopting them together, because they still aim at the same goal.

With its limited time span, this work could only focus on exploring one specific case study, choosing one experimental setup among the several proposed in the reference paper, and setting limits on the breadth of the research both in the green chemistry and in the emergy side of the journey. However, if someone ever wanted to come back on this path, here is some advice on more possible heights and sights.

1. This case study focused on one of the routes proposed in the reference paper (the one that appeared more promising according to LCA indicators), but the same analysis and comparison can be repeated for the other setups, to explore whether seemingly less advantageous processes in a LCA perspective can reveal further potential when inspected under another lens.

2. Due to lack of experimental or modeled data, information about electricity consumption, goods and machinery and labor and services had to be retrieved elsewhere. In doing so, we had to rely on data that was calculated for slightly different processes than the ones examined. As a potential research expansion, performing the same analysis (both emergy- and green chemistry-wise) with experimental data would allow more reliable estimates of metrics and indicators, hence more useful results.

3. For the same reason, it was not possible to perform emergy analysis on the full system of alt-LA, including also the production of pure DHA to sell on the market. A revealing development of this research would be repeating the emergy analysis and the green metrics calculation taking into account this step: the split in the DHA flow would cause a change in the lactic acid transformity and in the emergy indicators, modifying our overall judgment about the sustainability of the system. This research extension is particularly interesting because it compares two of the 'pillars' of sustainability that the present narratives claim are equivalent: since the purification of DHA is added to guarantee the economic sustainability of the plant, what would happen if this step revealed a decreased environmental sustainability? How would the mainstream perspective deal with inconsistencies between equivalent pillars? To this question, our present vision might already have an answer - but this is material for another journey. Even without further data about pure DHA production, knowing the transformity of acetone (calculated through the biobutanol emergy table) the

transformity of lactic acid could be related to the fraction of DHA dedicated to the purification through emergy algebra, enabling to explicit the mathematical correlation between lactic acid and DHA quantities. This would represent a way to explore the trade-off between economic and environmental sustainability of this lactic acid production route, potentially solving the conflict presented in the previous questions.

4. In the green chemistry side of the study, only the main metrics were calculated, adding an estimate of the EcoScale score. A further calculation of other metrics and other evaluations (e.g. GREENSCOPE, EATOS) coupled with toxicological data would provide a more comprehensive picture of the two processes.

5. The conventional production route uses methanol as a solvent in the last step of synthesis, to avoid a step of azeotropic distillation. However, methanol is toxic and decreases the reaction performance metric-wise, so it might be worth substituting it. A process model using another alcohol might be developed and studied with the same combination of emergy and green chemistry metrics, to explore how the substitution of a reagent changes the emergetic sustainability of the process.

6. As we have seen in this case study, calculating emergy indicators in totally human-dominated systems can be a daunting task. The lack of direct use of renewable sources such as solar energy, wind or rain, can make the algebra impossible to carry out. Similarly, not having clear information about whether a source is local or purchased leads to uncertainty in the calculation of these indicators. Some others, like the Unit Emergy Investment, cannot be estimated at all without having information on the "bigger picture". To overcome these difficulties, performing an emergy analysis on the extended systems for the two processes would provide quantitative information about the renewable and local sources involved, granting the possibility of calculating the same indicators (and more) with more reliability.

7. In the present work, the emergy analysis of the two systems was limited to energy and matter flows. However, information and money flows can heavily influence the functioning of can be developed to study the effect of information and money fluxes, mainly in terms of management and marketing of the product - especially related to the perception of sustainability towards the market.

More in general, we hope that this model of research, comparing emergy and green chemistry, will be reproduced in other case studies, to explore the consistency of the results obtained here. We also encourage the comparison between these and other environmental assessments, to find common ground and synergies for developing more integrated assessment methodologies. Last but not least, we virtually join the community of scientists who advocate for the creation of a common, open-source database both for green chemistry and for emergy analysis, to help overcome the lack of standardization and ambiguity to which the two disciplines are subjected.

