Biofuels from micro-organisms: Thermodynamic analysis of sustainability

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Biofuels from micro-organisms: Thermodynamic analysis of sustainability

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2022

Declaration

I hereby declare that, the contents and organization of this dissertation constitute my own original work and does not compromise in any way the rights of third parties, including those relating to the security of personal data.

Giulia Grisolia
2022

* This dissertation is presented in partial fulfillment of the requirements for **Ph.D. degree** in the Graduate School of Politecnico di Torino (ScuDo).

I would like to dedicate this thesis to my loving parents

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Abstract

Nowadays, the societies' awareness is continuously growing in relation to the need to change the actual trends in exploiting natural resources, and in a more general framework, in the way in which the present societies interact with their environment, the Earth system. Just in this context, almost fifty years ago, the concept of Sustainable Development was introduced. During the last thirty years, the spotlight has been put into this concept, which has its roots in three different domains: economy, society and environment. However, how to measure sustainability still remains a tricky open problem. Furthermore, this century is characterised by several challenges, which must be addressed by considering the consequences of the present choices for future generations. Among these challenges, environmental pollution and greenhouse gasses (GHGs) emissions have gained attention, due to their harmful impact on climate change and human life. Energy represents the key-enabler for life. However, the societies' reliance upon fossil fuels is one of the major contributors to GHGs emissions and pollutants. Thus, a global energy transition is required, switching from fossil fuels to renewables.

The aim of this PhD Thesis is to develop a method to evaluate the sustainability of a country, by introducing an approach based on the link among the social, economic, and environmental domains to the engineering thermodynamics optimisation one. To do so, an indicator has been developed, by introducing the Gouy-Stodola theorem related to GHGs emissions into the Human Development Index, HDI, the United Nations (UNs) indicator based on three main aspects: long and healthy life, knowledge, and a decent standard of living. The resulting index, named Thermodynamic Human Development Index ($THDI$), considers the domains of the sustainable development, including a link with the technological pillar. Moreover, an improvement of the UNs' Education Index (EI) is proposed, to consider both the schooling years, as already set by the UNs, and the students' skills and knowledge, which are required to build the knowledge bases for the future citizens and workers in advanced technologies for

sustainability. Thus, the Education Index-more-professional-oriented (EI_p), and the related Thermodynamic Human Development Index - professional-oriented ($THDI_p$) are obtained.

An approach to mitigation strategies is carried out by considering the biofuels production from micro-organisms. Thus, the irreversible thermodynamic analysis of the micro-organisms membrane heat and mass flows with their environment is carried out in order to obtain an optimisation approach to biomass generation for biofuel production. To optimize this process, it is possible to exploit a natural positive interaction, a behaviour that exists between different species, called mutualism, in which one of the species supplies useful metabolites to the other one and *vice versa*, or acts by changing the neighbouring external environment, supporting the behaviour of the other one. This behaviour can be exploited during the anaerobic digestion process of biomasses, too.

Hence, in this Thesis, the valorisation of a field residue - the rice straw - has been considered to obtain biomethane from the anaerobic digestion process. Actually, rice straw is acknowledged as an agricultural waste, because of its physico-chemical properties, which do not allow its use in the industrial sector. However, rice is the third global staple food, and the actual disposal methods of the related rice straw induce negative impacts on the environment, because it is mainly burned or slowly incorporated in the field, causing GHGs and pollutant emissions. The potential amount of biomethane from rice straw for different countries has been evaluated, and the *THDI* has been applied in this context, to analyse the biomethane production from anaerobic digestion with respect to the actual disposal methods.

Structure of the PhD Thesis

This PhD Thesis focuses on the thermodynamic approach to the improvement of biomass formation for biofuels production from micro-organisms, in the context of sustainable development and on the measure of sustainability itself.

So, in Chapter 1, a brief summary of the present approaches to measure sustainable development, and their analysis is developed, in order to point out the actual needs to introduce new indicators, with the aim of overcoming the limits of the Gross Domestic Product (*GDP*). Indeed, at present, *GDP* still represents the main reference for any decision on countries' development policies. However, it is only an economic indicator. Consequently, it does not take into consideration the environmental, social and technological aspects, needed to achieve a sustainable development. Thus, due to the requirement of new sustainable technologies and future strategies, *GDP* should not be considered as an effective tool for this kind of decisions. Hence, in Chapter 1, some existing indicators are considered and analysed; in particular, the United Nations Human Development Index, *HDI*, emerges as an interesting index to assess the countries' development level, in relation to socio-economic and human well-being conditions, because it is defined as the geometric mean of three socio-economic milestones: the Life Expectancy at birth (Life Expectancy Index), knowledge (Education Index) and a decent standard of life (Income Index). But, among these indexes, any impact to the environment is considered; so, *HDI* does not provide any information on the efficiency of the technological level of a country, in relation to anthropic impact on the environment. The result of the analysis is the need to improve this indicator towards a new approach, to include also the environmental domain.

As a consequence of this analysis, a question arises: how is it possible to approach the measure of sustainability, starting from and engineering viewpoint, maintaining also the socio-economic evaluations? To try finding an answer to this question, a thermodynamic analysis of the considered system must be carried out. This is the topic of the next Chapter, which lays the thermodynamic foundations of all the PhD Thesis project, in relation to the improvement both of the biomass formation for biofuels production for which a thermodynamic model is carried out, and of the *HDI*, with the result to define a new indicator, named *THDI*, which represents the tool for the measure of sustainable development, proposed in the research here developed.

Consequently, in Chapter 2, micro-organisms are considered as the functional unit of a biorefinery, or as its *workers*. Their work consists in the biomass formation, useful for the biofuels production. So, the non-equilibrium thermodynamics is introduced in the analysis of the micro-organisms *thermodynamic work*, with particular regards to the optimisation of the biophysical processes involved in the biomass formation, in order to improve the biofuels production itself. The result of the analysis is a thermodynamic approach to highlight the characteristics of the species and the conditions to improve the performance in the biomass formation. In particular, the result obtained points out that the better micro-organisms are the species which are able to realise mutualistic conditions, in which a species support the life and activities of the other, and *vice versa*.

Thus, on the bases of the thermodynamic results, obtained in Chapter 3, the improvement of the *HDI* can be developed by introducing a measure of the environmental impact of the process that occur within a country, by measuring their irreversibility. In this way, the Thermodynamic Human Development Index, *THDI*, has been built on the basis of the Gouy-Stodola theorem and the entropy generation evaluation, related to the pollutant emissions. Moreover, also the $OECD - PISA$ program results are introduced in the Education Index component, in order to consider the abilities acquired by students during their schooling period, to consider their groundwork knowledge for the future jobs, when the sustainable development will require more technical competences, related to advanced technologies. In summary, the *THDI* has its bases on:

- The expectancy of life at birth, implicitly related to healthy life style, the health care system, the access to water and food, etc.;
- The primary access to knowledge and education, related to the schooling years and students' skills and knowledge abilities;

- The Income Index, related to the sustain of a decent standard of living in a country;
- The environmental impact, related to the efficiency of a productive system with respect to their GHGs emissions.

Last, in Chapter 4, the previous results represent the tool for the analysis of the valorisation of a field residue, with particular regards to rice straw. Indeed, rice straw is considered a field residue without any other industrial use, due to its chemical-physical characteristics. Here, the rice straw is proposed as an energy resource for the bio-methane production by means of anaerobic digestion, which is carried out in mutualistic conditions. The use of the $THDI$ shows the interesting potential of rice straw as a biomass resource for the bio-methane production in the major rice producing countries over the world, due to its availability. Indeed, rice represents the third global staple food, with the related unavoidable production of its straw. The use of rice straw for bio-methane production from anaerobic digestion is analysed first in an Italian context (the Novara district), then extended to Italy and last in other major rice producing countries, in all continents.

Publications

The results of this PhD Thesis have been published in the following papers:

1. G. Grisolia, D. Fino & U. Lucia. Biomethanation of Rice Straw: A Sustainable Perspective for the Valorisation of a Field Residue in the Energy Sector. *Sustainability* **14**, 5679 (2022).
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5. U. Lucia, D. Fino & G. Grisolia. A thermoeconomic indicator for the sustainable development with social considerations. (A thermoeconomy for sustainable society) *Environment, Development and Sustainability* **24**, 2022-2036 (2022).
6. E. Açıkkalp, O. Altuntas, H. Caliskan, G. Grisolia, U. Lucia, D. Borge-Diez & E. Rosales-Asensio. Sustainability analyses of photovoltaic electrolysis and magnetic heat engine coupled novel system used for hydrogen production and electricity generation. *Sustainable Energy Technologies and Assessments* **52**, 102094 (2022).
7. U. Lucia & G. Grisolia. Biofuels Analysis Based on the *THDI* Indicator of Sustainability. *Frontiers in Energy Research* **9**, 794682 (2021).
8. G. Grisolia & U. Lucia. Thermoeconomic Analysis of Alessandria District: A Case Study for an Engineering Thermodynamic Indicator for Sustainability. *Tecnica Italiana - Italian Journal of Engineering Science* **65**, 151-156 (2021).
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10. U. Lucia, D. Fino & G. Grisolia. Thermoeconomic analysis of Earth system in relation to sustainability: a thermodynamic analysis of weather changes due to anthropic activities. *Journal of Thermal Analysis and Calorimetry* **145**, 701-707 (2021).
11. U. Lucia & G. Grisolia. Irreversible Thermodynamics and Bioeconomy: Towards a Human-Oriented Sustainability. *Frontiers in Physics* **9**, 659342 (2021).
12. U. Lucia & G. Grisolia. The Gouy-Stodola Theorem - From Irreversibility to Sustainability - The Thermodynamic Human Development Index. *Sustainability* **13**, 3995 (2021).
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14. M.F. Torchio, U. Lucia & G. Grisolia. Economic and Human Features for Energy and Environmental Indicators: A Tool to Assess Countries' Progress towards Sustainability. *Sustainability* **12**, 9716 (2020).
15. U. Lucia & G. Grisolia. How Life Works – A Continuous Seebeck-Peltier Transition in Cell Membrane? *Entropy* **22**, 960 (2020).
16. U. Lucia & G. Grisolia. Thermal resonance and cell behaviour. *Entropy* **22**, 774-785 (2020).
17. G. Grisolia, D. Fino & U. Lucia. Thermodynamic optimisation of the biofuel production based on mutualism. *Energy Reports* **6**, 1561-1571 (2020).

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1. G. Grisolia & U. Lucia. Why does thermomagnetic resonance affect cancer growth? A non-equilibrium thermophysical approach. *Journal of Thermal Analysis and Calorimetry* **147**, 5525–5531 (2022).
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3. U. Lucia & G. Grisolia. Thermal resonance in living cells to control their heat exchange: Possible applications in cancer treatment. *International Communications in Heat and Mass Transfer* **131**, 105842 (2022).
4. L. Bergandi, U. Lucia, G. Grisolia, I. C. Salaroglio, I. Gesmundo, R. Granata, R. Borchiellini, A. Ponzetto & F. Silvagno. Thermomagnetic Resonance Effect of the Extremely Low Frequency Electromagnetic Field on Three-Dimensional Cancer Models. *International Journal of Molecular Sciences* **23**, 7955 (2022).
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7. U. Lucia & G. Grisolia. Resonance in thermal fluxes through cancer membrane. *Atti dell'Accademia Peloritana dei Pericolanti* **98**, SC1-SC6 (2020).

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Chapter 1

Introduction and problem identification

Summary. In this Chapter, the problem to which this PhD Thesis is addressed is argued and the frameworks on which it is embedded are summarised. In particular, the sustainable development is discussed in relation to the environmental concerns of the present days. In this context, a way to measure the sustainability of processes, systems, and countries emerges as a need. So, some considerations are introduced in relation to indicators of sustainable development. Consequently, the objective and the subjects of this PhD Thesis are presented, by laying the foundations for the next Chapters, which will develop the thermodynamic approach, the new indicator of sustainability, and their use in the valorisation of the rice straw, at present considered as a field residue, and here proposed as a new resource in the energetic supply chain.

1.1 Introduction

Contemporary time represents a crossroad in the history of humanity, but also of the whole Earth system, because the complex dynamics both of widening and growing the poverty distribution, and of rising of environmental and socio-economic issues, are producing a complex unbalanced socio-economic system, and it has been highlighted that it is very difficult to untangle this yarn [197]. A hope of addressing this problem is represented by real advances in access for all to basic services such as energy and healthcare, increasing the global awareness of environmental concerns.

Humanity has started its wider impact on the environment, since Europe has undertaken its development path towards a technological society, during the industrial revolution. Indeed, since 1950, the environmental consequences have increased mostly due to the technological, industrial and economic developments, such as [197]:

- The hole in the ozone layer, which is the region of the stratosphere that absorbs harmful ultraviolet radiation;
- The loss of more than the 65% of the land that was before arable;
- The desertification of the 15% of the Earth's land surface, that means its conversion into deserts;
- The emission of long-live chemicals and toxic substances into the atmosphere, ground, and water;
- The induced disappearance of a wide number of plants and animal species every year;
- The increase of the global mean temperature which is rising of an average of 0.5°C up to 2.0°C [535].

Moreover, from an economic and financial viewpoint less than the 20% of the global population, earns approximately two hundred times more than the remaining 80% [197]; one of the consequences of this condition is represented by human fluxes that occur from poorer regions to the richest ones.

In order to allow access to energy, which is meant to represent a decent standard of living, decisions on future energy supply should be effectuated mostly in relation to renewables and to viable alternatives to fossil fuels, in order to reduce the related CO_2 emissions, and to guarantee security in the energy supply chain.

In this context, the International Energy Agency (IEA) offers medium to long-term energy scenarios by using the World Energy Model (WEM), which simulates how the energy markets could evolve, providing also sector-by-sector and region-by-region projections for the World Energy Outlook (WEO) scenarios. The WEM encloses data on the global energy system and has three main modules: (i) final energy consumption, (ii) energy transformation, and (iii) energy supply. Among the outputs from the model greenhouse gases emissions are included. The WEM contains four main different scenarios, and their results in terms of CO_2 emissions are shown in Figure 1.1:

1. The Net Zero Emissions by 2050 Scenario (NZE): which considers energy-sector pathway to achieve net zero carbon dioxide emissions by 2050. This scenario fulfils central UNs Sustainable Development Goals (SDGs) related to energy (including global energy access by 2030 and improvements on pollution levels). This scenario assumes that all the non-energy sectors will decrease with the same proportion as energy emissions, and it is coherent with the limitation to the maximum increase of the global Earth temperature of 1.5°C, without overshooting it with a probability of 50%.

2. The Announced Pledges Scenario (APS): which considers the commitments of governments (including Nationally Determined Contributions) and the longer term net zero targets, assuming they will be met all on time, highlighting the gap that should be closed to achieve targets of the Paris Agreement. In the APS (COP26) are included the new pledges by different countries to reduce their emissions, with this scenario the threshold of the increase of the average global temperature below 2.0°C is obtained.

3. The Stated Policies Scenario (STEPS): which considers the actual policies in place in each country sector-by-sector, and the already announced ones. Thus, it provides the projection to measure the potentially achievable targets with present developments in the energy and climate policy.

4. The Sustainable Development Scenario (SDS): which considers SDG 7 (Ensuring universal access to affordable, reliable, sustainable and modern energy services by 2030), SDG 3.9 (Reducing significantly pollution), and SDG 13 (Effective actions to fight against climate change).

The projections of the emissions in Figure 1.1 are the result of a deep analysis on different policies regarding the energy sector, and highlight how energy policies can dramatically affect the global emissions. The energy sector accounts for about 75% of the emissions, that have pushed global average temperatures 1.1°C above the pre-industrial era, with related consequences on the environment. Thus, the energy sector has to be the core of the solutions to climate change. Contemporarily, energy should be available for all people (with an increasing trend in the population), that means pushing up demand for energy. By now the energy system is not able to meet all these challenges, meaning that a new strategies are required. In Figure 1.2 are

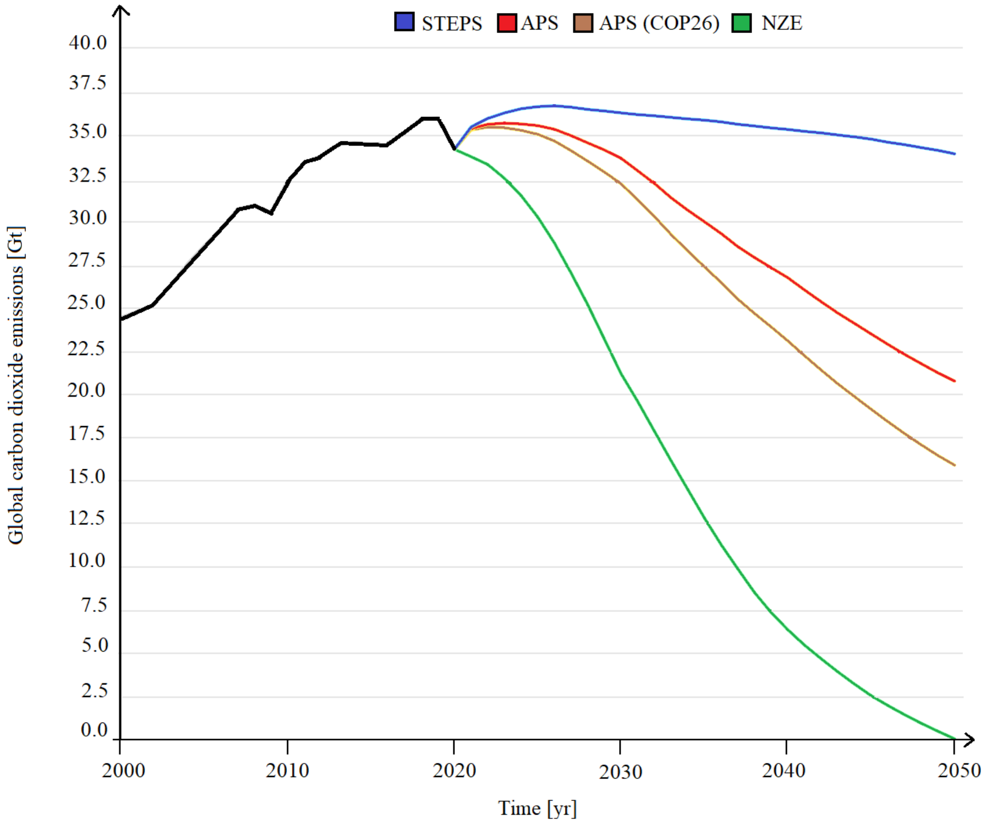

Figure 1.1 CO_2 emissions related to different WEM Scenarios by 2050, adapted from Ref. [214]

represented the patterns of CO_2 emissions in function of time, from 2000 to 2040 in other scenarios realised by the IEA in 2018: the New Policies Scenario, Sustainable Development Scenario, Future is Electric Scenario and considering the latter one but performing a decarbonisation on energy supply (in figure indicated with FiES dec). It is evident, how different policies could influence carbon dioxide emissions and, it is fundamental that governments pursue the goal of their reduction. Before imposing stronger policies, a particular attention has to be paid in long/mid- term decisions, the short gap between FiES and NPS CO_2 emissions is significant in this context. Thus, a change on the global energy supply must be compulsory if we want to reach an inversion on carbon dioxide emissions; so, low-carbon development patterns and technologies are attracting always more attention, also due to strong shocks to societies and to economies that have been originated from climate changes. Thus, moving towards a low-carbon society is necessary and, this transformation requires not only engineering solutions to develop low-carbon technologies but also institutions, systemic structures, industrial players, governments and individuals.

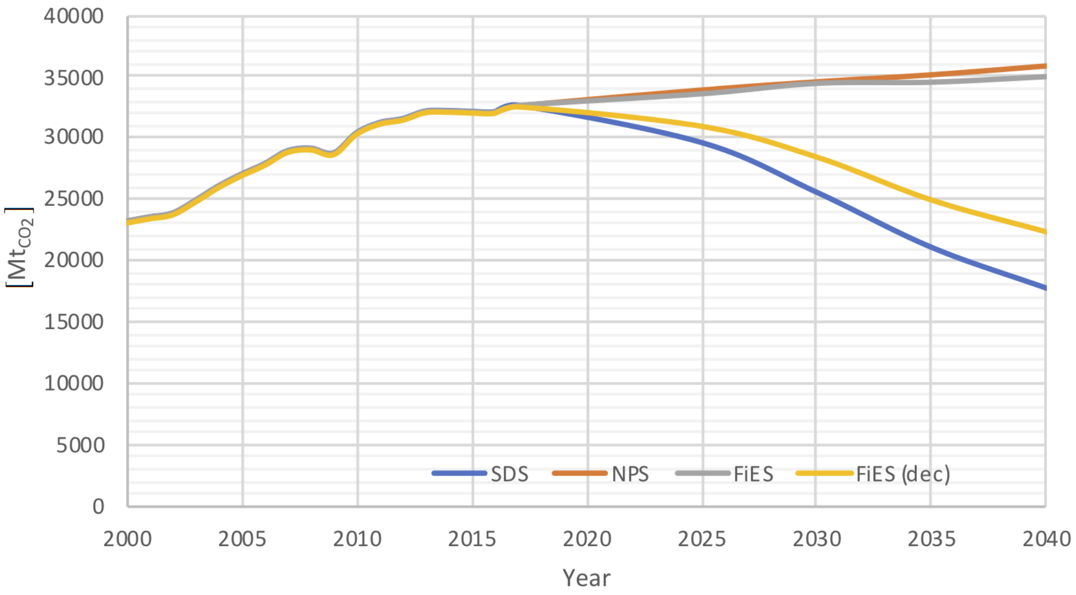

Figure 1.2 CO_2 emissions related to Sustainable Development Scenario, New Policies Scenario, Future is Electric Scenario and Future is Electric Scenario decarbonising energy supply; data from International Energy Agency [214]

On the other hand, in the Chapter 40 of *Agenda 21* the need of availability of information and data related to the conditions of each Country has been highlighted, together with the requirement of the definition of indicators of sustainability, in order to [326]

> *provide solid bases for decision-making at all levels and to contribute to a self-regulating sustainability of integrated environment and development systems*

Thus, the aim of this Research is to build an indicator of sustainability by using thermodynamics, which allows us to introduce concepts of engineering optimization. This leads to solutions targeted to minimize the irreversibility. Moreover, this tool will be applied to the biofuels production from living micro-organisms, which results also in accordance with the goal of reducing anthropic carbon dioxide emissions.

The need to dispose of a non-fossil fuel is still an issue, although steps forward have been done. The question that could rise is *Why are we still interested in fuels, which implicitly imply combustion?*. The answer to this question can be find looking at the patterns of the different IEA scenarios in Figure 1.2. The silver bullet does not exist and a myriad of trade-offs are needed if really has to be a *global* energy transition. Electrification must be carried-out conscientiously to avoid the induction of further impacts on the environment and the related negative consequences. Moreover, the actual disparity between countries and policies can not be neglected. So, biofuels can represent an anchor also in mid-long term time, where the conditions are still unripe. Biofuels are considered as having a carbon-neutral route in their production process so they are considered as having a great potential to abate carbon dioxide emissions [333]. They are considered a possible alternative to fossil fuels, because of the fossil fuels depletion and also environmental issues [333].

Some characteristics required for biofuels are the following [263]:

- To be easily available;
- To be technically and environmentally feasible;
- To be economically competitive.

An interesting characteristics is diversification in terms of supply related to their production from different biomasses consists, because the row materials required can locally be produced in each Country [267]; indeed, biomasses are generated thanks to the photosynthesis process during their living cycle, using carbon dioxide as a feedstock. In addition, biofuels can be classified in relation to their origin, as follows:

- The first biofuels generation, obtained mainly by food crops [212], which are usually obtained from sugars, starches, and vegetable oils; only to cite some of them, bio-ethanol, bio-propanol, and bio-butanol are produced by the micro-organisms and enzymes activity *via* the fermentation of sugars or starches, or cellulose;

- The second biofuels generation, are obtained by non edible biomasses, or lignocellulosic biomasses [407], comprising the food and agricultural discards, agro-industrial and urban wastes;
- The third biofuels generation, obtained by photosynthetic microorganisms as micro-algae and cyanobacteria [7];
- The fourth biofuels generation, are the result of the development of metabolic engineering in the field of carbon capture and storage technique on micro-organisms.