3. What for?

Beyond our results and recommendations, the goal of applied scientific research cannot be only that of producing new information. Once we obtain some results, we must ask ourselves: how can these be useful to society?

In our case, environmental assessments are the methodologies to direct industrial and societal development, and indicators are the tool to facilitate communication of this change: they provide scientific knowledge in an accessible form to a non-specialized audience, helping build environmental awareness; they can influence consumers' perception of goods and their value, aid informed purchases and direct consumption towards a sustainable pattern; and they offer invaluable help in providing advice to policymakers, to enable informed and scientifically sound decision making. Overall, we believe in the benefit of creating an open dialogue based on free but aware opinions and choices. We hope the methodologies to calculate these indicators will be strengthened and standardized to provide more and more reliable information to the audience and enable the systemic change we need, to build a sustainable present and allow our posterity to have a future.

There is still some confusion between sustainability-related terms (such as green versus sustainable chemistry, or sustainability versus sustainable development), but we hope this work focuses attention on the need to create a uniform lexicon for scientists and non-specialists, to navigate the world of sustainability with more awareness.

Closing remarks - Call to action

A statistician once told me that when studying climate change and sustainability, scientists are perhaps "too cautious" in what they say. Perhaps following too strictly the precautionary principle, the risk is avoiding exposing an uncomfortable truth due to "excessive" uncertainty in measurements. If we really have a few decades to avoid a catastrophe, does it make sense to wait to be 99% sure before taking action?

To change our "business as usual", science is not enough. The climate conferences from Rio to today have largely proven that gaining proof of climate change is not enough. We should start being a bit less scientists and a bit more activists (Woodhouse and Breyman, 2005). The situation demands us to turn to epistemic politics and take into account the "societal and political context of knowledge production" (Iles, 2011). We need to take a step out of academia and enter the rest of the world to spread our message. Glavovic (2021) has even proposed a moratorium on climate research as a "protest" against the lack of action of public institutions. We have to go out of our scientifically sound comfort zone, give up our jargon, and start talking to people in their terms. "Why would I have to be the one going out of their way to adapt my language to others?" Because you are, perhaps, the most educated one in the room, and part of your job as a researcher consists of disseminating your results and making this information accessible.

We must agree on clear definitions for this vision. Since unlimited growth is impossible on a physically constrained planet, we must agree on a path to reach a society that this planet can sustain. For this goal, we here propose reframed definitions to sustainable development and sustainability: the first as a transition stage that bridges the gap between the current detrimental status-quo to the aimed "final" stage of "eco-friendly" living; the second as the final stage itself, in which no development is strictly necessary to reach a society in harmony with the environment. In "emissions policies" terms, sustainability corresponds to the "net zero", and sustainable development is the path to get there. When Köhler (2014) highlighted the "ecological time scale violation" of our industrial society, he asserted that "Besides the long-term sustainability of the global economy, we need a "temporal sustainability" for the development of our technical culture." If we want to pursue "sustainable development" even beyond our "steady state", we must change its meaning in human development, whose goal is not unlimited growth or richness, but fostering human well-being.

Last but not least, we must make this vision systemic, overcoming the reductionism inside and between sciences. As with details in a painting, we too often focus on the single brushstrokes without observing the landscape they create. It is easy to feel that the image on the canvas is much more than the mere sum of the brushstrokes or the colors: the single spots merge to create a picture that can be seen only at a distance, at a higher level of awareness. We will know we will have reached our goal when green will go back to being another color on the Venn diagram. Once industries and policymakers will dismiss the need of using green as a sign of sustainability, and advertisements of sustainable practices will become red, blue, pink or black-and-white, it will mean sustainability has finally entered the realm of "common sense", as it is supposed to be.

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Chapter 5 - Comparison

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Closing remarks

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