Although the first generation of biofuels constitutes the majority of the biofuels used today, several concerns on the first biofuels generation have been highlighted:

- They come mostly from edible or specific crops dedicated to energy purposes, with all the relative consequences, also involving the competition with edible crops;
- The cultivation can bring to biodiversity loss, land-use changes and water depletion [114], that are neither sustainable [97] nor ethical,

and, for the second generation, the trouble on their use use is more related to their production energy needs and costs [84]. However, this generation has a pivotal role in the context of moving towards a circular economic system, where wastes should be strongly reduced. These wastes, specially the agricultural ones, can be effectively exploited as raw biomass materials to produce biogas and other valuable biofuels, such as biomethane but also hydrogen and liquid fuels. In order to explore new routes to obtain bio-fuels, the third generation has been introduced. Biofuels from microalgae and photosynthetic micro-organisms are widely studied and, their advantages have been pointed out as follows:

- Their cultivation do not present a competition with edible crops;
- They are able to absorb carbon dioxide during their life cycle [94];
- They present a relatively high efficiency in performing photosynthesis [367].

Furthermore, in comparison with higher plants,

- They present major oil yield, that allows them to deliver a higher amount of lipids with respect to all other biomass feedstock [558];
- They can require less fresh water than terrestrial plants;
- They may grow in any kind of water, including wastewater, or non-arable lands, avoiding the competition with terrestrial crops;
- For their harvesting pesticides or herbicides are not required;
- Their biomass can bring to a wide variety of biofuels.

But, the third generation of biofuels does not present a large scale production process, due to a non completely mature technologies. The main lack of competitiveness in relation to fossil fuels is related to their production costs and extraction, related to the quantity of fuel per litre of culture that can be obtained [144], and to the understanding of the micro-organisms behaviour.

Consequently, biofuels production has to be studied in order to optimize their production processes [323], for the necessary transition from fossil to renewable fuels. Furthermore, this requirement is imposed by the legislation, and, in the last decade, the biofuels production advancement has mostly been developed in order to fulfil government policies [412], e.g., with regards to the European Union, the *Directive on the Promotion of the Use of Biofuels or Other Renewable Fuels for Transport* (2003/30/EC), the *Renewable Energy Directive* (2009/29/EC), recently modified by the *Renewable Energy Directive II* (2018/2011/EC), the overall target for renewable energy sources use (to achieve within 2030) has been raised to 32%. In relation to the sub-sectors of road and rail transport, the minimum level has been setted to 14%, with a limitation for biofuels of first generation, due to their nature and to their *Indirect Land Use Change* [109]. The latter can be summarised by considering that, by now, the majority of the produced biofuels derive from croplands, which were previously used for agriculture. That implies a switch of other areas into arable lands, remaining agriculture a primary necessity. This can bring to the expansion of arable lands into non-cropland, encompassing areas that constitute a high carbon stock as wetlands, peatlands, and woods/forests, and that process is known as Indirect Land Use Change (ILUC), which can cause the release in the atmosphere of the carbon stocks in the form of CO_2, more informations can be found in the *Delegated Regulation on indirect land-use change* ((EU) 2019/807).

Moreover, the European Commission is revising its overall targets, in order to achieve the goalpost in the reduction of GHGs emissions of at least 55% by 2030 (considering 1990 as the reference year), and climate neutrality by 2050. Moreover, in the last months the ambitious target of 45% of renewable energy has been proposed by the European Commission in power generation, buildings, transport and industry.

1.2 The environmental issues

Since the beginning of the XIX century, Fourier[1] analysed the data on the Earth temperature, by relating them to the Earth-Sun distance. He pointed out that the partial out-flowing of infrared (IR) radiation from the atmosphere was the cause of the subsisting higher Earth's temperature than it should be expected: nowadays, this effect is named *greenhouse effect*, and it was empirically proven in 1859, by John Tyndall[2], who proved the radiant heat trapping property of CO_2 and water vapour. These studies allowed Arrhenius[3] to reveal that a doubling carbon dioxide concentration in the atmosphere could bring to the increase of the Earth's temperature of approximately 4°C.

Despite the controversy on global climate change, at present, the consequences of the anthropogenic activities on the weather, and also on climate, are often accepted by the greater number of scientists [20]. Indeed, industrialised society needs large amounts of energy for all activities, including: the power generation, industrial, agricultural, buildings, and transportation sectors, still generated mainly by adopting fossil fuels as primary sources. The greenhouse gas emission is a well established consequence [376], because of the combustion processes involved in the energy productive systems. In recent times, the effect of the correlated wasted heat, due to human activities, is attracting the interest of scientists and engineers [160, 296], in relation to the global warming and the climate change, but more generally speaking, to the continuous growing environmental concerns. In fact, one of the main problems

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[1] Jean Baptiste Joseph Fourier, Auxerre, March 21th, 1768 - Paris, May 16th, 1830

[2] John Tyndall, Leighlin Bridge, August 2nd, 1820 - Hindhead, December 4th, 1893

[3] Svante August Arrhenius, Wik Castle, February 10th, 1859 - Stockholm, October 2nd, 1927

of industrialized countries is the management of carbon dioxide emissions [298], being energy the fundamental requirement to enable human well-being.

The need of a continuous increasing amount of power has characterised human history and development [45]. As a matter of fact, energy represents a requirement to live and, only by means of access to energy to all people we can reach equity. Indeed, energy is also implicitly related to several inter-linked human rights (i.e. living standards, work, food, health, housing and public participation in decision-making, etc.), furthermore it promotes their practical realisation [480].

Considering the World's demographic & Total Primary Energy Supply ($TPES$) data of the last thirty years, it has been registered:

- A relative increment of approximately 44% of the global population;
- A relative increase of approximately 64% of the Total Primary Energy Supply (see Table 1.1).

The total amount of these two quantities, between 1990 and 2019, has been reported in Figure (1.3), while in Figure (1.4) are shown the graphs of the Total Primary Energy Supply per capita for different World's broad areas, during the same reference period of time. As can be observed, there is a net disparity among the *TPES per capita* values of the different World's regions.

Table 1.1 World's Total Energy Supply by source [215], between 1990 and 2019.

Year	Total Energy Supply [ktoe]							
	Coal	Natural gas	Nuclear	Hydro	Renew.	Biofuels & Waste	Oil	Total
1990	2220587	1662187	525520	184064	36571	904162	3233212	8766303
1995	2207669	1806624	608098	212766	42391	967469	3373297	9218314
2000	2317134	2071233	675467	224663	60262	1014659	3669477	10032895
2005	2990601	2360022	721706	252334	70143	1088960	4010067	11493833
2010	3649798	2735952	718713	296474	110200	1205287	4127360	12843784
2015	3842742	2928795	670172	334851	203821	1271235	4328233	13579849
2019	3878857	3362950	728480	363046	322442	1356645	4475972	14488392

It results quite obvious that the amount of energy that would be needed in the next future will tend to increase, specially considering the regional distribution of energy. Indeed, at least two facts stand out:

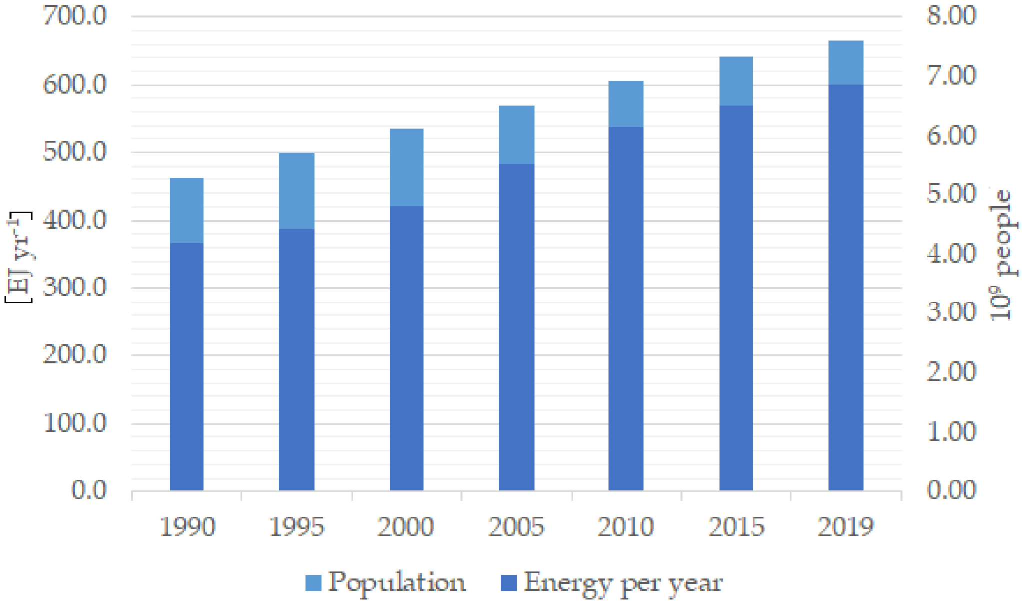

Figure 1.3 World's Total Primary Energy Supply data [215] vs Population data [531], between 1990 and 2019

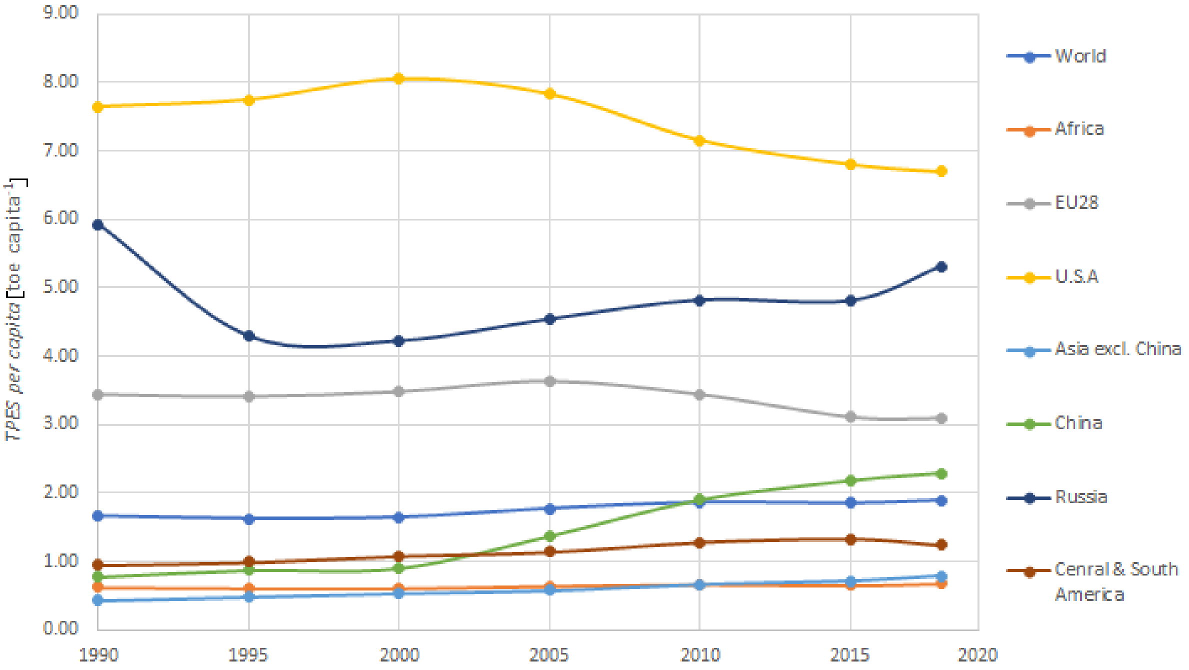

Figure 1.4 Total Primary Energy Supply per capita [215] of different broad areas between 1990 and 2019

- A continuous global population growth is expected for the next years (a population projection of 10.9×10^9 is expected by 2100 [225]);
- To achieve the SDGs, the less developed Countries must increase their energy consumption *per capita*.

This represents a challenge within a challenge: we must reduce our greenhouse gases emissions (GHGs) to preserve the environment but, we also need to "ensure access to affordable, reliable, sustainable and modern energy *for all*" [498]. So, the four overlapping pillars on which is based Goal 7 are: i) affordability, ii) reliability, iii) sustainability and, iv) modernity and they can not be considered mutually exclusive, as occurs for the three dimensions of the sustainable development. All that concerns energy, can not be decoupled from economics and from environment. Indeed, the issues of clean energy generation, storage and distribution are fundamental and, these challenges have to be addressed not only from an engineering point of view but in an interdisciplinary way, involving all the players at all levels, together. In this context, deals between Countries and Institutions are essential, such as the *Paris Agreement* [491], dealing with GHGs and Climate Change and based on *mitigation*, *adaptation* and *support*. The principal aim of this agreement is related to decrease global warming by:

1. Maintaining the increase of the global mean temperature below 2.0°C above pre-industrial levels, pursuing efforts to limit it to 1.5°C, reducing risks and impacts of climate change;
2. Raising the capability of adaptation against impacts of climate change, based on the concept of resilience;
3. Investing finance flows in developing technologies and instruments with a low impact on carbon dioxide emissions.

So, this strategy is directly correlated to energy and climate policy. In this Agreement, it also emerges the concept of *capacity-building*, which implies the transferring of the know-how from the developed Countries to the developing Ones, in order to put in act measures for adaptation and mitigation based on local strategies and on local labour and strengths. So, all the previous considerations are clearly interlinked with Human Rights, Cooperation and Policy-making.

The pattern and profile of the World's energy use which prevail today raises important questions about the relationships between energy and the economy, environmental protection, social issues, and security [493]. Without belittling and forgetting the importance of the human rights, it has to be considered that guarantee access to energy for *all people* will be always more difficult and unsustainable, without changing the actual vision. It results a tricky phase, considering the axiom of correlation between economic growth and energy consumption [493]. In the last decade, as the European Commission [148] has pointed out the environmental issues related to human activities have not been solved but, on the contrary have grown. A shift towards a more responsible way in producing/consuming in "a cleaner" way is needed to reach the above mentioned targets. The World's energy system still relies strongly on the use of fossil fuels (approximately 80%), as can be seen in Figure (1.5).

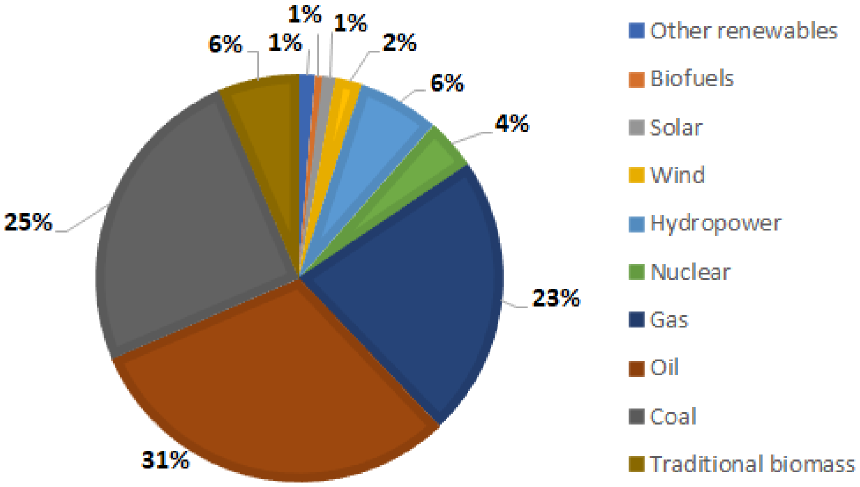

Figure 1.5 World's primary consumption by source in 2019 [215]

The related GHGs emissions are constantly increasing all over the world: from 1960 to today their concentration has been almost quadruplicated. In 2021, as highlighted by the American Society of Meteorologists members in their report [60], the annual global average carbon dioxide concentration in volume has been 414.7 ± 0.1 ppm, that is 11.9 ± 0.1 ppm greater than that of 2016, representing the highest annual concentration ever registered. An important contribution to the increment of greenhouse gases emissions is due to the land-use change and to the increase of fossil fuel consumption [148]. In Figure 1.6 are shown the percentages by sector of greenhouse gases emissions related to 2019. The sum of emissions by sector corresponds to 52.4 $\mathrm{Gt}_{\mathrm{CO}_{2e}}$ [216].

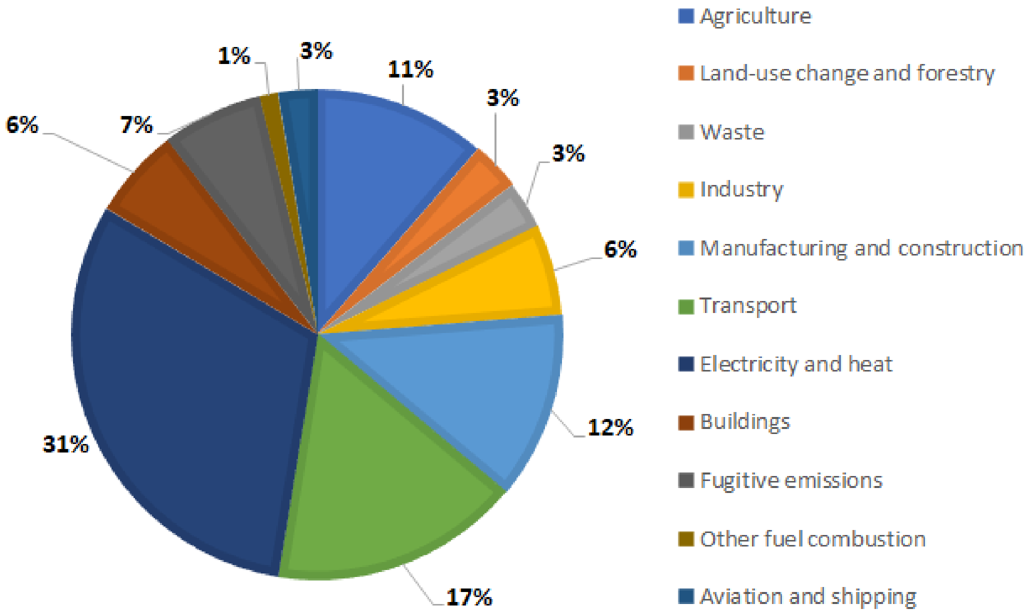

Figure 1.6 Global GHGs emissions by sector in 2019 [216]

Following an increasing demand for resource exploitation, including land, water, soil and ecosystems in general, an environmental degradation and impoverishment is occurring, leading also with the loss of biodiversity and an increase in deforestation. Furthermore, as is known, the scarcity of resources and the difficulties to access them are by now a global issue.

Another related problem with the exploitation of Earth's resources is the water pollution, including the contamination of water bodies and oceans; according with the present data, if the situation remains unchanged from today, in 2025 at least one third of the global population will face the problem of water scarcity [497]. We can not ignore the problem of at least 8×10^6 t yr^{-1} of plastics that end up into the Oceans and all the related consequences. This has been identified by the International Union for Conservation of Nature (IUCN) as one of the emerging issues affecting the environment, with also direct consequences on climate change [219].

Plastic is one of the fundamental substances in our everyday life; indeed, it has led to many technological, medical and societal advantages. The advantages related to the use of plastics are due to: its light weight, its durability, its strength, its corrosion-resistance, and its high thermal and electrical insulation properties. It is used in the industries with particular regards to food industry as they have versatile properties: strength and stiffness, barrier to gases, moisture, transparency and grease, resistance to food component attack and flexibility. Consequently, the plastic production and use have heavily grown in the last fifty years. In 2017, the use of plastic in the US was 109 kg yr^{-1} per capita, while in Europe, it was 65 kg yr^{-1} per capita [257].

Table 1.2 Most important kinds of plastics: percentage production and wasted [257]

Polymer	Production [%]	Waste [%]
Polyethylene	30-34	40-47
Polypropylene	12-15	12-19
Polystyrene	8-10	13-17
PET	2-5	5-12
PVC	19-22	10-11
Polyurethan	5-7	4-8
Other Thermoplastic	7-12	8-9
Other plastic	7-20	6-11

But, it is difficult to decompose synthetic plastics, so a high quantity of them have accumulated in landfills and environment; it has been evaluated that the 90% of the rubbish that actually is contained in the Oceans is represented by plastic, and more than its 10% comes from the municipal wastes [32]. More than the 33% of plastic consumption is in favour of packaging; that amount is commonly used once and then wasted: it requires the 4% of the world's oil production and another 4% is required for energy in the process [472, 471]. Oil-based polymers are non-biodegradable and difficult to recycle or re-use.

Plastics possess lots of advantages because of their versatility, however they also present some drawbacks:

- Environmental pollution issues;
- Sustainability issues;
- Human health issues.

To overcome these concerns, various methods can be introduced [181]:

- Recycling, for environmental pollution, oil and energy use reduction;
- The use of only decomposable plastic bags;
- The production and the use of bioplastics.

Bioplastics are polymers made from biomass, they are usually biodegradable and biocompatible, with several advantages [431, 436]:

- Their production is independent from fossil resources;
- Their decomposition is usually much faster than decomposition of oil-based plastics;
- They are less or not harmful to human health.

In particular, the bio-based packaging material must remain stable without changes in mechanical and barrier properties and must function properly during storage, until disposal [257]. Thus, considering the importance of plastic materials in our daily life, it becomes essential finding bio-based solutions, in order to substitute fossil derived polymers with biomaterials, which are synthesise by micro-organisms and can be degradable.

The reduction of CO_2 emissions, as already suggested in the Kyoto Protocol (in 1997), can be achieved by promoting three primary actions:

- The use of renewables as energy sources;
- The carbon dioxide sequestration, which implies estimated high investment costs, with the related difficulty of achievement;
- The implementation of existing high efficiency technologies, and the introduction of new advanced low-CO_2 emission energy systems, due to the direct relation of CO_2 reduction to plant thermodynamic efficiency. Consequently, energy policies for the promotion and adoption of best existing technologies could be carried out.

Thus, in the Kyoto Protocol already were proposed three mechanisms for the reduction of the greenhouse gas (GHG) emissions:

- The *Clean Development Mechanism* (CDM), that in developing countries enabled the development of credits (CERs, Certified Emissions Reductions), to be introduced with investment in carbon-reduction projects to offset emissions;
- The *Joint Implementation* (JI), analogous to the previous mechanism, but linked to emissions concerning deforestation, decay of biomass, change and forestry, fossil fuel use, perfluorcarbons, hydrofluorcarbons, etc., in relation to the following substances: (i) methane (CH_4), (ii) nitrous oxide (N_2O), (iii) carbon dioxide (CO_2) from ;
- The *International Emissions Trading* (The allowed emissions are divided into assigned amount units, AAUs trading).

The overall CO_2 equivalent emissions may be affected by several factors, such as: economic growth level, technological development, and production process chosen for any particular production [204]. On the other hand, the carbon dioxide emission issue should also serve as a concrete opportunity to promote high-efficiency design of conventional equipments and plants, with the related diffusion of advanced technologies. In fact, the European Union (EU) also established the *Strategic Energy Technology* (SET) *Plan*, to develop researches on new technologies, particularly linked to the ones related to climate change [180]: measurement, tracking, and program evaluation are important to assess the sustainable policies' impact, particularly related to the emissions reduction.

In the history of science and engineering, thermodynamicists tried to achieve universal principles in order to evaluate the system behaviours [348, 349, 372, 373] with particular interest for the dissipative systems, that are adopted in several energy efficiency issues, in designing and optimizing thermal and power systems [38, 39, 52]. Lowenthal and Kastenberg [285] firstly introduced the entropy approach in industrial ecology. Their results were to assign an entropy value, interpreted as a cost, to stages in a product's life cycle, but its use was also a thermodynamic measure for the resource use, or waste generation [560]. Exergy may be introduced in order to determine how far a process, or a system, is from its maximum thermodynamic performance [514]; therefore, exergy losses and thermodynamic efficiency are related to assess thermo-economic costs [423].

Thus, the energy transition requires the achievement of both new strategies and technologies, and more sustainable and decarbonized societies [235]. So, policies aimed to sustainable consumption and production represent the central points for the achievement of the sustainable development, particularly directed towards the environmental sustainability and the reduction of greenhouse gases emissions. In this context, socio-economic well-being, environmental recovery and protection, and anthropic emissions reduction have to be introduced into the every-day activities [306].

But, a measure of the sustainability is required to design any action; thus, indicators are required to establish policies and disseminate their communication. Indicators represent the fundamental tool to determine and establish policies, collect data and perform future projections; this tool is mainly required to inform policy-makers, scientists, and citizens on actual conditions, and to aid in the identification of suitable and concrete actions, and in evaluating their effectiveness [305]. The requirement to dispose of sustainable development indicators, as the primary tool to quantify and assess the Countries performances towards sustainability, has been pointed out also in Chapter 40 of the United Nations Action Plan *Agenda 21* [326, 461].

Science and technology are *de facto* crucial to the advancement and to the socio-economic development of countries; in fact, the development in technologies affects the income distribution, the economic growth, the job market, the finance sector, the environmental and industrial structures [5]. The 1992 *Earth Summit* ratified that countries, at national level, as well as governmental and non-governmental organizations, at international level, must create indicators of sustainable development in order to support actions and decisions in countries concerning sustainable development [5]. Thus, science and technology present a fundamental role in this context, because scientific knowledge and technologies represent the basis of challenging economic, social, and environmental issues, in order to achieve sustainable conditions. The analysis of technological processes can be developed using a thermodynamic approach in relation to the whole system, but also to all its interactions both to the process (inside the technological system), and to the environment and society (outside the technological system). The result is a quantitative assessment of the flows of matter and energy for the system and of the consumption rate of the available resources for the environment. This information can be a key support for policy planning and resource management [427].

Indicators are required also to assess the technological stage, and the development level of industrial processes. Every enterprise implements different production processes, causing different carbon emissions or environmental impacts, thus as concerns the environmental consequences, the process itself results more decisive than the product realised. Several indicators can be introduced to analyse both the environmental impact and the technological level acquired by the countries. Indicators can be defined as [425]:

> *An aggregate, a quantitative measure of the impact of a 'community' on its surroundings (environment).*

It entails that:

- The environmental indicators have to be used for any *community*;
- They are considered as aggregated, because of they are not limited to a single individual;
- They may consider only the effects produced on the environment that surrounds the community under analysis.

As a consequence of these definitions, the community and the environment can be considered as two separate, interacting systems [425], as occurs in thermodynamics, where the system and its environment are considered. The subsequent properties of the environmental indicators can be outlined as follows:

- They have to be assessed using unambiguous and reproducible methods under a well defined set of underlying assumptions;
- They have to be defined by a numerical expression whose results can be ordered in an unambiguous way;
- They have to be calculated on the basis of intrinsic properties of the community and of the environment;
- They have to be normalized in order to compare different communities or environments;
- They should be defined on the basis of the well established laws of thermodynamics.

Moreover, Sciubba analysed in detailed a lot of indicators and pointed out their limits [425], which can be summarised as follows:

- *MTA* (*Material Throughput Analysis* or *Material Inventory Analysis*): an indicator founded on the assumption that the lifestyle of a community may be measured by the global equivalent material flow, related to the production of the commodities on which it thrives. The method involves highly disaggregated accounting of the material inputs/outputs and it requires detailed knowledge on production processes. But, it does not use the second law of thermodynamics;
- *EEn* (*Embodied Energy*): an indicator that obtains a direct measure of the environmental impact. The amount of energy used to build a product, in relation to resources and work done, is assessed, but it does not encompasses any measure of the quality of the energy flows;
- The *transformity*: in the Emergy Analysis the energy accounting is considered, but the fundamental assumption is that the only input form of energy is the solar radiation. All other flows of matter and energy are related to equivalent solar energy necessary to obtain them. This evaluation is carried out by using a proper set of coefficients, the transformities. It does not include any measure of the different quality of the energy flows.

One charachteristic that can be highlighted in these methods is that they do not take into account the energy quality, even if this property results fundamental in the analysis of the technological level involved in a process. Indeed, just in the early '80s, Wall and others thermodynamicists analysed territorial systems by introducing exergy flows balance, related to the first and second law of thermodynamics [425]. Exergy introduces considerations on the quality of the energy used. The focus of this PhD Thesis is the exergy dissipation, due to its link to the available energy dissipated into the environment; indeed, the less is its value the higher is the technological level used in a process.

Furthermore, in relation to the global economic development and population growth, an increment of the energy demand in all sectors can be conjectured; if we consider the analysis of the world energy consumption related to 1965, it resulted in 155.69 EJ, while in 2021 it resulted 595.15 EJ [66], with an interlinked decrease in its availability, and the requirement of changing the energy use and production, before 2050 [20].

As a consequence of all the previous considerations, a new approach is needed for the analysis of sustainability [113].

1.3 The Sustainable Development & its link with thermodynamics

Sustainability lays down its roots in the concept of sustainable development. This concept was introduced during a prosper period of development for many societies and technologies, in the early ’70s by means of the work, commissioned by the Club of Rome, *The limits to Growth* [307]. The latter presented the earliest environmental concerns, related to the effects of the demographic and economic growth, with particular regards to the presence of finite and limited natural resources, highlighting the limits and constraints imposed by the Earth system. Thus, the human-planet interaction was simulated by means of five variables hypothesised to growth exponentially: i) population ii) non-renewable resources consumption, iii) industrialisation, iv) pollution, and v) food, while the technological ability to improve resources was simulated with a linear behaviour. Three different scenarios were obtained by changing the variables growth trends. The authors concluded that without switching the increasing behaviour of exploitation of resources, a limit would have been achieved within hundred years, with a possible related abrupt peak in demographics and industrial capacity. Moreover, it was highlighted that for each citizen a basic material need should be satisfied, in order to have an equal opportunity to realize his individual potential. Thus, in 1972 the need to integrate conservation with development for all citizens already came out, with the requirement to manage sustainably the Earth’s *limited* resources.

The term sustainable development was firstly used in an official document in 1980, with the *World Conservation Strategy Report* [220], where the need for a global strategy to administrate resources was highlighted, in relation to ecosystems, and the counter-effects of local actions on the whole system. Nevertheless, the most commonly cited definition of sustainable development is the one that was introduced in 1987, with the release of the Brundtland report. There, the definition of sustainable development was clearly stated as [524]:

> *The Development that meets the needs of the present without compromising the ability of future generations to meet their own needs*

But, in the human history, business activity has been highlighted always to be dominated every stage of the value creation and production chain [113, 513]. These activities use a great amount of resources with impact on the natural environment [113].

Sustainability is an interdisciplinary topic of research, so different approaches have been developed in order to supply the implications of sustainability related to the economic value, to the societal and human aspects of business behaviour, to the industry and technological level, to the environmental and resource impacts of products and services. So, the Life Cycle Analysis (LCA) has been developed, on the bases of the efficient use of resources at each stage of the process, for products and services, analysing design, manufacture, distribution, use, end-of-life of the products, and CO_2 emission. But, the economic, environmental and social sustainability, i.e. the business's processes, must also be considered. In fact, sustainability implies also socio-economic equity, which is related to the social well-being of the society and employees.

Thus, sustainable development results as a completely multi- and inter-disciplinary topic, that combines together economy, science, engineering, educational and social sciences, even if these disciplines maintain their specific methodologies and approaches for its study. But, a unified approach is required to be concrete. In this context, an indicator can be introduced in order to highlight both the economic needs of analysis and the engineering optimisation, with the aim of considering the social consequences, too. In fact, indicators have many functions [481]:

- They should simplify, clarify and aggregate information in order to consent the policy-makers to perform consciously their decisions;
- They should include engineering and social sciences information into decision-making, by measuring and calibrating progress toward sustainable development;
- They should emphasize eventual risks in order to prevent economic, social and environmental set-backs.

In literature, a great number of indicators exist for the analysis of sustainability [481], so, in order to develop a new viewpoint for an effective approach, a subset of indicators must be identify on the bases of three fundamental criteria [481]:

- They should cover issues relevant for sustainable development in as large amount as possible countries;
- They should supply crucial information for policy-makers;
- They should be calculated for most countries, with data available within reasonable time and costs.

The result was the disposal of a core of more than sixty indicators, which however are difficult to merge and consider contextually.

From a sustainable engineering viewpoint, this concept means a constraint which must be added to the technical ones, and the link of the technological indicators to the sustainable ones usually results difficult. In order to avoid this difficulty, a new rational approach to sustainable policies, based on concrete designing and effective results, is required.

In the '80s, reconsiderations on the optimization of energy and process systems started [118], and Bejan proved that maximum power corresponds to minimum entropy generation rate [36], or maximum entropy generation, in accordance with the Gouy-Stodola theorem. Consequently, entropy generation analysis resulted a design tool to recognize system improvements, but also a measure of sustainability for processes and technologies. The process, which presents the lower entropy generation rate, results more sustainable, due to its more efficient energy conversion process [251, 202].

Furthermore, the introduction of thermodynamics in the analysis of economy and society, was developed by many authors [167, 226, 228, 227, 331]. Thermodynamics has a large amount of applications and an integration of many methodologies for the analyses of both energy and material flows, and economics [332, 233, 556, 552, 538, 543, 527, 523, 429].

During the last three decades, environmental economics has become from a fringe activity to one of the most active fields of economic researches. It has now a major, even dominating, influence within significant areas of policy debate, including global concerns, such as climate change and biodiversity loss. It formulates and analyses the two key issues of concern: the valuation of ecological assets, and the design of policy instruments for their management. These are brought together, in the contemporary study of sustainable development. Thus, environmental economics represents essentially a branch of applied welfare economics. The various methods for the evaluation of external costs and benefits are all open to criticism [188, 189].

As previously cited, the fundamentals of sustainable development are related to economics, environment and society. Consequently, a sustainable system must [195]:

- Be able to supply goods and services, to provide manageable levels of government and external debt and to avoid damages to agricultural or industrial production;
- Provide a stable resource base, biodiversity, atmospheric stability;
- Achieve fairness in distribution, opportunity and adequate provision of social services.

These elements of sustainability bring to a multi-dimensional approach, based on the balance of different needs [195]:

- Economic sustainability means that manufactured capital, natural capital, human capital and social capital have to be maintained over the long term;
- Conservation of ecosystems and natural resources results vital for sustainable economic production and intergenerational equity;
- Social equity has to be the basic element of development and is correlated with environmental sustainability.

Moreover, these considerations are linked to the technological development, and its evaluation in relation to the processes adopted during the production activities. Furthermore, lots of applications of *exergy analysis* were developed in cleaner production, industrial ecology and LCA, for the analysis of depletion of resources, activities and production also in transports and building materials, and to consider and introduce the effects of new and more sustainable alternatives, such as wind and solar power, and bio-fuels [331].

1.4 Circular Economy

Other important necessary framework in which this Research is included, beyond the sustainable development and the energy transition, is the one of circular economy. Indeed, these frameworks result closely interlinked each other, and future choices and actions should be taken by considering them as a whole.

The main feature of the circular economy concept is the new paradigm of switching from the well-tested - but no more sustainable - linear model, based on take-make-dispose sequence in production, to a more circular model. In this model, the economic growth should be decoupled from resources use as long as possible, by reducing and reusing natural resources and wastes. However, it should be noted that circular economy not consists only in the *4R*s paradigm (or the combination of reducing, reusing, recycling and recovering activities), that requires new business models, but even more in a systemic shift of the entire system. The latter should be focused on a sufficiently prosper economic system, where environmental quality has a pivotal role, together with social equity. In this context, an interesting perspective associated to circular economy is the one given in the work of Blosma and Brennan [59], who have applied the Hirish and Levin's *umbrella* notion (which represents a broad concept that is used to encompass and account for a set of different phenomena) to circular economy, highlighting its catalytic function in the resource and waste management and the ability to envelope old and new paradigms under a common framework, pointing out the key role of circular economy in the context of social aspects of industrial ecology, too.

As it has occurred for sustainable development, also circular economy presents several discussed definitions, and related interpretations among different stakeholders and sectors, as the academic, entrepreneurial, policy-making and governmental ones. Many reviews about its definition have been developed during the last decade, such as in Refs. [242, 371]. The abundance of its definitions points out that the circular economy concept presents different meanings for different stakeholders. Among circular economy definitions, the most recurring one, is the one given by the Ellen McArthur Foundation [166]:

> *Circular economy is restorative and regenerative by design and aims to keep products, components, and materials at their highest utility*

> *and value at all times, distinguishing between technical and biological cycles.*

From many viewpoints, including the the European Commission and United Nations Environment Assembly ones, circular economy has been interpreted as an effective way to implement, and a necessary step achieve sustainable development. On the other hand, it has been criticized as a vague and limitless concept, without specific boundaries, or only as a way to manage primary resources. Nevertheless, the fundamental role of circular economy cannot be neglected, due its inclusion within the actual policy framework, specially in developed and developing countries.

1.4.1 The role of Circular Economy in the European context

Circular economy has been set as one of the pivots for the actual and future European policies. Indeed, since 2011, with the development of the *Roadmap to a Resource Efficient Europe* [147], and in 2015 with the *Circular Economy Package*, or *EU Action Plan for the Circular Economy* (CEAP) [149], the European Commission has pointed out the need to improve the European resource efficiency and the transition towards a circular economic approach [135]. This transition is considered the nucleus to achieve the European 2050 climate neutrality target. In order to do so, legislative and non-legislative measures have been introduced to reduce anthropic pressure on the natural capital, and to support the creation of sustainable production chains and new jobs. Thus, circular economy has been designated as one of the bases of the *European Green Deal*, which constitutes the European Agenda for a sustainable growth.

In 2015, the European Commission adopted the *EU Action Plan for the Circular Economy* (CEAP) [149], which consists in a programme of actions, with large ambitions in the context of the whole life cycle of products - from production to waste management - involving also the consumption phase and the secondary raw materials market, in order to close the loops of products life cycles. In particular, this action plan aims to [149]:

- Maintaining in the economy for as long as possible the value of products, materials and resources, and
- Minimising the wastes,

by following sustainable policies, focused on an economy: (i) resource efficient, (ii) low carbon, and (iii) competitive.

In 2020, the European Commission has adopted the *New Action Plan for Circular Economy* (New CEAP), which constitutes the foundations of the *European Green Deal*, that is the European roadmap towards the target climate-neutrality by 2050. The actions proposed within the CEAP aim to lower the European consumption footprint, and to double the circular material use by 2030. Moreover, this document points out the requirement to dispose of a fully developed circular economic system to achieve the carbon neutrality target by 2050. Some of the main proposes of the CEAP concern the following sectors, aiming to ensure less wastes: electronics and ICT, textiles, plastics, construction and buildings, packaging, batteries and vehicles, food. Furthermore, the CEAP included the introduction of a Global Circular Economy Alliance to set a possible international agreement on the management of natural resources.

In 2021, the *Global Alliance on Circular Economy and Resource Efficiency* (GACERE) has been launched. In its working paper *Circular Economy and Climate Change*, some insights on how circular approaches can intensify climate action are provided. The GACERE has highlighted that the present nationally determined contributions (NDCs), established with the *Paris Agreement*, must be collectively modified by increasing at least by three times the ambitions of each country to reach the 2.0°C goal, and by more than fivefold to the 1.5°C target. Moreover, the GACERE has pointed out that the key sectors to achieve the *Paris Agreement* goals in mitigating the anthropic impact on the environment must include energy production and transmission, water, construction, consumer goods or agriculture and food production.

The transition towards a circular economy should preserve markets against scarcity and depletion of resources, volatile prices, by creating new business opportunities, switching from the actual production, consumption and disposal pathways. It is expected to promote the creation of new jobs locally, with related new chances for social integration. Concurrently, it should favour energy saving and reduce anthropic climate pressure, biodiversity loss, and pollution of air, soil and water. Thus, the transition to a circular economy involves multifaceted and multilevel processes. In all this contexts, it results clear the pivotal role of the energy sector, and in wider terms the energy transition must be included within it.

1.5 The need for a measure: Indicators

Sustainability is a multi facet and interdisciplinary concept, with the final goal to guarantee the needs of all people in the next future, enclosing the idea of improving the aspects within the "human system" and outside from it, because of in order to live the main constrain is the forced interaction with its external environment. One of the main issues that actually exist in the context of sustainable development is how to measure actions, policies, processes, etc. in relation to sustainability. In this context, in 2000, the *Millenium Declaration* was signed by the representatives of 189 different countries, who agree to pursue 8 common measurable goals, or the Millenium Development Goals (MDGs). These goals constitute a milestone because of they provided a common agreement to achieve targets for all the actors involved, by means of eight measurable goals, itemised as follows: (i) Eradicating extreme poverty and hunger; (ii) Guaranteeing universal primary education (iii) Ensuring gender equality; (iv-v) Reducing child mortality and improving maternal health; (vi) Fighting against diseases such as HIV, malaria, etc.; (vii) Ensuring environmental sustainability; (viii) Developing a global partnership for development. Thus, just in 2000 the goal to commonly implement policies related to environmental and socio-economic sustainability was set. In the following fifteen years some progresses have been achieved concerning the MDGs. However, as stated also by the UNs, the achievements were uneven, and the focus was needed to build more sustainable societies, by encompassing social inclusion and equity, economic development and well-being, and environmental protection and preservation, which have to be equally valued. Thus, in the 2012' *United Nations Conference on Sustainable Development* the process to build the *Sustainable Development Goals* (SDGs) started, with the aim to create a more people-centered *Development Agenda*. In 2015, the 17 SDGs were officially approved by the UNs General Assembly, with their related 167 targets. These goals are defined by the UNs as targets for an "*urgent call for action by all countries - developed and developing - in a global partnership*".

Thus, International Organizations, governmental panels, researchers, stakeholders, etc. have tackled huge efforts to build and to introduce several sustainability indicators, even if some concerns have came up in their definition and efficient use, in relation to the multi-stakeholder and interdisciplinary process of sustainable development, with the need of considering together all different sectors and actors involved [312, 416, 138]. Consequently, a great number of works have been carried out in developing and reviewing indicators of sustainability, such as in Refs. [321, 529, 61, 314, 336, 457, 158, 151, 136, 279, 327], including some of them recommended to specific sectors, like those related to the energy topic, such as in Refs. [185, 426, 183]. As concerns the role of energy in sustainable development, it is interesting to observe that what may seem us quite obvious, actually has not been so foregone. Indeed, in Figure 1.7 are shown on a time-harrow, the main efforts to include energy in the sustainable development policies. The central role of energy has been somehow underestimated or difficult to be accounted, if we consider that in the 2000 Millenium Development Goals, energy related targets were not considered.

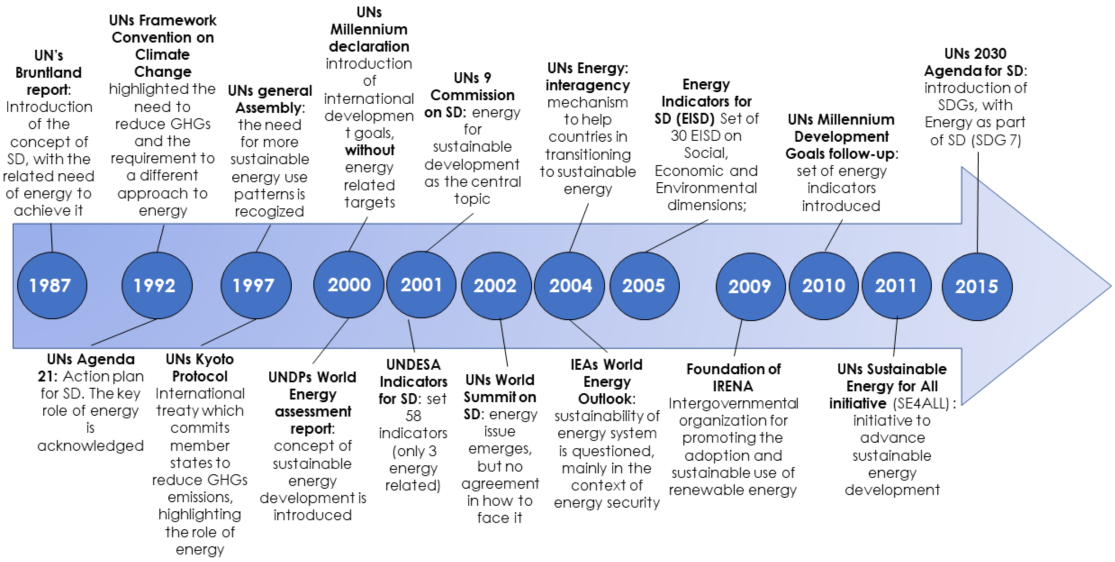

Figure 1.7 The energy role in the context of Sustainable Development (SD), time-harrow from 1987 to 2015.

In this section, a short summary of the more used sustainability indicators is presented, some of their main features are reported in Table 1.3.

The *Index of Sustainable Economic Welfare* (*ISEW*) [103], introduced to be an alternative quantity to the Gross Domestic Product (*GDP*), considers also the different domains of sustainability [104, 105], by it improvement which is the Genuine Progress Indicator (*GPI*), even if the principal weak point of the latter has been identified in the non-unique methodology for its evaluation [354].

The *Ecological Footprint* (*EF*) represents an account-based system of indicators, that takes into account the consumption of the finite Earth resources [275], measuring the consequences of the anthropic behaviours and activities on the environment. It accounts the productive land, effective to support a given population in relation to its consumption level [386, 512, 313], evaluating the anthropic load on the ecosystems and biodiversity: EF encompasses only the environmental domain of sustainability, without presenting an unified method to its calculation.

The *Genuine Savings Indicator* (*GSI*) determines a measurement of the annual change in the total broad capital stocks, giving an indication on how the capital stocks are managed by different societies, with the aim to generate stream of well-being over time [187, 259]. But, recently, as a consequence of its analysis on a Swedish broad time series (1800-2000), no one-to-one relationship between the *GSI* and the well-being has emerged [276].

The *Environmental Sustainability Index* (*ESI*) is a composite index to measure sustainable development, considering 21 different indicators (covering environmental, economic and social aspects), combined together with a finite number of variables (from 2 to 8) [146]. Furthermore, this composite index has undergone many changes has in order to consider other environmental indicators, and human health related indicators, obtaining the *Environmental Performance Index* (*EPI*) [208].

The *Sustainable Society Index* (*SSI*) is another index composed by 22 different indicators, sub-classified in five main groups (i. Personal development, ii. Clean environment, iii. Well-balanced society, iv. Sustainable use of resources, and v. Sustainable world) [501]; all these aspects have not been aggregated into an overall score, because of the correlation between human and environmental well-being [74].

The *Climate Change Performance Index* (*CCPI*) gives information on the climate protection level of the countries, which, at present, emit more than 90% of global energy-related CO_2 emissions. Its value is the results of the overlap of three main categories, weighted in different way in relation to emissions trend, emissions level and climate policies [73].

The *Economy-wide material flow indicators* are a framework of aggregated indicators introduced by Eurostat, which have their foundations on the economy-wide material flow analysis. These indicators are focused on the environmental domain of the sustainable development.

The same attribute is possessed by the *European Environment Agency* (EEA) *core set indicators* [312]. In parallel, the OECD has proposed its own *Core Environmental Indicators* (*CEI*), too.

Furthermore, the *Living Planet Index* (*LPI*) has been proposed, with the aim of measuring the state of the world's biodiversity, too: it includes data from human pressures on natural ecosystems, related to the consumption of natural resources, also including the negative impacts of pollution.

The *Well-being Index* (or barometer of sustainability) is obtained by combining 36 indicators with other 51 into two indexes, then aggregated in one single index: it gets the measurement of the human well-being in a nation, weighting its relative effect on the environment [312].

The *Happy Planet Index* (*HPI*) was introduced in 2006, as another alternative to *GDP*, with the aim of obtaining a measure of the environmental impact of a nation, with particular regards to the capability of its citizens to conduct long and happy lives. The *HPI* considers 3 variables: i. the Life Expectancy at birth, ii. the Ecological Footprint, and iii. Life Satisfaction. Just the latter represents the main concern about *HPI*, because it constitutes a subjective variable to measure well-being [79].

In the earlies 1990s, United Nations Development Programme proposed the Human Development Index (*HDI*) [483], then updated and improved [485, 486, 203], in order to obtain a multidimensional index, able to measure the development of a country from a socio-economic point of view, focused on human well-being (human centred), by taking into account the social development as reference [405, 203]. The main advantage of this index is the small number of variables considered, even if this advantage represents also its weak point for many researches. The *HDI* is a composite index, which measures a country's average achievements in three fundamental aspects of human well-being. But, the major critique moved to *HDI* is that to be advocated as an indicator of sustainable development, it should take into account the environmental domain. However, by now, *HDI* does not contain information on environmental aspects, which are instead fundamental, examining that life (and consequently also well-being) can occur only in presence of interaction with the external environment.

Table 1.3 Brief list of already existing indexes of sustainability, with the related domains enclosed within each one, with some notes.

Index	Economic	Environmental	Social	Notes
EF	×	✓	×	It covers deeply the environmental domain, measuring the results of the anthropic activities on nature. The main criticism moved to *EF* has been its non uniform definition needed to evaluate it.
ISEW–>GPI	✓	✓	✓	*ISEW* was born to substitute *GDP*, then implemented to obtain the *GPI* by considering the other domains, too. The main concern on *GPI* has been its non-sole definition.
GSI	✓	✓	✓	It includes all forms of capital and measuresdis-savings. However, its account methodology has failed in evaluating the economies and results of some countries.
ESI–>EPI	×	✓	✓	Composite index, combination of 21 indices (derived from 68 indicators), and other variables (up to 8). It has been considered too articulated in its construction, causing methodological issues such as: aggregation problem, cause and effect problem ad weighting variables issues.
SSI	✓	✓	✓	It synthesizes 3 basic dimensions through 8 categories and 21 indicators. Being a complex indicator its most debated point has been the weighting method.
HPI	×	✓	✓	It was born as the counterpart of *GDP*. However it introduces a subjective variable, the Life Satisfaction Index.
HDI	✓	×	✓	It presents the advantage of being simple and widely used. However, the environmental domain is not considered in any form.

1.6 The objective of this PhD Thesis

As the results of the analysis developed in this Section, the concern of reducing CO_2 emissions associated to human activities represents one of the main challenges required in this century. Furthermore, in relation to the global climate change, two main different approaches have been suggested: mitigation [30] and adaptation [359]. In this PhD Thesis, any discussion on adaptation will be developed, but, on the contrary, mitigation by the use of biofuels will be the focus of the research.

Mitigation actions are rooted on the reduction of the CO_2 and GHGs concentrations in the atmosphere, by reducing the emissions, increasing the storage and introducing renewable energy sources. For example, in relation to the transport sector (composed by aviation, maritime, rail, heavy-duty vehicles, light-duty vehicles, passenger vehicles, etc.), its consumption results approximately the 20% of the total global energy produced, accounting for approximately 24% of the total direct CO_2 emissions [217]. Consequently, using alternative fuels (i.e. biofuels) in this sector, and in any other sector where the present technologies can not be replaced by more sustainable ones, can be an answer to reduce their environmental impact [126]. Indeed, decarbonising transport requires a wide range of bio-based fuels [68, 9], especially advanced low carbon fuels. In this context, micro-organisms-based biofuels represent an interesting technology both to improve energy security and to reduce the CO_2 emissions from the transportation sector [12].

Biofuels are derived from biomasses, or from their residues. They contain around 80% of renewable materials constituted by biomass, obtained by photosynthesis processes, which represent carbon sequestration with energy storage and little sulphur content.

Biofuels can be classified in four main categories [125, 398]:

- The first generation: it involves the use of agricultural biomass products, mainly derived from food-based biomasses or *ad hoc* energy crops (i.e. corn, sugar-cane, soybean, oil seeds, vegetables, etc.); consequently, ethical criticisms have been moved in relation to the food supply chain, with the consequence that this generation of biofuels can no more be considered sustainable (this concept has been received also from the newest renewable energy directives). Nevertheless, it represented the first response to energy security and global warming, by involving the use of sugar and lipid platforms, without the need for new infrastructures for feedstock delivery and biomass-to-biofuel conversion [126];

- The second generation: it introduces the use of non-edible biomasses (i.e. cellulose and hemicellulose) and agricultural waste products. However, these biofuels present the issue of not being yet profitable, due to the need of technological improvements for bio-refineries, related to the use of waste lignin as a feedstock for new chemical products [126];
- The third generation: it uses micro-organisms biomasses such as algae, microalgae, yeasts, fungi, bacteria and cyanobacteria; algal technology coupled with wastewater treatment facilities and the anaerobic digestion represent some of the present improvements of biofuels use towards a sharper sustainability;
- The fourth generation: it uses engineered micro-organisms, or genetically modified living organisms, for improving the production of their useful co-products.

Today, the largest production of biofuels consists in bioethanol and biodiesel [125], even if mostly derived from edible crops. It has been highlighted by International organisations and governments that this trend can not be considered sustainable, because of ethical concerns (food competition) and adverse after-effects on the use of land (Indirect Land Use Change) [355]. With the aim of reducing these negative effects, the production of biofuels must be based on alternative methods and feedstock, ensuring policies to obtain biomasses in a sustainable and replicable way [108]. Thus, the interest on bio-refineries with multi-generation technologies is continuously growing by developing also their integration into the already adopted and built fuels networks. In relation to this subject, biofuels based on micro-algae and cyanobacteria may result a significant answer to the above mentioned limitations for biofuels production and use [126], like sustainability, reduction in GHGs emissions, energy conservation, local food security, soil, air, and water protection, land preservation. Therefore, to improve the required circular economy approach, particular attention should be given to those lignocellulosic biomasses that actually do not present any second use, and are disposed of as wastes, causing negative impacts on the environment. Furthermore, other crucial features of sustainability are referred to the biofuel production, such that human and labour rights, rural and social development, technology improvements and wastes treatments [126]. There is the risk that producing biofuels could cause some negative effects on biological diversity *via* land conversion, introduction of eutrophicating species, soil and water consumption in agriculture, habitat loss, and nutrient pollution. Moreover, society, environment, and economy must be considered in order to allow them to get improvement from a sustainable biofuels production and use. All these aspects have to be considered in the study of biofuels production and considering their subsequent next developments.

The basic idea of this PhD Thesis is the application of thermodynamic concepts to socio-economic systems, starting from the analysis of irreversibility. Thermodynamics is a physical theory based on two corresponding concepts: one approach is based on the first and second laws of thermodynamics and leads to engineering thermodynamic analysis of cycles, engines, heat pumps and refrigerators, while the other is the free energy approach, which leads to the concept of interaction in physics and chemistry.

In fact, in relation to natural resources, their thermodynamic quality is not considered by the energy analysis. The latter allows to estimate energy or heat losses, but yields only limited information about the optimal energy conversion. On the contrary, the Second Law of Thermodynamics states that, it is not possible to completely convert the input heat into useful work, while as a consequence of dissipation and irreversibility it is possible that the work is converted into heat, by friction. Thus, the Second Law highlights the requirement of nw thermodynamic quantities for the evaluation of the maximum amount of work that can be obtained in a system by using different energy sources. This parameter is known as the *exergy*; indeed, exergy quantifies the available energy that can be converted from a reservoir with a reference to a specified datum, usually represented by the environmental conditions. It can be interpreted as the thermodynamic quality of the energy. Kline has pointed out that the irreversibility, perhaps better defined as exergy degradation or exergy destruction, can be explained as the dissipated available energy (or exergy) that ends up as random thermal fluctuations of the atoms and molecules in the outflow of physical devices [190, 188, 189].

In relation to the approach and to the measure the sustainable development, the result of this PhD Thesis will be the Thermodynamic Human Development Index $THDI$. This indicator will be developed in order to introduce also the environmental pillar of sustainable development into the HDI, taking into account the GHGs emissions in terms of the fundamental thermodynamic quantity, the entropy generation. In fact, by combining the first and the second law of thermodynamics, the Gouy-Stodola theorem is used, and it represents a powerful tool for the analysis of irreversibility in any process, and in this context, in this PhD Thesis, it will be used also as a measure the related environmental impact.

Chapter 2

Thermodynamic approach to micro-organisms for biofuels production

Summary. In this Chapter, the thermodynamic bases of the biophysical analysis of the micro-organisms behaviour is developed, in order to obtain a model to improve the biomass formation for biofuels production. To do so, first the thermodynamic approach to biosystems is introduced, based on the non-equilibrium thermodynamic analysis of mass transport (ions and metabolites) through the living system membrane. The result is a thermophysical model to improve the efficiency of biomass productions. In this context, irreversibility are introduced and evaluated by the Gouy-Stodola theorem obtaining biophysical and biochemical conditions to constrain the micro-organisms behaviour in order to improve the biomass formation for biofuels production.

2.1 Introduction: The thermodynamic standpoint

Nowadays, fossil fuels still remain one of the main source of energy. But, two weaknesses must ne pointed out [392]:

- The risk of geopolitical turmoil;

- Environmental pollution (well established) and climate change (still discussed).

It has been well established that entropy generation influences many Earth system processes [246, 508, 526], firstly related to the thermal fluxes in the atmosphere, but not only confined to them [243, 245, 244, 508, 526]. Global thermometric measurements, dated from 1850 up now, point out that the last decades have been the hottest in human history [478]; indeed, global temperatures are predicted to continually increase by 2-4°C before the end of this century, and the cause of this increase has been identified in the anthropogenic activities related to the emissions of greenhouse gases.

At the 2017 UN's IPCC Conference held in Morocco (Marrakesh), it was proposed a limitation of 2°C temperature increase with respect to the pre-industrial era, in order to prevent exceeding a thermal threshold for *possible disastrous* climate change [478]. Surely, pollution also lowers quality of life due to its human-health and environmental consequences [106, 31]. Consequently, more sustainable practices in human activities are required to be adopted in order to limit the environmental effects of pollution and climate change. This, improvements are required in technologies for power generation and transportation, industrial production, and agriculture. Among the possible strategies to achieve these improvements, a alternative and more sustainable biofuels are highly recommended. Indeed, biofuels offer [333, 116, 86] three main advantages over fossil fuels [263, 267]:

- Availability: biofuels can be obtained from different types of biomasses;
- Technical and environmental feasibility: biofuels can be obtained from biomasses of living organisms that photosynthetically consume, the same amount of CO_2 emitted by the combustion of the same biofuels;
- Economic competitivity: countries can cultivate locally the raw biomass material for biofuels production.

There are three different, classifying generations of biofuels [162]:

- The 1st generation [212], which are obtained from food crop yields and compete directly with food;
- The 2nd generation [407], which are obtained by non-edible biomasses like energy terrestrial crops or wastes from the agricultural, municipal or food

sectors, and compete with non-arable land: in this context, the field residues are very interesting because they are considered wastes without any possible use, and often burned in the field, while their biofuel production could give them an economic value with sustainable consequences;

- The 3^{rd} generation [7], which are obtained from photosynthetic microorganisms like microalgae and cyanobacteria, that can grow on non-arable land and in saltwater or brackish waters with no need for pesticides, fungicides or herbicides. These biofuels do not compete with resources of the 1^{st} or 2^{nd} generation feedstocks and are considered more sustainable with respect to maintenance of biodiversity [114, 97], ethical responsibility, energy and costs requirements [84, 94, 299, 367, 558, 270, 395]. However, 3^{rd}-generation biofuels aren't yet as competitive as fossil fuels due to their higher costs of production and maintenance, in relation to the amount of fuel obtainable per unit volume of culture [144].

In this context, microbial, phototrophic biofuel production requires scientific interest in relation to its modelling, simulation, analyses, in order to optimize its production [323, 412, 462]. A thermodynamic approach has been highlight as a fundamental tool for biophysical processes [236].

Micro-organisms outer membranes, comprised typically of phospholipids and proteins, are crucial for life. Such microorganisms continuously interact with their environment through such membranes, and modify it via secretion of enzymes, toxins or pheromones, and macromolecules on their outer membrane surfaces. Outer membranes represent a partial barrier to the diffusion and/or active transport of water-soluble compounds and isolate the cytoplasm from external environment [294]. Membranes modulate inflow of nutrients and outflow of waste products with a consequent restoration of ionic gradients varied by the transport systems. Cells maintain their ionic concentration at a pH of ~ 7.5, usually 10 mmol L^{-1} for Na^+, 200 mmol L^{-1} for K^+, and 0.1 mmol L^{-1} for Ca^{2+}, etc., by using external sources of energy like adenosine triphosphate (ATP) hydrolysis generated by electrochemical ion gradients [294]. Indeed, microbial electrical signalling was experimentally proven to regulate a great variety of physiological processes like cellular proliferation [460], which is mediated by membrane electric potential [374, 448, 303].

Many theoretical modelling and computational studies have been developed on cellular membrane mechanics, but they are not able to give a comprehensive description of membrane dynamical and chemical behaviour [21], leaving open some questions on the membrane behaviour [410, 439, 238, 112, 201, 95, 379, 460].

In this PhD Thesis, I consider the thermophysical result obtained at the Department DENERG on cancer interaction with environment, always experimentally confirmed both from oncologic results [541, 463, 420, 110] and from ophthalmologic studies [438, 43]. Thus, based on the irreversible thermodynamic approach developed at DENERG, I wish to further determine how known conditions of micro-organisms environments can be used to control and improve biofuel production. In particular, I extend to microbial life cycle the thermophysic simplified model based on a Peltier-Seebeck transition in membrane ion fluxes, in order to predict the influence of outer membrane potential in microbial behaviour and biofuel production. By the Peltier-Seebeck analogy, microbial life cycles are represented by two thermodynamic processes:

- Continuous microbial energy generation (metabolism), due to ion fluxes: ionic and metabolic fluxes are described by imposing a null heat flux;
- Continuous heat fluxes from microbial cells to their environment: the outwards heat transfer from cell to its environment is described by imposing null ion fluxes.

This allows the analysis of the thermodynamic behaviour of the micro-organisms. Indeed, the recent results on the structure information on proteins have been highlighted their useful application in nanotechnology. The requirement to develop more studies emerged, in order to obtain a quantitative understanding of a comprehension of the complex phenomena in the bio-systems. In particular, bio-systems have been highlighted to be open systems able to convert energy in the most efficient way by the transport of energy and mass through their membrane [127]. Indeed, the adaptative bio-systems adapted behave in some different way [127]:

- The evolution towards maximum statistical thermodynamic disorder [510];
- The spontaneous sustenance of a high degree of organization, for which living organisms need to pair chemical and metabolic reactions with transport processes [82], which occur irreversibly and they may pair obtaining a new effect.

In this context, irreversible thermodynamics represents a fundamental tool for the investigation of the transport processes and the micro-organisms biophysical and biochemical behaviour, with the aim of their control in bio-refineries. Indeed, the analyses of living systems have highlighted the bases for their living activities [419]:

- Bio-systems are able to convert an exergy source into entropy;
- Bio-systems must be in a state far-from-thermodynamic equilibrium;
- Bio-systems are constituted by subsystems.

Therefore, life results an organizational process, from cooperation among components, with an interconnection among sub-systems and super-systems, such that the survival of the super-system requires to export equal or more entropy products than its sub-systems produces, towards maximum conversion of available exergy sources to entropy products [419]. Thus, biochemical reactions produce or consume external metabolites, accumulated inside the system, and they connect internal metabolites, in constant concentrations in the cells at their steady states [373].

The exergy of a system is defined as the maximum shaft work that could be done by the composite of the system and a specified reference environment that is assumed to be infinite, in equilibrium, and ultimately to enclose all other systems: the environment is specified by stating its temperature, pressure and chemical composition [41]. Exergy is not simply a thermodynamic property, but rather it is related to the reference environment [41]. Exergy is a measure of the potential of the system or flow to cause changes, as a consequence of not being completely in stable equilibrium relative to the reference environment.

2.2 Concepts from equilibrium thermodynamics

Equilibrium thermodynamics is essentially concerned with the study of heat and temperature. Following the usual historical approach, thermodynamics began in 1822 with Fourier's publication of the *Théorie analytique de la chaleur*, where he was able to derive the partial differential equation for the temperature distribution in a rigid body [320].

Then, in 1824, Sadi Carnot introduced the bases of thermodynamics as a science for engineers, with his book *Réflexions sur la puissance motrice du feu et sur* *les machines propresà développer cette puissance* [320]. Carnot understood the fundamental role of the steam power in the context of the industrial revolution, with its implications in economical and social life.

Improvements in the scientific development of thermodynamics were given by James P. Joule, who experimentally proved that heat is a form of energy, laying the foundation for the future formulation of the first law of thermodynamics [320].

In 1851, William Thomson (Lord Kelvin) introduced in his *On the dynamical theory of heat*, the conjecture that the mechanical action of heat could be interpreted by referring to two laws, later recognized as the first and second laws. In this context, Clausius[1] first introduce the concepts of *internal energy* and *entropy* [320].

In the next time, Gibbs[2] made thermodynamics become a deductive science, pointing out the theory of stability by using the properties of convexity for the thermodynamic functions, and laying the foundations for the modern chemical thermodynamics, in his *On the equilibrium of the heterogeneous substances* [320].

Then, equilibrium thermodynamics became the present well structured, universal, and undisputed science under the contributions of Carathéodory[3], Cauchy[4], Clapeyron[5], Duhem[6], Einstein[7], Helmholtz[8], Maxwell[9], Nernst[10], and Planck[11] [320].

Equilibrium thermodynamics is the macroscopic physical science which describe the transformations of energy in all its forms, based on [247]:

- The concept of state and the state variables;
- The notion of internal energy;

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[1] Rudolf Julius Emanuel Clausius, Köslin, January 2nd, 1822 - Bonn, August 24th, 1888

[2] Josiah Willard Gibbs, New Haven, February 11th, 1839 – New Haven, April 28th, 1903

[3] Constantin Carathéodory, Berlin, September 13rd, 1873 – Munich, February 2nd, 1950

[4] Augustin-Louis Cauchy, Paris, August 21st, 1789 – Sceaux, May 23rd, 1857

[5] Benoît Paul Émile Clapeyron, Paris, January 26th, 1799 - Paris, January 28th, 1864

[6] Pierre Maurice Marie Duhem, Parigi, June 10th, 1861 – Cabrespine, September 14th, 1916

[7] Albert Einstein, Ulma, March 14th, 1879 - Princeton, April 18th, 1955

[8] Hermann Ludwig Ferdinand von Helmholtz, Potsdam, August 31th, 1821 – Berlin-Charlottenburg, September 8th, 1894

[9] James Clerk Maxwell, Edinburgh, June 13th, 1831 – Cambridge, November 5th, 1879

[10] Walther Hermann Nernst, Briesen, June 25th, 1864 – Zibelle, November 18th, 1941

[11] Max Karl Ernst Ludwig Planck, Kiel, April 23rd, 1858 – Gottinga, October 4th, 1947

- The notion of entropy, in relation to which Clausius formulated the second law for isolated systems as a principle of entropy increase [236]:

  $$\Delta S \geq 0 \tag{2.1}$$

  Thus, entropy was proven to continuously increase during irreversible processes until it reaches a state of maximum value [247], corresponding to the equilibrium state, such that [325, 236]:

  $$\begin{aligned} dS &= 0 \\ d^2S &< 0 \end{aligned} \tag{2.2}$$

  As a consequence of this result, the enthalpy $H = U - TS$ results minimum at the equilibrium state [325].

But, when a system is not isolated (closed and open systems), the entropy variation can be decomposed into two components:

- One, d_eS, related to the inflow and outflow of energy and matter with the environment: it can be positive or negative;
- Another one, d_iS, related to internal irreversible processes: this component is always positive or null (at the equilibrium state);

so, the total entropy variation results [236, 247]:

$$dS = d_eS + d_iS \geq 0 \tag{2.3}$$

and, consequently, the enthalpy results [265, 247]:

$$dH = -T\, d_iS \leq 0 \tag{2.4}$$

A fundamental result, related to the link of the first to the second law, is the Gibbs' equation, formulated for a closed systems [78, 247]:

$$dU = T\, dS - p\, dV + \sum_{k=1}^{n} \mu_k\, dm_k \tag{2.5}$$

where μ_k is the chemical potential of the $k-$th chemical species and m_k is its mass, while the total number of chemical species is denoted by n.

The Gibbs' equation expresses that internal energy is a single-valued function of extensive state variables, which contains all thermodynamic information about the system. Indeed, introducing the constitutive equation for the internal energy [247]:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,\{m_k\}_{k\in[1,n]}} dS + \left(\frac{\partial U}{\partial V}\right)_{S,\{m_k\}_{k\in[1,n]}} dV + \sum_{k=1}^{n} \left(\frac{\partial U}{\partial m_k}\right)_{S,V,\{m_i\neq m_k\}_{i\in[1,n]}} dm_k \tag{2.6}$$

and comparing it with the (2.5), it is possible to obtain the explicit definition of the internal energy [247]:

$$U = TS - pV + \sum_{k=1}^{n} m_k \mu_k \tag{2.7}$$

from which the Gibbs-Duhem's equation has been obtained, as follows [247]:

$$SdT - V\,dp + \sum_{k=1}^{n} m_k\, d\mu_k = 0 \tag{2.8}$$

which links together the intensive variables that result not independent from one another.

The fundamental problem of equilibrium thermodynamics consists in maintaining a system in the designed equilibrium state; to do so, thermodynamics constraints must be introduced. If some of them are removed, the system will change its equilibrium state into a new one, with the need of finding a tool to determine it, in relation to the operative condition of the system considered.

In this context the Gibbs' free energy, $G = H - TS$ represents a fundamental quantity; indeed, G was proven to reach its minimum at the equilibrium state [265]:

$$dG \leq 0 \tag{2.9}$$

This quantity is very interesting due to its link to the chemical potential, which plays a fundamental role in bio-systems behaviour; indeed, the chemical potential is defined as follows:

$$\mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{S,V,\{n_i\neq n_k\}_{i\in[1,n]}} \tag{2.10}$$

where n is the number of moles of the chemical species. Considering the chemical equation:

$$\sum_{reactants} \nu_{reactants} X_{reactants} \quad = \sum_{products} \nu_{products} X_{products} \quad \Rightarrow \quad \sum_{k=1}^{n} \nu_k X_k \tag{2.11}$$

where ν_k is the stoichiometric coefficient of the $k-$th chemical element X_k, with $\nu_k < 0$ for the reactants and $\nu_k > 0$ for the products. The numbers of moles, dN_k, of the chemical species change in accordance to the condition [503]:

$$\frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \cdots = \frac{dN_n}{\nu_n} = d\xi \tag{2.12}$$

where ξ is the degree of advancement of reaction, such that at the beginning of the reaction $\xi = 0$ and its time derivative, $d\xi/dt$ is related to the velocity of reaction which results null at chemical equilibrium [503]:

$$\frac{dN_k}{dt} = \nu_k d\xi \tag{2.13}$$

and

$$dm_k = \bar{M} \nu_k \xi \tag{2.14}$$

with $\bar{M}$ molar mass.

Chemical reactions supply or absorb heat, the reaction heat, h_r, which can be evaluated by considering the first law of thermodynamics, obtaining the van't Hoff relation [503]:

$$h_r = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p} + T\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \xi}\right)_{T,p}\right]_{p,\xi} = -RT^2 \frac{\partial \ln K(T,p)}{\partial T} \tag{2.15}$$

which is positive for exothermic reactions and negative for endothermic reactions, and $K(T,p)$ is the equilibrium constant, defined as [503]:

$$K(T,p) = \frac{\prod_{products,i} X_{products,j}^{\nu_j}}{\prod_{reactants,i} X_{reactants,i}^{\nu_i}} \tag{2.16}$$

2.3 Concepts from irreversible thermodynamics

In summary, equilibrium thermodynamics develops the analysis of ideal processes which occur at infinitely slow rate, under the hypothesis of as a sequence of equilibrium states. Consequently, for any arbitrary process, this approach allows us only to compare the initial and final equilibrium states, without any possibility to a deep analysis of the process itself. The analysis of physical processes are carried out by introducing an equivalent reversible process, named *quasi-static* process [265]. When a perturbation acts on a thermodynamics system, it is supposed to adapt by changing its state variable very slowly. The fundamental characteristic of the quasi-static process can be summarised as follows [265]:

- The final state of the thermodynamics system is the most stable;
- The thermodynamics state functions can be evaluated at the equilibrium states.

But, in real systems there are no quasi-static processes [265, 372]. Indeed, for complex thermodynamics systems, the relationships among different thermodynamics processes play a central role in their analysis. Thus, in order to develop the study of real processes, with finite evolution time and inhomogeneous effects, the Classical Theory of Irreversible Processes [265, 247], nowadays called *Classical Irreversible Thermodynamics*, has been introduced.

This thermodynamic approach improves the concepts and the tools of Equilibrium Thermodynamics by transposing them at a local scale [247], due to the inhomogeneous characteristics of non-equilibrium states, where the thermodynamic quantities vary both in place and time. This theory was introduced on the bases of the scientific results of some scientists and engineers, among them we can remember Onsager[12] [348, 349], Nobel Laureate in Chemistry in 1968, Meixner[13] and Reik, Prigogine[14] [372], Nobel Laureate in Chemistry in 1977, de Groot[15] and Mazur[16], and Gyarmati[17].

The first aims of Classical Irreversible Thermodynamics can be summarised as:

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[12] Lars Onsager, Kristiania (Oslo), November 27th, 1903 – Coral Gables, October 5th, 1976

[13] Josef Meixner, Percha, April 24th, 1908 – Aachen, March 19th, 1994

[14] Ilya Prigogine, Moscow, January 25th, 1917 – Bruxelles, May 28th, 2003

[15] Sybren de Groot, 1916 - 1994

[16] Peter Mazur, Vienna, December 11th, 1922- Lausanne, August 15th, 2001

[17] Istvan Gyarmati, 1929 - 2002

- Developing a thermodynamic improvement to the classical transport equations of heat, mass, momentum, and electrical charge;
- Providing an approach for the description of the coupling between thermal, mechanical, chemical, and electromagnetic effects;
- Studying the stationary non-equilibrium dissipative states.

The fundamental hypothesis of Classical Irreversible Thermodynamics is the local equilibrium hypothesis, for which the local and instantaneous relations between thermodynamic quantities in a system out of equilibrium are the same as for a uniform system in equilibrium. The local equilibrium hypothesis states that at a given instant of time, equilibrium is achieved by any subsystem of the control volume considered, but any state of equilibrium is different from one subsystem to the other; consequently, mass and energy are exchanged among neighbouring subsystems. Therefore, in each individual subsystem, the equilibrium state changes during time course [504].

In order to evaluate the correctness of this hypothesis two timescales have been considered:

- The equilibration time inside one subsystem, τ_m, related to the microscopic behaviour of the particles component the subsystem;
- The characteristic time related to the range of observation, τ_M, related to the macroscopic behaviour of the system.

The ratio of these two times is named Deborah number *De*:

$$De = \frac{\tau_m}{\tau_M} \tag{2.17}$$

Two possible cases can occur [186]:

- $De << 1$, then the local equilibrium hypothesis is fully justified because the relevant variables evolve on a large timescale τ_M and do not change over the time τ_m;
- $De >> 1$, then the local equilibrium hypothesis is not justified.

As a consequence of the local equilibrium hypothesis, all the thermodynamic variables defined in equilibrium are univocally defined outside equilibrium, even if they can vary with time and space [247]. Moreover, the local state variables are related by the same state equations as in equilibrium. It is particularly interesting for the Gibbs' relation (2.5) between entropy and the state variables. Last, the, locally, the system results stable. From the kinetic theory point of view, the local equilibrium hypothesis [247] is justified only for conditions where the Maxwellian distribution is approximately maintained [265, 247].

Thus, the state variables can be identifies by some theoretical constrained, explicitly required by the thermodynamic approach to irreversibility:

- The state variable are related to the system under consideration, under the degree of accuracy required for the investigation of the process;
- Their timescale is larger enough in relation to the microscopic levels of description;
- Theoretical predictions must always be experimentally confirmed;
- Any result must be reproducible.

So, the local equilibrium hypothesis allows us to build the space of the state variables as an ensemble of extensive thermodynamic quantities, which can be related by the Gibbs' equation (2.5), together with fields of mechanical, equilibrium thermodynamic and chemical quantities. Just the local equilibrium hypothesis allows the definition of temperature and entropy in non-equilibrium conditions [265].

Consequently, any change in the system state is caused by an interaction between the system and its environment: this interaction is evaluated by fluxes through the control surface (the border) of the system [41], with a related set of balance equations [265]:

$$\begin{aligned}
&\frac{d\rho}{dt} = \nabla \cdot (\rho \mathbf{w}) \\
&\rho \frac{dc_k}{dt} = -\nabla \cdot \mathbf{J}_k + \sum_{j=1}^{N} \nu_{kj} J_j \\
&\rho \frac{du}{dt} = -\nabla \cdot \mathbf{q} - \mathbf{P}^t : \nabla \mathbf{W} + \rho\, r \\
&\rho \frac{dw}{dt} = -\nabla \cdot \mathbf{P} + \rho\, \mathbf{F}
\end{aligned} \tag{2.18}$$

where $\mathbf{w}$ is the velocity, w is its modulus, $\rho = 1/v$ is the mass density and v the specific volume, $c_k = \rho_k/\rho$ is the mass fraction of the $k-$th chemical species, $\mathbf{J}_k$ is its fluxes through the border of the system, $\sum_{j=1}^{N} \nu_{kj} J_j$ is its source due to chemical reaction, with N the number of the chemical species involved in the chemical reaction where the $k-$th species is produced, J_j the fluxes of the chemical species involved in the reaction and $\nu_{kj} = \bar{M}_k \nu_k$, with $\bar{M}_k$ is the molar mass of the $k-$th chemical species and ν_k its stoichiometric coefficient, $\mathbf{P} = p\mathbf{I} + \Pi$ is the pressure tensor, with p the hydrostatic pressure, $\mathbf{I}$ the unit tensor, Π the viscous tensor, r is the energy source per unit mass, ":" is the double-dot product such as it can be easily evaluated the Frobenius inner product with an additional transposition on the second dyadic, $\mathbf{A} : \mathbf{B} = \mathrm{Tr}(\mathbf{A}\mathbf{B}^t)$, u is the internal energy, and $\mathbf{F}$ is the external body force per unit mass.

Thus, the entropy rate can be evaluated by considering a control volume bordered by a surface of area A, by introducing the balance equation [247]:

$$\frac{dS}{dt} = \frac{d_iS}{dt} + \frac{d_eS}{dt} \tag{2.19}$$

where [247]:

$$\begin{aligned} \frac{dS}{dt} &= \int_V \rho \, s \, dV \\ \frac{d_eS}{dt} &= -\int_A \mathbf{J}_s \cdot \hat{\mathbf{n}} \, dA \\ \frac{d_iS}{dt} &= \int_V \sigma \, dV \end{aligned} \tag{2.20}$$

where ρ is the mass density, s is the specific entropy, $\mathbf{J}_s$ is the entropy flux, i.e., the entropy crossing the boundary surface per unit area and unit time, σ is the entropy density, named rate of entropy production, i.e., the entropy produced per unit volume and unit time inside the system, V is the volume, A is the area of the border, $\hat{\mathbf{n}}$ is the versor to the border surface, in relation to the control volume. Considering the divergence theorem the Equation (2.20):

$$\frac{ds}{dt} = v \cdot (-\nabla \cdot \mathbf{J}_s + \sigma) \tag{2.21}$$

where v is the specific volume.

In the classical irreversible thermodynamics, for a non-isolated systems, the second law is analytically stated as follows [372, 247, 265]:

$$\left.\begin{array}{ll} \dfrac{d_iS}{dt} > 0 & \text{for irreversible processes} \\[2ex] \dfrac{d_iS}{dt} = 0 & \text{for reversible processes or at equilibrium state} \end{array}\right\} \Rightarrow \sigma \geq 0 \quad (2.22)$$

Considering the balance equations (2.18) into the Gibbs' relation (2.5), from the entropy equation (2.21) it is possible to relate the entropy production rate σ to thermodynamic generalise fluxes $\mathbf{J}_\ell$ and thermodynamic generalised forces $\mathbf{X}_\ell$:

$$\sigma = \sum_\ell \mathbf{J}_\ell \cdot \mathbf{X}_\ell \tag{2.23}$$

The rate of entropy production is important in engineering because it allows as to measure dissipation of energy in systems, in accordance to the Gouy-Stodola theorem for which the power lost for irreversibility $\dot{W}_\lambda$, can be expressed by the following relation [247, 41]:

$$\dot{W}_\lambda = T_0 \dot{S}_g = T_0 \int_V \sigma \, dV \geq 0 \tag{2.24}$$

where $\dot{S}_g$ is the entropy generation rate [41], such that

$$\dot{S}_g = \int_V \sigma \, dV \geq 0 \tag{2.25}$$

and the sign "=" represents the reversible and/or the equilibrium state, while inequality sign ">" represents irreversible and/or stationary state.

Thermodynamic fluxes, $\mathbf{J}_\ell$, have been proven to be linked to the thermodynamic forces, $\mathbf{X}_\alpha$, by a linear relationship [348, 349]:

$$\mathbf{J}_\ell = \sum_\alpha L_{\ell\alpha} \mathbf{X}_\alpha \tag{2.26}$$

where $L_{\ell\alpha}$ are the Onsager's phenomenological coefficients, generally depending on the intensive variables T, p, and c_k, such that they satisfy the Onsager-Casimir's reciprocity relations [85]:

$$L_{\ell\alpha}(\mathbf{p},\omega,\mathbf{B},t)=L_{\alpha\ell}(-\mathbf{p},-\omega,-\mathbf{B},-t) \tag{2.27}$$

where **p** is the momentum, ω is the angular velocity od a rotating reference frame, **B** is an external magnetic field, t is the time, and [348, 349]:

$$\begin{cases} L_{\ell\ell}\geq 0 \\ L_{\ell\ell}L_{\alpha\alpha}-\frac{1}{4}\left(L_{\ell\alpha}+L_{\alpha\ell}\right)^2\geq 0 \end{cases} \tag{2.28}$$

Stationary states play an important role in continuum physics, because the property of the system remain unchanged in the course of time. These states are characterized by the principle of minimum entropy production [372], corresponding to the principle of maximum entropy generation [41], due to the one order of differential between their analytical expressions (2.23) and (2.25).

In the case of non-linear phenomena, the *general evolutionary criterion* was established by Prigogine [373], as follows:

$$d_{\mathbf{x}}\left(\frac{d_iS}{dt}\right)=\sum_{\ell}J_\ell\,dX_\ell\leq 0 \tag{2.29}$$

2.4 Biofuel production from micro-organisms: The results obtained

Micro-organisms can be modelled as black-box thermodynamic engines which exchange exergy and mass with their environment through their outer membranes. Polychromatic light, from the Sun or artificial sources, represents the external heat and light intensity source used for photosynthesis, while external molecular oxygen and organic carbon represents the energy source for aerobic respiration.

Cellular outer membranes are a double lipid layer that separates internally-bound cytoplasm from the cell's external environment. Thermo-physical properties of the outer membranes (i.e. conductivity, convective and radiative heat transfer coefficients, effective diffusivity, thickness, porosity, surface area, etc.) relate to heat and mass transfer, while the optical properties are influenced by the outer membrane as well as the network of internal folded membranes housing organelles (i.e. mitochondria, chloroplasts, Golgi apparatus) or lipid bodies containing neutral triacylglycerides that serve serve as pre-cursors to biofuels. Such optical properties in turn influence the gradient in solar or artificial light intensity and wavelength inside the micro-organisms cell. Outer membrane proteins may serve as channels, across which for the inflows and outflows of mass and ions can occur. These trans-outer membrane fluxes influence internal and external ion concentrations and related pH and trans-internal membrane electric potential variations.

Micro-organisms metabolic and biochemical processes, like cellular aerobic respiration and photosynthesis, are internal thermodynamic transformations needed for cellular maintenance, nutrient uptake, heat dissipation, growth, division, and proliferation. These electrochemical gradients occur across either internal mitochondrial membranes or internal chloroplast thylakoidal membranes and are, respectively, created via electron transport chain with O_2 as final electron acceptor of oxidative phosphorylation or created via proton motif force with $NADP^+$ as final electron acceptor for non-cyclic or cyclic photophosphylation.

An irreversible thermodynamic approach to simulate cellular membrane phenomena can be developed by introducing the Onsager phenomenological relations (2.26):

$$\begin{cases} \mathbf{J}_e = -L_{11}\dfrac{\nabla\mu_e}{T} - L_{12}\dfrac{\nabla T}{T^2} \\ \\ \mathbf{J}_Q = -L_{21}\dfrac{\nabla\mu_e}{T} - L_{22}\dfrac{\nabla T}{T^2} \end{cases} \tag{2.30}$$

where $\mathbf{J}_e$ [A m^{-2}] is the net current density, if the effect of multiple different species of ions are considered, or the effect of one species if only one ion species is considered, $\mathbf{J}_Q$ [W m^{-2}] is the heat flux, $\mu_e = \mu + ze\phi$ [J mol^{-1}] is the electrochemical potential, with μ [J mol^{-1}] the chemical potential, ze [A s mol^{-1}] is the electric charge, and ϕ [V] the membrane potential, T is the living cell's outer environmental temperature [K] and L_{ij} represent the adimensional phenomenological coefficients, such that [236] $L_{12}(\mathbf{B}) = L_{21}(-\mathbf{B})$, $L_{11} \geq 0$ and $L_{22} \geq 0$, and $L_{11}L_{22} - L_{12}L_{21} > 0$ [236].

Following the usual approach of thermodynamics to cycle analysis, the cellular life cycle of micro-organisms can be by modelled by introducing two related processes:

- A continuous energy generation (metabolism), due to the ion fluxes: ionic and metabolites fluxes are described by imposing $\mathbf{J}_e \neq \mathbf{0}$ and $\mathbf{J}_Q = \mathbf{0}$;
- A continuous heat fluxes from microbial cell to its environment: heat transfer from the cell to its external environment can be described by imposing $\mathbf{J}_e = \mathbf{0}$ and $\mathbf{J}_Q \neq \mathbf{0}$.

Consequently, we can divide the cellular life cycle into two thermodynamic processes, in accordance with the thermodynamic approach to complex processes. If the ions and metabolites fluxes occur, $\mathbf{J}_e \neq \mathbf{0}$ and $\mathbf{J}_Q = \mathbf{0}$. Therefore, Equations (2.30) are used to obtain [247] the following relation:

$$\frac{d\mu_e}{dT} = -\frac{L_{21}}{L_{11}}\frac{1}{T} \tag{2.31}$$

with a related heat flux:

$$\frac{du}{dt} = -\nabla \cdot \mathbf{J}_Q \tag{2.32}$$

where u [J m^{-3}] is the internal energy density. Considering the living microorganisms in a fluid, conductive heat transfer can be neglected because it is very small compared to convective and radiative heat transfer. Consequently, living phototrophs exchange heat with their environment primarily by convective transmission and thermal infrared emission. Based on the First Law of Thermodynamics, it follows:

$$\frac{du}{dt}\,dV = \delta\dot{Q} = -\alpha\,(T - T_0)\,dA - \varepsilon_{irr}\,\sigma_{SB}\left(T^4 - T_0^4\right)dA \tag{2.33}$$

where $\varepsilon_{irr} \approx 0.97$ is the emissivity factor [115], $\sigma_{SB} = 5.67 \times 10^{-8}$ W m^{-2}K^{-4} is the Stefan-Boltzmann constant, $\alpha \approx 0.023\,Re^{0.8}\,Pr^{0.35}\,\lambda/\langle R\rangle$ is the coefficient of convection, A [m^2] is the area of the external surface of the cell membrane, V [m^3] is the cell volume, T [K] is the mean temperature of the external surface of the microorganisms membrane, and T_0 [K] is the temperature of their external environment. Equations (2.32) and (2.33), together with the Divergence Theorem, can be combined to yield the heat flux results:

$$J_Q = \alpha\,(T - T_0) + \varepsilon_{irr}\,\sigma_{SB}\left(T^4 - T_0^4\right) \tag{2.34}$$

from which it follows:

$$\dot{Q} = \int_A \mathbf{J}_Q \cdot \hat{\mathbf{n}} dA \approx \alpha (T - T_0) A + \varepsilon_{irr} \sigma_{SB} \left(T^4 - T_0^4\right) A \tag{2.35}$$

Equation (2.30) and the second hypothesis previously introduced ($\mathbf{J}_e = \mathbf{0}$, $\mathbf{J}_Q \neq \mathbf{0}$) are used to obtain the following:

$$\frac{d\mu_e}{d\ell} = \frac{T J_Q}{\left(L_{22}\frac{L_{11}}{L_{12}} - L_{21}\right)} = -\frac{\alpha T (T - T_0) + \varepsilon_{irr} \sigma_{SB} T \left(T^4 - T_0^4\right)}{\left(L_{22}\frac{L_{11}}{L_{12}} - L_{21}\right)} \tag{2.36}$$

where ℓ is the length of microbial outer membrane [m] and $|\nabla \mu_e| \approx d\mu_e/d\ell$. Equation (2.36) represents a link between the microbial outer membrane electrochemical potential and external temperature with heat exchange. Now, Equations (2.34) and (2.36) allow us to obtain:

$$J_Q = \alpha (T - T_0) + \varepsilon_{irr} \sigma_{SB} \left(T^4 - T_0^4\right) \approx -\frac{1}{T} \left(L_{22}\frac{L_{11}}{L_{12}} - L_{21}\right) \frac{\partial \mu_e}{\partial \ell} \tag{2.37}$$

Considering that $\varepsilon_{irr} \sigma_{SB} \left(T^4 - T_0^4\right) << \alpha (T - T_0)$, Equation (2.37) can be simplified as:

$$\alpha T (T - T_0) = -\left(L_{22}\frac{L_{11}}{L_{12}} - L_{21}\right) \frac{\partial \mu_e}{\partial \ell} \tag{2.38}$$

Considering that [177]:

$$\left(L_{22} - L_{21}\frac{L_{12}}{L_{11}}\right) = \lambda T^2 \tag{2.39}$$

where λ is the thermal conductivity [177], the following is obtained:

$$\frac{\partial \mu_e}{\partial \ell} = \frac{\partial \mu_e}{\partial T} \frac{\alpha}{\lambda} \left(T_{surf} - T_0\right) \tag{2.40}$$

which, considering that $\mu_e = \mu + ze\phi$, is used to obtain the following:

$$\frac{\partial \mu}{\partial \ell} = -ze\frac{d\phi}{d\ell} + \frac{\partial \mu_e}{\partial T} \frac{\alpha}{\lambda} \left(T_{surf} - T_0\right) \tag{2.41}$$

The chemical potential is defined as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{k\neq i}} \approx \frac{G}{n_i} = g \tag{2.42}$$

where G [J] is the Gibbs energy, g [J mol^{-1}] is the Gibbs molar specific energy, n is the number of moles, and p [Pa] is the pressure. Gibbs Free energy is related to the membrane electric potential by the Nernst equation [179]:

$$\Delta g = F\,\Delta\phi - 2.3\,RT_0\,\Delta\text{pH} \tag{2.43}$$

where $F = 96485$ A s mol^{-1} is the Faraday constant and $R = 8.314$ J mol^{-1} K^{-1} is the universal constant of ideal gas. Incorporation of Equation (2.43) into Equation (2.41) yields the following:

$$\frac{\partial \mu_e}{\partial T} = \frac{\lambda}{\alpha}\frac{F + ze}{T_{surf} - T_0}\frac{d\phi}{d\ell} - \frac{\lambda}{\alpha}\frac{2.3RT_0}{T_{surf} - T_0}\frac{d\text{pH}}{d\ell} \tag{2.44}$$

Furthermore, the characteristic length in Equation (2.41) is defined as $\langle R\rangle = V/A$ [m]. For this work, the membrane refers to the entire outer cellular envelope. For instance, the cyanobacteria envelope usually consists of an outer gelatinous membrane, a peptidoglycan cell wall and an inner plasma membrane.

The Equation (2.41) represents a fundamental link between the chemical potential gradient and the electric potential gradient across the outer membrane of a photosynthetic micro-organism, the thermo-physical properties of the outer membrane, and the external environmental conditions like temperature, weighted by the Carnot coefficient. The electro-chemical potential variation with temperature in Equation (2.44) depends on the trans-membrane pH gradient. This result agrees with the previously analysed behaviour of lipid membranes and their relationship with external chemical stimuli. In fact, lipid membranes are extremely responsive to chemical stimuli, particularly to pH gradients, as experimentally shown for synthetic membranes [453].

The second fundamental quantity in Equation (2.41) is the characteristic length $\langle R\rangle = V/A$, which represents a geometrical property related to the shape or morphology of microorganisms. Its role is important in heat, mass, momentum, and light transfer. Recently, cell mechano-adaptation was related to the interplay between membrane tension and curvature generation [435, 316], further suggesting a fundamental role of characteristic length in the bio-logical behaviour of microorganisms.

The third fundamental quantity of Equation (2.41) governing microbial behaviour of the microorganisms is controllable, external environmental temperature. In general, as environmental temperature increases and approaches the intracellular temperature of microorganisms, the cellular outer membrane potential increasingly depolarizes. When environmental temperature exceeds the microorganism's intracellular temperature, hyperpolarisation occurs.

Microbial electrical signalling is an overlooked topic of research. Greater interest in the analysis of the cellular membrane dynamics of membrane is emerging. Research on intra- and inter-cellular signalling has pointed out its role in the regulation of fundamental physiological processes [53, 460]. A greater understanding of the effects of the exogenous stimuli and electrophysiology on micro-organisms can be used to enhance biofuel production via synthetic biology or other tools [418]. Indeed, biofuel production is related to cellular growth rate and proliferation, which are in turn controlled by a multitude of factors, including by membrane electric potential and resulting ATP synthesis [250, 380, 231, 459].

As a consequence of the previous processes, a density entropy rate due to irreversibility (dissipation function) is generated:

$$\sigma = -\frac{1}{T_0}\sum_{i=1}^{N}\mathbf{J}_i\cdot\nabla\mu_i = \sum_{i=1}^{N} J_i\frac{z_i e}{T_0}\frac{d\phi}{d\ell} + J_Q\frac{\alpha}{\lambda}\left(1-\frac{T_{surf}}{T_0}\right)\sum_{i=1}^{N}\frac{\partial\mu_{e,i}}{\partial T} \tag{2.45}$$

where T_0 is the environmental temperature, $\sum_{i=1}^{N}\mu_i\mathbf{J}_i$ is the contribution of the inflows and outflows, and μ is the chemical potential. Considering that $\sigma \geq 0$, the condition of control can be obtained for the previous relations:

$$\begin{aligned}\sum_{i=1}^{N} J_i\frac{z_i e}{T_0}\frac{d\phi_i}{d\ell} \geq -J_Q\frac{\alpha}{\lambda}\left(1-\frac{T_{surf}}{T_0}\right)\sum_{i=1}^{N}\frac{\partial\mu_{e,i}}{\partial T} \Rightarrow \\ \Rightarrow \sum_{i=1}^{N} J_i z_i e\nabla\phi_i \geq J_Q\frac{\alpha}{\lambda}(T_{surf}-T_0)\sum_{i=1}^{N}\frac{\partial\mu_{e,i}}{\partial T}\end{aligned} \tag{2.46}$$

which represents a constraint to improve the production of biomass.

The model here obtained is supported by experimental validation in literature [194, 252, 17]. In particular, exogenous electrical stimulus was proven to shape the proliferative capacity of microorganisms, by inducing hyper-polarisation in the cells [460]. Experimental estimation of the energy requirement required by the bacterium *Escherichia coli* to maintain its membrane electric potential is around the half of its total energy consumption [310]. This result highlights the fundamental role of the membrane electric potential in microbial life.

Biomass dry weights and/or cell densities are evidently higher at 37°C (ethanol and acetate result, respectively, 3.43 ± 0.08 g L^{-1} and 0.93 ± 0.12 g L^{-1}, for *Clostridium carboxidivorans* [433]) compared to at 25°C (ethanol and acetate result, respectively, 1.58 ± 0.03 g L^{-1} and 0.61 ± 0.15 g L^{-1}, for *Clostridium carboxidivorans* [433]).

Higher microbial growth temperatures generally shortens the lag period and stimulates nutrient uptake, metabolism, and cellular division [370]. In the thermodynamic model here developed, micro-organisms metabolism is accounted for by the surface temperature, while conditioning is accounted for by the environmental temperature. Particularly for photosynthetic micro-organisms as 3^{rd}-generation feed-stocks to sustainable biofuels, additive and multiplicative Monod's growth law relates microbial growth rate as a function of the limiting nutrient concentration and light intensity [400]. The results of the model here developed regarding the influence of environmental temperature are also validated by the following previous studies [157, 381, 460]: the biomass concentrations (cell dry weights) results for ethanol 3.43 ± 0.08 g L^{-1} and acetate 0.93 ± 0.12 g L^{-1} *Clostridium carboxidivorans* at 37°C [433], higher than at 25°C, (ethanol 1.58 ± 0.03 g L^{-1} and acetate 0.61 ± 0.15 g L^{-1} [433]).

During the second half of the 20th century, many experiments were conducted to measure heat production during microbial growth to evaluate the entropy variation in growing cells and their environment. Thus, growth and decaying rates of dissipated heat, and the maximal rate of self-replication increase with heat dissipation [400]. Furthermore, replication rates increase with higher internal entropy. In this context, the results here obtained suggest to link the active ion flux to heat flux across cellular outer membranes.

Experimental validation of the present results can also be shown in the review [509], where thermodynamics was applied to simulate living microbial cultures and explore their possible practical use. A study of the energy dissipation effects in industrially fermented cultures, both in terms of heat and Gibbs energy dissipation, has been developed by considering experimental techniques for calorimetric measurements, with particular regards to their use for monitoring and control. The analysis of the dissipation of Gibbs free energy, in chemotrophic growth, is a consequence of both accounting for the irreversibility (analytically represented by the entropy production) by metabolic processes in the cells and the driving force (energy sources of the biological processes), for growth and metabolism. Using experimental measurements from growth experiments involving a variety of microbial strains, the model here obtained predicts that the driving force for growth and metabolism decreases as the growth yield increases. It was proven that the Gibbs function and metabolic process rates are inversely proportional.

The modelling results here obtained suggest a predictive tool for metabolic pathway optimization to improve the techno-economics and efficiency of photosynthetic bio-refineries [557]. Indeed, a variation in metabolite exchanges across microbial outer membranes is related to the change of ion concentration and, consequently, to the pH gradient [128].

Now, the question which arises from these results is related on the biological mechanisms to realise the optimisation process obtained. A possible solution could be mutualism. Mutualism is a common type of ecological interaction which describes the ecological interaction between two or more species where each species has a net benefit [67]. Therefore, a proposed immediate application of the model here obtained is the simulation of co-cultivation of two different microbial species, which can enhance intracellular accumulation of lipid biomolecules for biodiesel production [383]. Several studies have investigated the co-cultivation of different micro-organisms to improve their lipid concentration. For instance:

- In Ref. [277], the species *Chlorella pyrenoidosa* and *Rhodospiridium toruloides* were co-cultivated, obtaining 4.60 g_{lipid} L^{-1} (compared respectively to 3.00 g_{lipid} L^{-1} and 3.40 g_{lipid} L^{-1}, respectively for each single species);
- In Ref.[537], the species *Arthrospira platensis* and *Rhodotorula glutinis* were co-cultivated, obtaining 0.467 g_{lipid} L^{-1} (compared respectively to 0.013 g_{lipid} L^{-1} and 0.135 g_{lipid} L^{-1} for the single species);
- In Ref. [356], the species *Chlorella sp.* and *Toluraspore* were co-cultivated, obtaining 2.42 g_{lipid} L^{-1} (compared respectively to 0.052 g_{lipid} L^{-1} and 1.141 g_{lipid} L^{-1} for the single species);

- In Ref. [553], the species *Chlorella sp.* and *Monoraphidium sp.* were co-cultivated, obtaining an improved lipid productivity of 29.52 ± 1.13 $\mathrm{mg_{lipid}}$ $\mathrm{L^{-1}}$ $\mathrm{d^{-1}}$ (compared respectively to 17.99 ± 3.39 $\mathrm{mg_{lipid}}$ $\mathrm{L^{-1}}$ $\mathrm{d^{-1}}$ and 17.70 ± 1.19 $\mathrm{mg_{lipid}}$ $\mathrm{L^{-1}}$ $\mathrm{d^{-1}}$ for the single species).

These examples represent some application of the mutualism in the context of biodiesel production, while other promising consortia [542] are involved in the production of biohydrogen [261], biomethane [337], and bioethanol [300, 441]. These processes use a large amount of exchanged metabolites, molecular signals, and transporters, which induce a variation in the fluxes between the micro-organisms and their environment, through their membrane, with related variation of their membrane potential and pH gradients.

The results obtained in this Section agree with the recent open problems, pointed out in the new frontiers of microbiological researches for industrial use of bacteria [53]. One practical example of industrialised bacterium is represented by the *Bacillus subtilis* which is used in the hydrolysis of polypeptides through its secreted proteases, and in the conversion of amino-acids into advanced biofuels and ammonia fertilizers [258]. Indeed, some experiments on stimulation of the *Bacillus subtilis* membrane by an electric stimulus of 60 mV $\mu\mathrm{m}^{-1}$ AC 0.1 kHz for 2.5 s have been carried out [460], with the result of obtaining a hyperpolarization response: the result is that electrical stimulation generates the efflux of K^+ cations. *Bacillus subtilis* was highlighted to react to external stimuli by maintaining the resting-state membrane potential, but its response requires a consumption of a constant amount of ATP to keep the intracellular K^+ level. Furthermore, the opening of voltage-gated K^+ channels, with the related hyperpolarization due to K^+ efflux, has an effect on the proliferative capacity of the cell [460]. These experimental results represent a further proof of the thermodynamic results and considerations. In fact, cell membranes contain enzymes complexes that further the oxidative phosphorylation along which electrical potential of H^+ ions, and chemical potential of reduced transporters (i.e., NADH, etc.), play a fundamental role in ATP production. Last, mutual interactions among different species can be highlighted to represent an interesting approach to improve the production of biofuels, with a related optimisation of their production.

In this context, the technical potential of macro-algae and micro-algae, bacteria (or micro-organisms in a wide viewpoint) for biomass production and, greenhouse gases abatement can represent a possible response to sustainable energy production.

Indeed, biofuel production from these resources is becoming an interesting topic of research, in particular with possible waste water treatment or polluted natural resources, but also in relation to co-production of high value products for an economic development [525]. Today, algal biofuel production represents an important economic sector for its application in the transportation of people and goods, by trucks, ships and boats, while biomethane represents an important production for domestic and power generation uses.

Around one hundred thousand species of algae are believed to live on the Earth, but only about twenty species of them are involved in industrial and economical processes [525]. Macro-algae produce a great amount of biomass, evaluated in of $7-30$ t $\text{ha}^{-1}\text{yr}^{-1}$, but their major problems are related to the off-shore growth [71]. On the contrary, micro-algae live both in marine and in freshwater environments. They present a photosynthetic mechanism similar to ground plants, but their simple cellular structure, together with their aqueous environment, allows them to obtain a more efficient light energy conversion into biomass [525].

Old and abandoned mines and quarries could represent an ideal location for algae culture, because of:

- There is often water, but polluted, so it is not useful for human use;
- Mines are circumscribed places, so, invasive species could not escape from the site;
- In underground mines, algae can live by using LED light, and the temperature remains constant, too;
- Mines are inexpensive, so, companies can use them for new economic activities, with the social consequence of employment creation;
- Algae support land reclamation, because they sequester metals from previous mining activities.

In this chapter, I wish to highlight the possibility to exploit old and abandoned mines and quarries in order to cultivate and produce biofuels and other useful co-products. So, I develop a preliminary quantitative evaluation of the biomethane and ammonium production from microalgal biomass grown in a typical dismissed quarry in the Alessandria district (Piedmont, Italy), starting from the data collected during a study [368] at the Politecnico di Torino.

The characteristics reported in the study [368] can be summarised as follows:

- Flooded area, named lake: 17 ha;
- Maximum lake depth: 26 m;
- Walkable area: 15 ha;
- Water temperature range in the lake: 5-15°C.

Usually, the depth considered as exploitable, for the microalgal growth in open ponds, is about 30×10^{-2} m [150, 428]. Moreover, the temperature is a crucial factor to select the proper microalgal strain that can grow in the environment conditions considered [58, 159, 430]. There exists an optimum temperature for each species: it usually varies in the range $15-30$°C [255]. At lower temperatures, a limit in the cell growth can occur [475]. In Table 2.1 are reported the range temperatures in which particular microalgal strains have been exposed to verify their growth [466, 382, 544, 446, 8, 210, 10, 72, 152, 141, 464].

Now, in order to determine the theoretical methane and ammonium yields of the anaerobic digestion, it is necessary to known the composition of the examined organic matter [16]. The maximum potential yields can be obtained by considering a theoretical approach (which does not consider the requirements to cell maintenance and anabolism) from the following reaction [440]:

$$\begin{aligned} &\mathrm{C}_a\mathrm{H}_b\mathrm{O}_c\mathrm{N}_d + \left[\frac{4a+3d-b-2c}{4}\right] \mathrm{H_2O} \longrightarrow \left[\frac{4a-3d+b-2c}{8}\right] \mathrm{CH_4} + \\ &+ \left[\frac{4a+2c+3d-b}{8}\right] \mathrm{CO_2} + d\, \mathrm{NH_3} \end{aligned} \tag{2.47}$$

The specific theoretical methane yield $[\mathrm{L_{CH_4}} \mathrm{g_{TS}^{-1}}]$ (TMY) can be evaluated as follows [440, 199]:

$$TMY = \frac{\tilde{V}_{\mathrm{CH_4}}}{8} \, \frac{4a+b-2c-3d}{12a+b+16c+14d} \tag{2.48}$$

being $\tilde{V}_{\mathrm{CH_4}}$ the normal volume of $\mathrm{CH_4}$.

Table 2.1 Growth temperature range for some microalgal and cyanobacteria strains presented in literature.

Specie	Range of temperature [°C]	Ref.
Ankistrodesmus falcatus	$5.0 - 35.0$	[466]
Arthrospira maxima	$16.0 - 33.3$	[447]
Arthrospira platensis (*Spirulina*)	$15.3 - 33.3$	[122]
Asterionella formosa	$-7.3 - 29.8$	[382]
Botryococcus braunii	$5.0 - 45.0$	[544]
Chaetomorpha valida	$17.0 - 32.0$	[446]
Chlorella minutissima	$10.0 - 35.0$	[8]
Chlorella pyrenoidosa	$5.2 - 45.8$	[382]
Chlorella sorokiniana	$13.0 - 45.0$	[210]
Chlorella vulgaris	$4.0 - 28.0$	[10]
Cryptomonas marssonii	$-2.4 - 30.0$	[382]
Euglena gracilis	$13.3 - 32.0$	[72]
Haematococcus pluvialis	$14.0 - 28.0$	[152]
Oscillatoria aghardhii	$5.0 - 35.0$	[466]
Scenedesmus acutus	$15.0 - 40.0$	[141]
Scenedesmus sp.	$-3.1 - 32.7$	[382]
Tetradesmus obliquus	$25.0 - 40.0$	[464]

From the Equation (2.47), it can be estimated the ammonium production yield TAY [mg $\mathrm{g}_{\mathrm{TS}}^{-1}$] [440]:

$$TAY = \frac{17 \cdot 10^3 \cdot d}{12a + b + 16c + 14d} \tag{2.49}$$

Moreover, when the composition of the organic matter considered is known, it is possible to estimate the biomethane higher calorific value obtainable from the biomass, by using the empirical Du Long equation Ref. [199], expressed in [MJ kg_{TS}^{-1}]:

$$HHV = \frac{1}{100} \cdot \left(34.1\ \mathrm{C} + 102\ \mathrm{H} - 9.85\ \mathrm{O} + 6.3\ \mathrm{N} + 19.1\ \mathrm{S}\right) \tag{2.50}$$

where C, H, O, N and S are respectively the carbon, hydrogen, oxygen, nitrogen and sulphur biomass percentage content in the microorganism.

Thus, in order to show a set of preliminary data on the theoretical methane yield and ammonium production, that can be obtained from some microalgae and cyanobacteria strains, I have considered an average composition and some biomass productivity values from literature data, as reviewed by Li *et al.* [273].

Following the theoretical approach suggested by Sialve *et al.* [440] and Heaven *et al.* [199], I have obtained the theoretical methane yield and the ammonium production, considering the following mean microalgal composition, as reported in [16]:

- Proteins: $C_{2.5}H_{3.5}O_{1.0}N_{0.5}$;
- Carbohydrates: $C_{6.0}H_{10.0}O_{5.0}$;
- Lipids: $C_{57.0}H_{104.0}O_{6.0}$.

In Table 2.2, the theoretical methane yield and ammonium production for the main components (proteins, carbohydrates and lipids) are summarised, calculated by using the Equations (2.48) and (2.49), by referring to the above reported mean chemical composition.

Table 2.2 Potential methane yield (TMY) and ammonium production (TAY), evaluated by using Equation (2.48) and Equation (2.49), and the average mean proteins, carbohydrates and lipids content given in Ref. [16]

Compound	TMY $\left[\mathrm{L_{CH_4}}\ \mathrm{g_{TS}^{-1}}\right]$	TAY $\left[\mathrm{mg}\ \mathrm{g_{TS}^{-1}}\right]$
Proteins	0.496	150
Carbohydrates	0.415	–
Lipids	1.015	–

By considering the average value of the percentage composition in proteins, carbohydrates and lipids given in Ref. [273] for some microalgal and cyanobacteria strains, it is possible to calculate their specific theoretical methane yield and the ammonium production, as shown in Table 2.3. Moreover, following Nwoba *et al.* [338], the mean value of biomass productivity given in Ref. [273] has subsequently been divided by a factor of 2.1, in order to consider the differences between the culture systems adopted. This value has been obtained by comparing the same strain microalgal growth in a photobioreactor with open ponds [338]. So, the productivity of the same culture in a photoreactor results 2.1 times higher than the one on open ponds. The latter presents a reduced productivity due to the external environmental conditions.

Table 2.3 Mean biomass productivity (P), average theoretical methane yield (TMY), ammonium production (TMY) and higher calorific value (HHV), calculated by using the average percentage composition values for some microalgal and cyanobacteria strains given in Ref. [273].

Strain	P [g L^{-1} d^{-1}]	TMY [L$_{CH_4}$ g$_{TS}^{-1}$]	TAY [mg g$_{TS}^{-1}$]	HHV [MJ kg^{-1}]
Arthrospira maxima	0.23	0.451	81.04	18.72
Arthrospira platensis	2.18	0.420	61.62	17.13
Botryococcus braunii	0.02	0.368	27.22	14.37
Chlamydomonas rheinhardii	1.41	0.521	59.39	20.81
Chlorella sp.	1.26	0.625	67.43	24.78
Chlorella pyrenoidosa	0.525	0.576	72.63	23.21
Chlorella vulgaris	0.11	0.644	67.43	25.47
Haematococcus pluvialis	0.055	0.553	59.39	22.12
Isochrysis galbana	0.915	0.443	33.41	17.31
Scenedesmus obliquus	0.039	0.559	41.94	21.74

Now, following the literature results, in relation to the quarry considered, I consider that the microalgae are cultivated in the first 15 cm of depth. Moreover, we consider that we can harvest them leaving at least the 50% of them, in order to allow them to continue their reproduction. Under these hypotheses, it is possible to evaluate, the annual energy data, for each strain, as summarised in Table 2.4.

In relation to the last data available for the methane energy consumption of the Alessandria district, which is reported to be 599471 GJ yr^{-1}, the annual energy values for each strain (Table 2.4) is considered as a possible supply source for the Alessandria district consumption. Consequently, we can highlight that the use of the quarry lake for the biomethane production from microorganisms could represent a sustainable supply, in order to reduce the consumption of fossil fuels.

Indeed, human life is related to a clean and healthy water, air, and environment, because humans need water to drink, water to grow food, unpolluted air to breathe, etc.

Recently, the growing pollution due to human activities has been pointed out. Today, we must intervene in order to obtain a mitigation of the increase of the global mean temperature and a reduction of pollutants and greenhouse gasses emissions.

Table 2.4 Mean annual energy which can be theoretically obtained from the quarry lake considered for the different algal species, introducing the previously cited hypotheses.

Specie	Annual energy [GJ yr^{-1}]
Arthrospira maxima	9540
Arthrospira platensis	82757
Botryococcus braunii	637
Chlamydomonas rheinhardii	65037
Chlorella sp.	69196
Chlorella pyrenoidosa	26998
Chlorella vulgaris	6208
Haematococcus pluvialis	2696
Isochrysis galbana	35106
Scenedesmus obliquus	1879

A possible contribution to sustainable activities can be obtained by using biofuels, with particular regards to biodiesel for heavy transportation, and biomethane for energy production and domestic uses.

In this paper, we suggest the use of the dismissed mines and quarries to produce biofuels for energy and domestic uses. In particular, we have taken in consideration a typical dismissed mine in Piedmont, in order to develop a theoretical quantitative evaluation of biomethane and ammonia production from microorganisms biomass and the annual energy obtainable from them. It have been registered 378 dismisses mines and quarries only in Piedmont [3]. Consequently, in relation to the previous theoretical evaluations and the great number of quarries and mines present in Italy, it could be interesting to develop studies to design future possible exploitation of this solution to obtain biofuels in a sustainable way, recovering dismissed places which can not be used in an alternative way.

Biofuels represent an economic opportunity with important environmental consequences, in relation to the reduction of climate emissions from the transport and energy sector. Biofuels are mainly produced from land based crops, with negative consequences on the agriculture. This effect is the well known Indirect Land Use Change [355].

In order to reduce this effect, it is important to produce biofuels in different ways. In particular, the use of the dismissed mines could be interesting, in order to upgrade them towards new sustainable economic activities, with social and ecological consequences for the districts where they are located. Indeed, the dismissed mines represent polluted areas, often abandoned, without activities, with the request of restoration. Brown et al. [70, 69] has investigated the possibility to use reclaimed surface mines in order to cultivate switchgrass to produce lignocellulosic biomass for biofuels production. Shang et al. [432] has studied the opportunity of exploiting the wasted water of mining industry coming from dewatering, for on-site microalgae cultivation in raceways, for biodiesel production.

If we consider dismissed mines as a new opportunity for the sustainable development, we can produce biomethane, biofuels and other chemical substances, with possible markets. In this way, these sites represent a new opportunity of economy for their district. Moreover, new activities require new workers. In this way, also social benefits can be obtained by these sites.

Thus, exploiting the abandoned mines to cultivate and produce biofuels by micro-organisms, such as microalgae, is a viable way to give a new lease of life to abandoned places, dispersed in our territories.

Moreover, micro-organisms can be a viable pathway to obtain biomass feedstock, for the biofuels production [559], due to different characteristics:

1. They are almost a continuous source in terms biomass supply, presenting a non seasonality for their harvesting [417];
2. They are able to growth in all types of water: freshwater, seawater, but also wastewater; thus, a fewer freshwater consumption is possible for their cultivation, including the use of areas not otherwise exploitable [299, 363];
3. They present a shorter doubling time during their exponential growth (usually below than 3.5 h) [94];
4. They have a high potential yield per unit of cultivated area, if compared to land-based crops, which results in a biofuel yield 10–10^2 times greater [123];

The result of this Chapter is the fundamental role of mutualisms in bio-refineries in relation to the control of the heat and mass fluxes trough the micro-organisms membrane in order to improve the biofuels production. But, the sustainability of this approach must be investigted, too. So, in the next Chapter, sustainability will be analysed by a thermodynamic approach in order to obtain an indicator to measure the sustainable development, based on thermodynamic analysis of irreversibility, linked to socio-economic condition of people.

Chapter 3

The Thermodynamic Human Development Index: An index to measure the sustainable development

Summary. In this Chapter, starting from the results previously obtained, the role of the entropy in the complex systems is introduced, in order to develop an approach to industrial processes, based on the exergy analysis. Then, the the United Nations socio-economic index is analysed and improved, obtaining a new thermodynamic index, which results a link between the socio-economic and the environmental issues. Last, the application of this new index brings to an approach of optimisation, where mutualism emerges as the condition for the improvement of the biomass formation for biofuels production.

3.1 Entropy in complex systems

The science that deals with energy and with the best use of available energy resources is the engineering and technical thermodynamics, including all aspects concerning energy and energy transformation, including power production, refrigeration, and the relationships among the properties of matter.

Energy is a thermodynamic property of a system, and that during an interaction, it can change from one form to another but the total amount of it remains constant [41]. The second law of thermodynamics states that energy has quality as well as quantity, and actual processes occur in the direction of decreasing quality of energy. Thermodynamics plays a key role in the analysis of systems and devices, in which energy transfer and energy transformation take place. Dincer and Cengel emphasize that *Nature allows the conversion of work completely into heat, but heat is taxed when converted into work* and, also, *a careful study of this topic* [energy] *is required to improve the design and performance of energy-transfer systems.* [131].

Entropy results the quantity useful to describe the progress of non-equilibrium dissipative processes [373]. Indeed, irreversible open systems develop on the thermodynamic path that maximises their entropy generation, under their present constraints [41].

The principle of maximum variation of entropy due to irreversibility is considered an important result in thermodynamic engineering, because it is a global theoretical approach to the analysis of the stability of open systems.

Classical science emphasized equilibrium and stability, while, more recently, it was pointed out the role of fluctuations, instability and evolutionary processes: irreversible processes are observed everywhere symmetry is broken. In thermodynamics the distinction between reversible and irreversible processes has been introduced by using the concept of entropy so that its formulation is fundamental for understanding thermodynamic aspects of self-organization, evolution of order and life that we see in Nature as it is recently pointed out [131].

The introduction of entropy in classical thermodynamics is related to equilibrium state and reversible transformation. In that context, entropy is a state function depending only on the equilibrium state of the system considered and only entropy differences can be evaluated [78]. The introduction of entropy generation comes from the necessity to avoid inequalities and use only equation from mathematical point of view. Nothing is really *produced* [373, 265]. Indeed, the second law states:

$$\oint \frac{dQ}{T} \leq 0 \tag{3.1}$$

defining the total entropy as [236]:

$$S = \int \left(\frac{\delta Q}{T} \right)_{rev} = \Delta S_e + S_g \tag{3.2}$$

then S_g is considered the generated entropy and it is always $S_g \geq 0$ and defined as [41]:

$$S_g = \int_{\tau_1}^{\tau_2} \dot{S}_g d\tau \tag{3.3}$$

with

$$\dot{S}_g = \frac{dS}{d\tau} - \sum_{i=1}^{n} \frac{\dot{Q}_i}{T_i} - \sum_{in} \dot{m}_{in} s_{in} - \sum_{out} \dot{m}_{out} s_{out} \tag{3.4}$$

and τ_1 and τ_2 the initial and final time of the process.

The quantity ΔS_e should be better defined as the entropy variation that will be obtained exchanging reversibly the same *fluxes* throughout the system boundaries. Thus entropy results a quantity which characterizes the thermodynamic state, while the component due to internal irreversibility, S_g, measures how far the system is from the state that will be attained in a reversible way [265].

In the second law analysis the definition and identification of the thermodynamic system is fundamental.

The open thermodynamic system has been analytically introduced in terms of advanced analysis in Refs. [41, 77]. Here, its phenomenological description is summarized as follows. Let us consider an open continuum or discrete N particles system. Every $i-$th element of this system is located by a position vector $\mathbf{x}_i \in \mathbb{R}^3$, it has a velocity $\dot{\mathbf{x}}_i \in \mathbb{R}^3$, a mass $m_i \in \mathbb{R}$ and a momentum $\mathbf{p}_i = m_i \dot{\mathbf{x}}_i$, with $i \in [1, N]$ and $\mathbf{p} \in \mathbb{R}^3$. The masses m_i must satisfy the condition:

$$\sum_{i=1}^{N} m_i = m \tag{3.5}$$

where m is the total mass which must be a conserved quantity so that it follows:

$$\dot{\rho} + \rho \nabla \cdot \dot{\mathbf{x}}_B = 0 \tag{3.6}$$

where $\rho = dm/dV$ is the total mass density, with V total volume of the system and $\dot{\mathbf{x}}_B \in \mathbb{R}^3$, defined as $\dot{\mathbf{x}}_B = \sum_{i=1}^{N} \mathbf{p}_i$, velocity of the centre of mass. The mass density must satisfy the following conservation law:

$$\dot{\rho}_i + \rho\nabla \cdot \dot{\mathbf{x}}_i = \rho\Xi \tag{3.7}$$

where ρ_i is the density of the $i-$th elementary volume V_i, with $\sum_{i=1}^{N} V_i = V$, and Ξ is the source, generated by matter transfer, chemical reactions and thermodynamic transformations.

For such system, the principle of maximum entropy generation was analytically shown [265]:

> *In a general thermodynamic transformation, the condition of the stability for the open system steady states consists of the maximum of the entropy generation.*

3.2 Energy and exergy analysis in industrial processes

In the last decades, the concept of exergy has gained increased interest in engineering applications [4, 315, 145]. But, on the other hand, exergy results still uncommon in the analysis of industrial processes, with particular regards to energy and materials sectors, but, overall, to economics.

The concept of exergy provides an estimate of the minimum theoretical resource requirement of a process, and this represents information on the maximum savings that can be achieved by making use of new technology and new processes [249].

In physics energy is usually defined as the ability to perform work, but in engineering this definition must be reintroduced as the ability to produce shaft or useful work. Energy is always conserved during every process. In 1824, Carnot described the relationship between the two different forms of energy, work and heat, analytically in the form [41]:

$$W = \frac{T - T_0}{T} Q \tag{3.8}$$

where W is work that can be extracted when heat Q flows from a heat reservoir with an absolute temperature T to a reservoir with an absolute temperature T_0.

Since 1873, Gibbs pointed out that this work can be evaluated as [78]:

$$\delta W = dU + p_0\,dV - T_0\,dS + \sum_i n_i\,d\mu_{0i} = dH - T_0\,dS + \sum_i n_i\,d\mu_{0i} \tag{3.9}$$

where U in the internal energy, V is the volume of the system, S is the entropy, and n_i are the number of moles of the $i-$th substance, while p_0 and T_0 are the environmental pressure and temperature respectively, and μ_{0i} is the chemical potential of the $i-$th substance evaluated at the environmental temperature, and H is the enthalpy.

The term exergy was proposed by Rant in 1953, and its complete definition was given by Baehr in 1965 [514]:

> *Exergy is the totally convertible part of the energy, i.e. that part which may be converted into any other energy form.*

The concepts of energy and exergy are related to the first two laws of thermodynamics; indeed, the first law state that the total energy is constant in a process, while the second law highlights how heat can only move spontaneously from a higher to a lower temperature reservoir. So, the thermodynamic synthesis of these two laws is the energy balance [514]:

$$E = H - H_0 - (T - T_0)\,S - V\,(p - p_0) + \sum_i n_i\,(\mu - \mu_0) \tag{3.10}$$

where exergy can be highlighted to approach zero as the system approaches equilibrium with the environment.

In the context of the biofuels analysis, my interest is focused in open systems. In 1824, Carnot introduced an ideal engine which works on a reversible cycle without dissipation. It converts the absorbed heat into work, without irreversibility. Carnot proved that [78]:

1. All ideal engines operating between the same two thermal reservoirs of temperature T_1 and T_2, with $T_1 > T_2$, have the same ideal efficiency $\eta_C = 1 - T_2/T_1$;
2. Any other engine, operating between the same temperatures, has an efficiency η such that it is always $\eta < \eta_C$.

The result consists in the existence of a definite upper limit for any conversion of the heat into kinetic energy and work. Just to quantify irreversibility in the dissipative processes, Clausius introduced the *entropy*, and, in 1889, Gouy and, in 1905, Stodola, independently, proved that the lost exergy in a process is proportional to the entropy generation. Exergy is the maximum amount of work which can be obtained by a system as it comes to equilibrium with its reference environment. Exergy is defined in relation to a reference, which is no more than the system environment [131]. It is a measure of the ability of a system to generate changes, due to its non-equilibrium related to the reference environment. So, we can point out that [131]:

1. The exergy of a system in complete equilibrium with its environment is null;
2. It does not exist a conservation law for exergy;
3. The exergy is carried in an amount proportional to the level of disequilibrium between the system and its environment;
4. The consumption of exergy allows us to measure any loss of energy quality.

Exergy allows the engineers to design system in order to obtain the highest efficiency at a least cost under the present technology, economic and legal conditions, but also to take into account the related ethical, ecological and social consequences; indeed, it allows us:

1. To take into account the impact of the use of energy resources on the environment;
2. To evaluate the more efficient use of the energy resources, and of the locations, types, and magnitudes of wastes and losses;
3. To evaluate the real possibility of designing more efficient energy systems in order to reduce the present technical inefficiencies.

So, we can highlight that the cause of any natural effect is always the dynamic balances of the interactions between the systems and their environment; in particular, the decrease of the free energy of the natural systems in the least time determine their evolution [40, 36, 38, 52, 48, 50, 41].

Following the first law of thermodynamics for open systems, any energy change is expressed by:

1. Flows of matter through the system boundary;
2. Heat through the system boundary;
3. Performance of work developed by or on the system.

so, any process, interaction, cycle, etc. evolves in a definite time τ, named lifetime, and, in during this time interval, the energy variation ΔE of the open system results:

$$\Delta E = \sum_i Q_i - W + \sum_j \int_0^\tau \dot{m}_i \big(h_j + e_{k,j} + e_{p,j} + e_{ch,j}\big)\, dt \tag{3.11}$$

where Q is the heat exchanged, W is the work done, $\dot{m}$ is the mass flow, h is the specific enthalpy, and e is the specific energy, and the subscripts k, p and ch mean kinetic, potential and chemical respectively, i and j are related to the number of fluxes of heat and mass respectively. The following entropy variation, ΔS, of the system occurs, related to the previous energy variation:

$$\Delta S = \sum_i \frac{Q_i}{T_i} + \sum_j \int_0^\tau \dot{m}_i s_i dt + S_g \tag{3.12}$$

where T is the temperature of any $i-$th reservoir, s is the specific entropy and $S_g = W_\lambda / T_0$ is the entropy variation due to irreversibility, named entropy generation [40, 36, 38, 52, 48, 50, 41] and W_λ is the work lost.

Combining these equations, the following exergy balance can be obtained [41]:

$$W_t = \Delta B + \sum_\alpha J_{ex,\alpha} + \sum_\beta Ex_{Q,\beta} - T_0 S_g \tag{3.13}$$

where:

- W_t is the net work done during the process;
- $\Delta B = E + p_0 V - T_0 S$ is the accumulation of non-flow exergy;
- $J_{ex} = \int_0^\tau \dot{m}\big(e - T_0 s\big) dt$ is the flow exergy due to mass flow;
- $Ex_Q = Q\big(1 - T_0/T\big)$ is the exergy transfer due to heat transfer;

and the subscript 0 means environment, while p is the pressure and V is the volume. The work lost W_λ can be obtained as [48]:

$$W_\lambda = \frac{Ex_{in} - Ex_{out} - W}{T_0} \tag{3.14}$$

where Ex means exergy and *in* and *out* mean inflow and outflow respectively. So, the final relation useful for our analysis becomes:

$$\begin{aligned} T_0 S_g = & \sum_j \int_0^\tau \dot{m}_i \big(h_j + e_{k,j} + e_{p,j} + e_{ch,j}\big)\, dt + \sum_\ell \int_0^\tau \dot{n}_\ell \nu_\ell \big(g_\ell^\oplus - ex_{ch,\ell}^\oplus\big)\, dt - \\ & - \sum_i \left(1 - \frac{T_0}{T}\right) Q - W_t - \int_0^\tau \frac{d}{dt}\big(E - T_0 S\big) dt \end{aligned} \tag{3.15}$$

where g is the molar specific Gibbs potential, $ex_{ch} = y\big(\mu - \mu_0\big)_{T_0,p_0}$ is the molar specific chemical exergy at the reference atmosphere, y is the molar fraction, $\dot{n}$ is the molar flux, ν is the stoichiometric coefficient, and μ is the chemical potential, $\oplus$ means standard conditions.

3.3 Exergy and entropy generation

Classical science emphasized equilibrium and stability, while, recently, it was pointed out the role of fluctuations, instability and evolutionary processes: irreversible processes are observed everywhere symmetry is broken. In thermodynamics the distinction between reversible and irreversible processes has been introduced by using the concept of entropy so that its formulation is fundamental in order to understand thermodynamic aspects of self-organization, evolution of order and life as we observe in Nature [131].

The introduction of entropy in classical thermodynamics is related to equilibrium state and reversible transformation. In that context, entropy is a state function depending only on the equilibrium state of the system considered and only entropy differences can be evaluated. The introduction of entropy generation comes from the necessity to avoid inequalities and use only equation from mathematical point of view. Nothing is really *produced* or *generated*. Indeed, the second law states:

$$\oint \frac{dQ}{T} \leq 0 \tag{3.16}$$

defining the total entropy as [41]:

$$S = \int \left(\frac{\delta Q}{T} \right)_{rev} = \Delta S_e + S_g \tag{3.17}$$

then S_g is the entropy generation, that is the entropy variation due to irreversibility, defined as [41]:

$$S_g = \int_{\tau_1}^{\tau_2} \dot{S}_g d\tau \tag{3.18}$$

with

$$\dot{S}_g = \frac{dS}{d\tau} - \sum_{i=1}^{n} \frac{\dot{Q}_i}{T_i} - \sum_{in} \dot{m}_{in} s_{in} - \sum_{out} \dot{m}_{out} s_{out} \tag{3.19}$$

and τ_1 and τ_2 the initial and final time of the process. It is always $S_g \geq 0$

The quantity ΔS_e should be better defined as the entropy variation that will be obtained exchanging reversibly the same *fluxes* throughout the system boundaries. Then entropy is not more then a parameter characterizing the thermodynamic state and the term due to internal irreversibility, S_g, measures how far the system is from the state that will be attained in a reversible way.

In the second law analysis the definition and identification of the thermodynamic system is fundamental.

The open thermodynamic system phenomenological description is summarized as follows. Let us consider an open continuum or discrete N particles system. Every $i-$th element of this system is located by a position vector $\mathbf{x}_i \in \mathbb{R}^3$, it has a velocity $\dot{\mathbf{x}}_i \in \mathbb{R}^3$, a mass $m_i \in \mathbb{R}$ and a momentum $\mathbf{p}_i = m_i \dot{\mathbf{x}}_i$, with $i \in [1, N]$ and $\mathbf{p} \in \mathbb{R}^3$. The masses m_i must satisfy the condition:

$$\sum_{i=1}^{N} m_i = m \tag{3.20}$$

where m is the total mass which must be a conserved quantity so that it follows:

$$\dot{\rho} + \rho \nabla \cdot \dot{\mathbf{x}}_B = 0 \tag{3.21}$$

where $\rho = dm/dV$ is the total mass density, with V total volume of the system and $\dot{\mathbf{x}}_B \in \mathbb{R}^3$, defined as $\dot{\mathbf{x}}_B = \sum_{i=1}^N \mathbf{p}_i$, velocity of the centre of mass. The mass density must satisfy the following conservation law:

$$\dot{\rho}_i + \rho \nabla \cdot \dot{\mathbf{x}}_i = \rho \Xi \tag{3.22}$$

where ρ_i is the density of the $i-$th elementary volume V_i, with $\sum_{i=1}^N V_i = V$, and Ξ is the source, generated by matter transfer, chemical reactions and thermodynamic transformations.

Inside this system, the principle of maximum entropy generation has been proved: *in a general thermodynamic transformation, the condition of the stability for the open system steady states consists of the maximum of the entropy generation.*

The exergy of a system is defined as the maximum shaft work that could be done by the composite of the system and a specified reference environment that is assumed to be infinite, in equilibrium, and ultimately to enclose all other systems: the environment is specified by stating its temperature, pressure and chemical composition.

Following Sciubba and Wall [427], exergy was implicitly introduced by Carnot[1] in 1824, and, starting from his results, Clapeyron[2], Rankine[3], Thomson[4] and Clausius[5] developed the Second Law of Thermodynamics. But, the first to introduce the concept of available work, including the diffusion terms, was Gibbs[6], even if Tait[7] and Lord Kelvin introduced a quantity similar to Gibbs availability, too, even if they haven't improved it [427]. The Gibbs results were developed by Duhem[8], while, independently from Gibbs' results, Gouy[9] proved his *useful energy theorem* (today known as Gouy-Stodola Theorem) and Stodola[10] used it in designing. Then, Keenan [239], Sciubba [422, 424, 421] and Wall [515–517, 427] improved and used in many engineering applications the concept of exergy.

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[1] Nicolas Léonard Sadi Carnot, Paris, June 1rd, 1796 - Paris, August 24th, 1832

[2] Benoît Paul Émile Clapeyron (Paris, January 26th, 1799 - Paris, January 28th, 1864

[3] William John Macquorn Rankine, Edinburgh, July 5th, 1820 – Glasgow, December 24th, 1872

[4] William Thomson, Lord Kelvin, Belfast, June 26th, 1824 - Largs, December 17th, 1907

[5] Rudolf Julius Emanuel Clausius, Köslin, January 2nd, 1822 – Bonn, August 24th, 1888

[6] Josiah Willard Gibbs, New Haven, February 11th, 1839 – New Haven, April 28th, 1903

[7] Peter Guthrie Tait, Dalkeith, April 28th, 1831 - Edinburgh, July 4th, 1901

[8] Pierre Maurice Marie Duhem, Paris, June 10th, 1861 – Cabrespine, September 14th, 1916

[9] Louis-Georges Gouy, Vals-les-Bains, February 19th, 1854 – Vals-les-Bains, January 27th, 1926

[10] Aurel Boleslav Stodola, Liptovský Mikuláš, May 10th 1859 – Zurich, December 25th, 1942

Exergy is a thermodynamic quantity related to the reference environment [131]. It is defined as *the maximum amount of work which can be produced by a system or a flow of matter or energy as it comes to equilibrium with a reference environment.* It represents a measure of the potential of the system or flow to cause changes, due to not being completely in stable equilibrium in relation to the reference environment. Some properties of the exergy can be highlighted [131]:

1. A system in complete equilibrium with its environment has null exergy;
2. The more a system deviates from the environment, the more exergy it carries;
3. When the energy loses its quality, it results in exergy destroyed;
4. An engineer designing of a system is expected to aim for the highest possible technical efficiency at a minimum cost under the prevailing technical, economic and legal conditions, but also with regard to ethical, ecological and social consequences. Exergy is a concept that makes this work a great deal easier;
5. Exergy is a primary tool in best addressing the impact of energy resource utilization on the environment;
6. Exergy analysis is a suitable technique for furthering the goal of more efficient energy-resource use, for it enables the locations, types, and true magnitudes of wastes and losses to be determined;
7. Exergy analysis is an efficient technique revealing whether or not and by how much it is possible to design more efficient energy systems by reducing the inefficiencies in existing systems;
8. Exergy is not a quantity subject to a conservation law.

Maximal possible conversion of heat Q to work L_t, known as exergy content of heat, depends on the temperature T at which heat is available and the temperature level T_a at which the reject heat can be disposed, that is the temperature of the surrounding. The upper limit for conversion is the Carnot efficiency $1 - T_2/T_1$, where T_1 and T_2 are, respectively, the higher and lower temperature of the transformation considered. Consequently, exergy exchanged is defined as [41]:

$$B = \left(1 - \frac{T_a}{T}\right) Q \tag{3.23}$$

Now, considering the relation (3.17), it follows:

$$S = \Delta S_e + S_g = \int \left(\frac{\delta Q}{T}\right)_{rev} = \int \frac{1}{T} d\left[\left(1 - \frac{T_a}{T}\right)^{-1} B\right] \tag{3.24}$$

As a consequence of the principle of maximum entropy generation and considering that:

$$\begin{aligned} \delta S_g &= 0 \\ d(\Delta S_e) &= 0 \end{aligned} \tag{3.25}$$

it follows that:

$$\frac{1}{T} d\left[\left(1 - \frac{T_a}{T}\right)^{-1} B\right] = 0 \tag{3.26}$$

and:

$$\frac{dB}{dT} = -\frac{\dfrac{T_a}{T^2}}{1 - \dfrac{T_a}{T}} B \tag{3.27}$$

It follows that:

1. if $T > T_a$ then $dB/dT < 0$, so dB/dt evaluates the maximum power generated during the process;
2. if $T < T_a$ then $dB/dT > 0$, so dB/dt evaluates the minimum power required during the process.

Thus, exergy output is not balance the exergy input for real processes in open systems because part of the exergy input is always destroyed, in accordance with the Second Law of Thermodynamics, as the maximum principle entropy generation states, too. Moreover, exergy analysis and entropy generation analysis allow us to evaluate the most efficient process, by minimizing the wasted and destroyed exergy, with the consequence of maximizing the available work, under the present constraints of the process and exergy inflow.

3.4 Human Development Index

The year 1990 has represented a turning point in relation to the attention for human development and human well-being, being people considered the wealth of a nation itself. Thus, since 1990, the United Nations Development Program (UNDP) has presented the concept of human development as the development towards a higher human well-being, introducing the need to measure it, pointing out the requirement to go beyond the only measure of economic growth, or Gross Domestic Product (*GDP*). Indeed, the economic growth does not necessarily imply human development. The definition given from UNDP for Human Development concerns the enlargement of people's choices, where the identified factors to fulfil it have been set as follows: lead a long and health life, have access to and carry out the educational pathway, and to enjoy a decent standard of living. If these three conditions are not satisfied, other opportunities can not be accessible. Beyond these choices, other ones have been identified as follows: the guarantee of human rights, political freedom and self-respect [483]. So, a switch of the focus from countries' economic well-being to people well-being has been introduced. Therefore, a new indicator to measure well-being has been proposed: the Human Development Index (*HDI*).

The UNDP publishes almost annually (excluding the years 2012 and 2017) the Human Development Report (HDR), a report that involves independent researchers, ensuring freedom from the United Nations General Assembly viewpoint. HDR represents a tool to raise awareness on global human development, a possibility to explore proposals for new possible more human centred policies, and to verify the improvements (or worsening) in fundamental factors for the human development of a country, such as healthy and long lives, education and income. Thus, the HDR provides also measurement and comparison tools by means of data and indicators, useful for researchers, policy-makers, NGOs in order to analyse the actual situation and to improve human development.

In order to measure and monitor human development, the ideal case would be to include many variables, to have a comprehensive picture of the well-being conditions of the country. However, the use of too many indicators could produce a picture too complex to be analysed, risking distorted assessment of the condition of the country itself and bring to an incorrect focus by the policy-makers. The key issue, therefore, is of emphasis [483]. Therefore, the UNDP goal was to: i) create a multidimensional index, with the focus on the ends of people's lives, ii) being simple to calculate, iii) easily understandable and usable. Moreover, iv) its calculation should be feasible with the available data.

3.4.1 The evolution of the Human Development Index

The Human Development Index, *HDI*, was developed by Mahbub ul Haq, in accordance with the Nobel laureate Amartya Sen's work on human capabilities, promoting a more ethical socio-economic development [164]. In this index, three fundamental ends of development are enclosed, or the access to: health, education and goods [456]. In this way, two main aspects of human development are considered: i) the formation of human capabilities by improving health and knowledge, and ii) the use that people make of their acquired capabilities. *HDI* was proposed in its first version in the 1990 HDR, highlighting the primary objective of development: to benefit people.

The *HDI* is a multidimensional index, which encases indexes of life expectancy, income, literacy and school enrolment. These indexes are combined together, giving a single value, in order to assess the performances of a country over time, and to compare the human well-being among countries. So, *HDI* represents an alternative to the previous progress-assessment approach of considering only the nations' *GDP*.

The first version of this index was based on different indicators, related to:

- *Life Expectancy*, where the hypothesis introduced has been that a long life is closely related to other basic aspects, such as good nutrition and health;
- *Knowledge*, where literacy has been emphasised as a crude key-enabler, or the first step, to build a knowledge and to learn, which are requirements to gain independence, freedom, and working abilities. Consequently, its role is fundamental in human development and well-being, even if is not just literacy that matters, but also the quality of the education path in terms of student's outcomes [483];
- Management of resources required for *a decent standard of living*, where the main difficulty has been reported to find a unique indicator, available for all countries and simply to measure, in which access to land, natural resources, credit, income and the other resources were included. Thus, the per capita income was established as a plausible measure. In order to limit the impact of non-tradable goods or services, the distortion due to exchange rates and taxes, the purchasing power parity has been adopted to allow the comparison among countries. Therefore, the adjusted real *GDP* per capita was selected as

the variable to take into account of the relative power to buy commodities and to obtain resources to reach a decent standard of living. Moreover, in order to take into account that an excessive amount of resources are not needed for transforming income into human capabilities, the logarithm of the income per capita has been considered, instead of its absolute value. Moreover, a zero weight factor to income above the poverty line was given.

Thus, the first *HDI* definition, given in Ref. [483], was based on the definition of the deprivation suffered from a country for each of the above mentioned variables (Life Expectancy, Literacy, and the logarithm of real *GDP* per capita). This deprivation, then was normalised with respect maximum and minimum values defined for each variable, making the countries' mean deprivation value within the range 0-1. Therefore, an arithmetic mean of the three deprivation indexes was carried out, and the Human Development Index calculated as 1 minus its average deprivation value.

The various steps to calculate HDI_{1990}, can be summarised as follows [483]:

1. Calculation of the single deprivation index (D_i) for each variable X_i for the considered j-th country:

$$D_{ij,1990} = \frac{Max(X_{ij,1990}) - X_{ij}}{Max(X_{ij,1990}) - Min(X_{ij,1990})} \tag{3.28}$$

   where D is the deprivation index, the subscript i means i-th variable: Life Expectancy (*LE*), Adult Literacy Rate (*LR*), the logarithm of real *GDP* per capita, j indicates the j-th country, 1990 indicates the year in which this formulation was introduced, X is the value of the i-th variable considered. The maximum and minimum values of the $X_{ij,1990}$ variables, respectively $Max(X_{ij,1990})$ and $Min(X_{ij,1990})$ are set from the UNDP.

2. Calculation of the average deprivation index of a country, $D_{j,1990}$, calculated as the simple arithmetic mean of the three deprivation indexes, obtained with Equation (3.28), as follows:

$$D_{j,1990} = \frac{1}{N}\sum_{i=1}^{N} D_{ij,1990} \tag{3.29}$$

   where $D_{j,1990}$ is the average deprivation index or the j-th country considered, and $N = 3$.

3. Therefore, the HDI_{1990} for a j-th country, was calculated as:

$$HDI_{j,1990} = 1 - D_{j,1990} \tag{3.30}$$

Along the years, the HDI formulation and reference values for the single indicators have been changed, evolving on time [28].

Firstly, in 1992 the concept of deprivation was abandoned, introducing the following normalisation, for the indicators considered in each HDI domain:

$$I_{ij,1992} = \frac{X_{ij} - Min(X_{ij})}{Max(X_{ij}) - Min(X_{ij})} \tag{3.31}$$

where: Ix is the normalised index, the subscript i stands for the i-th variable of the HDI domain, 1992 indicates the year in which this formulation was introduced, X_{ij} is the actual value of the i-th variable considered for the j-th country. Thus the HDI formulation, for the j-th country became:

$$HDI_{j,1992} = \frac{1}{3}\sum_{i=1}^{3} I_{ij,1992} \tag{3.32}$$

The 2010 has been the turning point year for the HDI aggregation formula. Indeed, the arithmetic mean of the considered indexes was substituted by the geometric mean, in order to not to favour countries that were improving in only one of the three dimensions. The single normalised indexes were calculated as in Equation (3.31). The geometric aggregation to obtain the HDI was then introduced:

$$HDI_{2010} = \left(I_{Health} \cdot I_{Edu} \cdot I_{Income}\right)^{1/3} \tag{3.33}$$

where I stands for normalised index, I_{Health} is the index based on Life Expectancy at birth (LE), I_{Edu} is the index based on Mean Years of Schooling (MYS) and on the Expected Years of Schooling (EYS), and I_{Income} is the index based on the natural logarithm of real Gross Domestic Product per capita $\ln(GDP_{pc})$.

The possibility to lead a long and healthy life has always been evaluated by means of the Life Expectancy at birth (LE), only its reference values (goalposts) have changed during the years. Moreover, as all the three indexes that constitute the *HDI*, since 1992 this indicator has suffered the methodological change from the deprivation index to the calculation by means of Equation (3.31).

The evolution over the time of the educational component has been more articulated, and can be summarised as follows:

- In 1990, the knowledge component was considered by means of adult Literacy Rate at 15 years and above (*LR*);
- In 1991, the variable Years of Schooling (YS) was added to the Adult Literacy Rate (*LR*), to reflect higher educational level than literacy rate, or to give a sense of educational attainment to people not covered by adult literacy rate. The variables were weighted with a factor respectively of $2/3$ and $1/3$: $D_{Edu,1991} = 2/3\ D_{LR} + 1/3\ D_{YS}$.
- In 1992, the Deprivation index related to knowledge became an index (I) with the same components, by using Equation (3.31) instead of Equation (3.28);
- In 1995, due to lack of data on the mean years of schooling, so the adult Literacy Rate (*LR*) was combined with the gross Enrolment Ratio (*ER*) as follows: $I_{Edu,1995} = 2/3\ I_{LR} + 1/3\ I_{ER}$;
- In 2010, the educational component was newly changed, by considering two different indicators, equally weighted by their arithmetic mean: the Mean Years of Schooling (MYS), or the average number of years of education received by people age 25 and older in their lifetime, based on education attainment levels of the population converted into years of schooling based on theoretical durations of each level of education attended, and the Expected Years of Schooling (EYS), or the number of schooling years that a pupil of school entrance age can expect to receive if prevailing patterns of age-specific enrolment rates were to stay the same throughout the child's life. Thus, the Education Index was calculated as follows: $Ix_{Edu,2010} = (I_{MYS} + I_{EYS})/2$.

As concerns the ability to have a decent standard of living, many variations over the time have been proposed by the UNDP:

- In 1990, $\log(GDP_{pc})$ was selected as the sole variable to consider the "command over resources", due to scarcity of data with respect to other information as: access to land, income and other resources needed for a decent standard of living. GDP_{pc} has been adjusted by purchasing power parity (PPP) to consider the relative power of the people of different countries to buy commodities;

- From 1991 to 1993, the logarithmic transformation for income was substituted with the Atkinson formula with threshold value derived from poverty line, for the utility of income (real GDP_{pc}), in order to give different weights to the different levels of income, and to reduce the over bearing influence of income indicator of high-income countries;
- From 1994 to 1998, as for the previous years, the Atkinson formula was adopted. However, the threshold value was derived from the global average. This methodology was abandoned, because of its severity on the middle-income countries [318];
- From 1999 to 2009, the 1990 approach was reintroduced, by considering $\log(GDP_{pc})$;
- In 2010, the real $\log(GDP_{pc})$ was substituted with the natural logarithm $\ln(GNI_{pc})$ at Purchasing Power Parity (PPP). *GNI* is derived from *GDP*, subtracting from it the primary income payable to non-resident units, and adding the primary income receivable from non-resident units. The logarithm base change was due to the fact that usually in economy natural logarithms are often used [293].

The variation on time of the goalposts set by the UNDP, which have been used to normalise each considered indicator, are summarised in Table 3.1. The values reported are those that have changed, if there is an empty value for the considered year, it means that it has remained unchanged.

3.4.2 *HDI* today

Nowadays, the *HDI* is evaluated following the 2010 HDR updated procedure:

- *Life expectancy*: the country's actual value of the Life Expectancy at birth (*LE*) and the respective goalposts (maximum and minimum values) are considered,

Table 3.1 Goalposts, or maximum and minimum values to normalise the indicators, to obtain the indexes which compose the *HDI* [483–486, 317, 302, 293].

Year	Indicator							
	Life expectancy		Education				Income	
	LE [yr]		*LR* [%]				GDP_{pc} [US$ PPP$_{pc}$]	
	Min	Max	Min	Max			Min	Max
1990	41.8	78.4	12.3	100.0			219	4786
			LR [%]		*YS* [yr]			
			Min	Max	Min	Max		
1991	42.0	78.6	12.3	100.0	0	15	350	5070
1994	25	85	0.0	100.0	0	15	200	40000
			LR [%]		*ER* [%]			
1995			0.0	100.0	0	100.0	100	40000
1999							200	40000
	LE [yr]		*EYS* [yr]		*MYS* [yr]		GNI_{pc} [US$ PPP$_{pc}$]	
	Min	Max	Min	Max	Min	Max	Min	Max
2010	20	83.2	0.0	20.6	0.0	13.2	163	108211
2011	20	83.4	0.0	18	0	13.1	100	107721
2016 – today	20	85	0.0	18	0	15	100	75000

in order to obtain the Life Expectancy Index (*LEI*):

$$LEI = \frac{LE - LE_{min}}{LE_{max} - LE_{min}} \tag{3.34}$$

The *LE* [yr] is the number of years that a newborn infant would live if prevailing patterns of mortality at the time of its birth were to stay the same throughout its life [470], and the maximum and minimum values are 85 and 20, respectively.

- *Knowledge*: for which two different indicators are considered, the Mean Years of Schooling (*MYS*) [yr], and the Expected Years of Schooling (*EYS*) [yr], obtaining respectively the Mean Years of Schooling Index (*MYSI*):

  $$MYSI = \frac{MYS - MYS_{min}}{MYS_{max} - MYS_{min}} \tag{3.35}$$

  where the actual maximum and minimum values [yr] are 15 and 0, respectively. The definition of *MYS* can be summarised as the average number of completed years of education, attended by the country's population aged 25 years and over [488],
  and the Expected Years of Schooling Index (*EYSI*):

  $$EYSI = \frac{EYS - EYS_{min}}{EYS_{max} - EYS_{min}} \tag{3.36}$$

  where the actual maximum and minimum values [yr] are 18 and 0, respectively. The definition of *EYS* can be summarised as: the amount of time (expressed in years), that a child, starting now his educational path, is expected to spend at school, or university (sum of the age-specific enrolment ratios for primary, secondary, post-secondary non-tertiary and tertiary education) [469].

  The two indexes are aggregated as follows, in order to obtain the Education Index (*EI*):

  $$EI = \frac{MYSI + EYSI}{2} \tag{3.37}$$

- *Decent standard of living*: the natural logarithm of real GNI_{pc} is adopted in order to obtain the Income Index (*II*):

  $$II = \frac{\ln(GNI_{pc}) - \ln(GNI_{pc,min})}{\ln(GNI_{pc,max}) - \ln(GNI_{pc,min})} \tag{3.38}$$

- The final aggregation of the three indexes is obtained by evaluating their geometric mean:

$$HDI = \left(LEI \cdot EI \cdot II\right)^{1/3} \tag{3.39}$$

The UNs have established four different levels of human development, in relation to their *HDI* values: the very high-human developed countries, which have $HDI \geq 0.800$, the high-developed countries, which present a $0.799 \leq HDI \leq 0.700$, the medium developed countries, with $0.699 \leq HDI \leq 0.550$, and the low-developed countries, which encloses all countries with $HDI \leq 0.499$.

3.5 The requirements for a thermodynamic and socio-economic indicator

In Economy, Gross Domestic Product (*GDP*) represents an economic indicator useful for the evaluation of the results of the national policies; indeed, its increase is related to the growth of the nations well-being. National policies base their choices on the principle that “ what is good for the market is good for Gross Domestic Product, and *viceversa*”. As a consequence of this approach, the economists consider the *GDP* as the indicator of profit of the countries production, and of their economic, social, and environmental welfare.

On the contrary, it was stressed that sustainable development indicators should be classified in four different and inter-related, domains [481]:

- Social pillar: concerning equity (income, sanitation, drinking water, access to energy and living conditions) and Global economic partnership (related to trade and development financing) including the following main aspects:
  - Poverty,
  - Governance,
  - Health,
  - Education,
  - Demographics,
- Economic pillar, including the following main aspects:

  - Economic development,
  - Global economic partnership,
  - Consumption and production patterns,

- Environmental pillar, including the following main aspects:
  - Natural hazards,
  - Atmosphere,
  - Land,
  - Oceans, seas and coasts,
  - Freshwater,
  - Biodiversity,
- Institutional pillar, including the following main aspects:
  - Natural hazards,
  - Governance hazards,

To which also a technological pillar, must be considered, being one of the fundamental bases of our society and directly related to the previous domains:

- Technological pillar, including the following main aspects:
  - Designing optimization,
  - Optimization of production processes,
  - Energy saving and reduced environmental impact of power production.

The multi-dimensional nature of the indicators points out that sustainable development is a complex topic and that these pillars have to be interrelated by using a holistic approach; consequently, other alternative indicators, related to sustainability, have been introduced recently:

- The Measure of Economic Welfare;
- The Economic Aspects of Welfare;
- The Index of Sustainable Economic Welfare;

- The Genuine Progress Indicator.

In relation to *GDP*, the latter two indicators have been shown to be more accurate than the *GDP* itself, when the well-being and progress are evaluated on the bases of a concrete sustainable economics and on new nation strategies for policy decisions; indeed, they consider factors related to the quality of life and the nation ability to sustain it into the future, e.g., pollution, crime, family breakdown, and community involvement. Thus, while the *GDP* evaluates the total monetary value of all the production transacted in the marketplace, the Index of Sustainable Economic Welfare, and the Genuine Progress Indicator, evaluate the effect of the production to the population for improving the quality of life, by non-market goods and services useful to human life included.

These indicators show that a new approach must be introduced into the analysis of the sustainable development. In fact, they consider an engineering approach to sustainability, and evaluate it also in the economic contest. Thus, a link between technological level and economic value i shown to be developed.

Growth is the fundamental target of the present economic system. Therefore, a link between energy and economic development has been pointed out, due to the fundamental role of energy in the development [476], and the promotion of the economic growth; indeed, just energy represents an essential factor of any production system and the economic processes, as the recent geopolitic events have highlighted, even if the present economic analyses of growth continue to consider only capital and labour.

Today, in industrialized countries, the management of CO_2 emissions is one of the actual compelling issues. In fact, improving the energy efficiency and its rational use is considered a fundamental economic strategy for the sustainable development of the industrialized countries.

Consequently, in this PhD Thesis some new indicators are considered in relation to the inefficiency, in order to evaluate:

- The equivalent primary wasted resource value;
- The technological level;
- The advancement level of industrial processes,

with the result of obtaining a link between the exergy cost and the inefficiency of the systems, introducing also considerations on the cost of the wasted exergy useful to sustain the processes themselves.

3.6 Thermodynamic Human Development Index

The aim of this Thesis is to introduce an indicator which links the sustainable development to socio-economic and technological indexes. To do so, the approach here developed can be summarised as in Figure 3.1

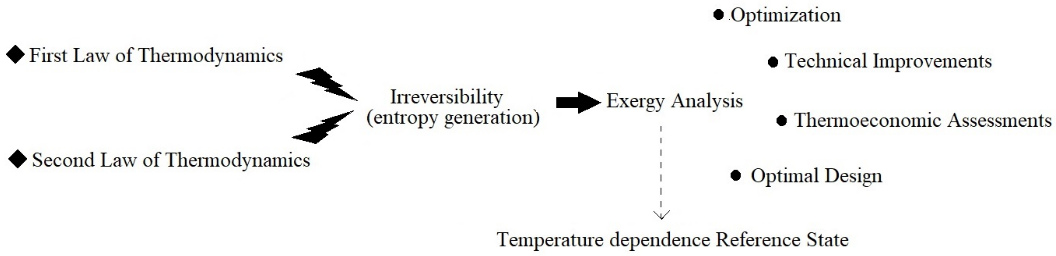

Figure 3.1 Scheme which shows the fundamentals of the technological analysis, that are represented by the first and the second law of thermodynamics. But, irreversibility is a natural intrinsic property of any system, that can be evaluated by using the concept of entropy generation. Entropy generation is also the fundamental quantity of the exergy analysis, allowing to evaluate the better thermodynamic pathway for the optimization of the engineering systems. This approach can be improved by introducing the Income Index in order to develop a more human well-being oriented analysis for sustainability. The limit of this approach is the temperature dependence of the exergy quantity, that must be evaluated for any Country and time.

Irreversibility in open systems represents a fundamental topic of investigation for engineering thermodynamicists, for the optimization of the design and development of industrial devices and processes. Today, the analyses of irreversibility is based on the Gouy-Stodola approach, called the entropy generation method, that states that the lost exergy in a process is proportional to the entropy generation. Exergy is the maximum shaft work which can be obtained by a system in relation to its specified reference environment. The reference environment is considered infinite and in equilibrium. The reference state is well known in relation to its temperature, pressure and chemical composition [131]. The fundamental step for the evaluation of exergy is just the definition of the reference state: exergy measures the ability of a system to generate changes, in relation to its non-equilibrium with respect to its reference environment [131].

The exergetic analysis is the basis of the present engineering in relation to the highest efficiency designing at the least cost, but it also allows us:

1. To take into account the impact on the natural environment;
2. To evaluate the more efficient use of the energy resources, and the magnitude of wastes and losses.

But, the cause of any impact is no more than the interaction between the system and its environment [40, 36, 38, 52, 48, 50, 41]; indeed, any change is always consequence of:

1. Flows of matter through the system boundary (money included);
2. Heat flow through the system boundary;
3. Work developed by or on the system.

Any process occurs in a proper time τ, and, during this time, the exergy balance can be obtained as follows [41]:

$$W = \Delta B + \sum_{\alpha} J_{ex,\alpha} + \sum_{\beta} Ex_{Q,\beta} - T_0 S_g \tag{3.40}$$

where:

- W is the net work done during the process;
- $\Delta B = E + p_0 V - T_0 S$ is the accumulation of nonflow exergy;
- $J_{ex} = \int_0^{\tau} \dot{m}\big(e - T_0 s\big) dt$ is the transfer exergy due to mass flow;
- $Ex_Q = Q\big(1 - T_0/T\big)$ is the exergy transfer due to heat flow;

and Q is the heat exchanged, W is the work done; $\dot{m}$ is the mass flow, h is the specific enthalpy, e is the specific energy, s is the specific entropy and $S_g = W_\lambda / T_0$ is the entropy variation due to irreversibility, named entropy generation [40, 36, 38, 52, 48, 50, 41, 39], and the subscripts 0 means reference environment, α and β are related to the number of fluxes of heat and mass, respectively. The entropy variation rate $\dot{S}$ of the system, related to the previous exergy variation, results:

$$\dot{S} = \frac{dS}{dt} = \sum_{\beta} \frac{\dot{Q}_{\beta}}{T_{\beta}} + \sum_{\alpha} \dot{m}_{\alpha} s_{\alpha} dt + \dot{S}_g \tag{3.41}$$

where T is the temperature of any $\beta-$th reservoir, W_{λ} is the work lost due to irreversibility, dissipation and frictions, and p is the pressure and V is the volume.

The power lost, $\dot{W}_{\lambda}$, due to irreversibility, dissipation and friction results [48]:

$$\dot{W}_{\lambda} = \frac{\dot{E}x_{in} - \dot{E}x_{out} - \dot{W}}{T_0} \tag{3.42}$$

where $\dot{E}x$ refers to exergy rate and *in* and *out* refer to inflow and outflow, respectively. So, we can obtain the explicit relation for the entropy generation, the entropy variation related to irreversibility:

$$\begin{aligned} T_0 \dot{S}_g = & \sum_{\alpha} \dot{m}_{\alpha} \big(h_{\alpha} + e_{k,\alpha} + e_{p,\alpha} + e_{ch,\alpha} \big) + \sum_{\ell} \dot{m}_{\ell} \big(g_{\ell}^{\oplus} - ex_{ch,\ell}^{\oplus} \big) - \\ & - \sum_{\beta} \left(1 - \frac{T_0}{T_{\beta}} \right) \dot{Q} - \dot{W} - \frac{d}{dt} \big(E - T_0 S \big) \end{aligned} \tag{3.43}$$

where g is the specific Gibbs potential, $ex_{ch} = y\big(\mu - \mu_0\big)_{T_0,p_0}$ is the specific chemical exergy at the reference atmosphere, y is the molar fraction, $\dot{m}$ is the mass flux, and μ is the chemical potential; $\oplus$ refers to the standard conditions, and the subscripts k, p and ch refer to kinetic, potential and chemical terms, respectively.

The sources of any physical process are the exergy gradients, while entropy generation allows us to evaluate its irreversibility [51, 42] and dissipations during any process, so we can introduce a new indicator, the *exergy inefficiency*, with the aim to measure the technological level of a process in relation to its *unavailability*:

$$\eta_{\lambda} = 1 - \eta_{II} = 1 - \frac{\dot{W}}{\dot{E}x_{in}} = \frac{\dot{W}_{\lambda}}{\dot{E}x_{in}} = \frac{T_0 \dot{S}_g}{\dot{E}x_{in}} \tag{3.44}$$

It allows us to quantify the effects of the process losses, so the lower the value of the exergy inefficiency, the more the industrial process is efficient in terms of energy use. Consequently, it allows us to quantify the technological maturity of a production system or a production sector.

The technological level, a thermoeconomic indicator can be introduced, in order to link economics to a technical approach:

$$I = \eta_\lambda \cdot ExI \cdot LP = \frac{\dot{W}_\lambda}{n_w \cdot n_h} \tag{3.45}$$

where η_λ is the inefficiency, and *ExI* is the Energy Intensity related to the power really used,

$$ExI = \frac{\dot{E}x_{in}}{GDP} \tag{3.46}$$

where $\dot{E}x_{in}$ is the exergy rate [41], *GDP* is the Gross Domestic Product and represents the well-being of a country or a productive system, *LP* is the Labour Productivity, defined as [551]

$$LP = \frac{GDP}{n_{wh}} \tag{3.47}$$

where $n_{wh} = n_w \cdot n_h$ is the total number of worked hours needed to obtain the *GDP*, with n_h number of worked hours and n_w number of workers. Now, considering the Gouy-Stodola theorem, the power lost due to irreversibility is related to the entropy generation, but we must consider the component related to environmental impact. To do so, we consider that the entropy generation presents many components related to heat transfer, mass transfer, friction, chemical reaction, interaction with external fields. The topic of research of this Thesis is related to air pollution and its mitigation, so the only component related to the greenhouse gas emission is considered, i.e. the carbon dioxide equivalent flux towards the environment. Consequently, the entropy generation can be evaluated as follows:

$$\dot{S}_g = \dot{m}_{\mathrm{CO}_2}\, s_{g,\mathrm{CO}_2} \tag{3.48}$$

where $\dot{m}$ is the mass flow, s_g is the specific entropy generation, and CO_2 means the equivalent carbon dioxide; so, the power lost results:

$$\dot{W}_\lambda = T_0\, \dot{m}_{\mathrm{CO}_2} s_g \tag{3.49}$$

where $\dot{m}_{\mathrm{CO}_2}$ is the CO_2 mass flow rate emitted for obtaining the required effect $\dot{W}$ and s_g is the specific entropy generation due to the process developed. Thus, the relation (3.45) becomes:

$$I = T_0 \, \frac{\dot{m}_{\mathrm{CO}_2}}{n_w \cdot n_h} \, s_{g,\mathrm{CO}_2} = T_0 \, \frac{\dot{m}_{\mathrm{CO}_2}}{\dot{W}} \, H_w \, s_{g,\mathrm{CO}_2} \tag{3.50}$$

where $\dot{W}$ is the power produced by a Country to obtain its economic objectives, and H_w is the mean work done by a worker, taken into account any sector of production. But, the indicator must considered the economic target of a Country, bound to the socio-economic conditions, the structure of the production system, the availability of resources, etc.; consequently, the value H_w can be considered a constant in a country, bound to the socio-economic condition of the worker, to his gratification in his work task, etc. Under these hypotheses, it is possible to introduce an indicator, which measure the technological level and the economic condition of a worker. So, this indicator, named I_T, can be introduced as follows:

$$I_T = \frac{I}{GNI_{pc} \, H_w} \tag{3.51}$$

where GNI_{pc} is Gross National Income per capita.

In order to improve the *HDI* by also using the indicator of Equation (3.45), now, we consider that the total number of workers is strictly related to the Gross National Income per capita, GNI_{pc}, and we combine its expression in relation to the Income Index, Equation (3.51), obtaining:

$$I_T = \frac{T_0 \dot{S}_g}{\dot{W} \cdot GNI_{pc}} = 0.01 \cdot \frac{T_0 \dot{S}_g}{\dot{W}} \cdot 750^{-II} \tag{3.52}$$

Now, we propose a Thermodynamic Human Development Index by introducing the following definition:

$$THDI = \left(\frac{LEI \cdot EI}{I_T} \right)^{1/3} \tag{3.53}$$

As a result, the *THDI* improves the usual *HDI* by also considering the technical and ecological level, introducing the CO_2 flows and the s_g quantities, evaluated in the I_T.

3.7 $THDI$ index and technical knowledge based job for sustainable development ($THDI_p$)

Recent facts as pandemics, extreme weather events linked to climate change, pollution, food production and its related security, affordable and clean energy for all, have demonstrated their complex nature for which non-trivial solutions are required [44, 45, 49]. These solutions need a dynamical use of scientific and technical knowledge. In particular, a deep knowledge of sciences and technologies is fundamental to achieve sustainable measures to respond to the previous mentioned issues, because of it requires workers' and engineers' abilities in advanced technologies applications, in order to reduce the CO_2 and pollutant emissions, to adopt new strategies, *etc*. Consequently, the need to measure the technical abilities of students emerges, in order to assess and bring out policies to improve them, just because students will be the workers in the next future. Indeed, sustainable development can be realised only by basing it on a creative approach to scientific and technological issues, as highlighted by Word Bank [165]:

> *Human capital accumulation is a complex process*

which represents the main driver towards a sustainable growth [27].

Thus, improving schooling and education constitutes an essential milestone to develop new strategies [57, 63], even if it has become controversial, because it has been highlighted that improvements in economic well-being are not guaranteed by expansion of schooling attendance. On the contrary, many studies on the role of cognitive skills in promoting economic well-being, particularly focused on the role of school quality and quantity [83, 117, 120, 172], highlighted a strong evidence that the cognitive skills of people, rather than mere school attainment, are powerfully related to individual earnings, to the distribution of income, and to economic growth, pointing out the fundamental role played by the level of skills, their complementarity and the robustness of the skills-growth relationship [192, 193].

In fact, looking back at the Millennium Development Goals actions [487] related to education, they were targeted towards strategies aiming to increase the populations' educational levels. However, some uncertainties and issues on these actions emerged [193]:

- Several differences, besides the educational level, exist within developed and developing countries, which make difficult to uniform actions to improve education;
- Several countries have accomplished steps towards schooling opportunities, nevertheless their well-being condition has not improved in the same way;
- Education programs need, at the same time, to have an effective management system, in order to achieve social goals, too.

So, some considerations should be developed in order to take also into consideration the socio-economic consequences of education, with particular regards both to the amount of time needed for schooling, and also to the abilities acquired by the students during their school pathway, focusing on the cognitive skills, which have been shown to have a central role, too [107, 1]. Indeed, these skills are related both to attending years and to the *quality* of schooling, as a consequence of the evidence that schooling activities which do not improve cognitive skills, present limited impact on economic development [98, 193].

Thus, a measure of the capabilities in solving complex problems and developing reasoning results fundamental for the ability and productivity of the future work force as a whole, with particular regards to organisation of the production sites, founded on the technological skills requirements. In fact, the main concern is that the work requirements are evolving quickly, and education should provide the knowledge to fill this gap, evolving faster in order to adapt competences to change, and conceptualize complex ideas in a multidisciplinary way [339–341, 343]. Thus, these competences and skills are required to overcome the actual global challenges and sustainability issues. The resulting choices must be taken in the correct way, from a multi- and inter-disciplinary viewpoint, covering always all the aspects that a choice implies (also from an environmental, social and economic viewpoint). In fact, moving towards sustainable societies requires the adoption of new technologies and solutions for the reduction of the environmental anthropic footprint, and in order to guarantee a decent quality of life for all people. Just with the aim to obtain a measure of the human well-being, the United Nations (UNs) have introduced an indicator to asses the progress and the well-being of any country, by considering its economic growth, as well as its population's education as well as its life expectancy, i.e. the Human Development Index, *HDI* [483, 405, 203], previously discussed in the Sections 3.4 and 3.4.1.

Thus, considering the UNs' results, in this PhD Thesis, *HDI* has been amended to yield an indicator with thermodynamic bases maintaining the UNs' characteristics, the Thermodynamic Human Development Index ($THDI$), as developed in the previous Section 3.6, in order to introduce also the second law concept and the one of the use of resources, with its related environmental impact of human activities.

But, in both indexes (*HDI* and $THDI$), the population's knowledge is accounted by using the Education Index, EI, considering its relevance for human development and well-being. It evaluates country's educational attainment by introducing the average adult years of schooling and the expected years of schooling for students that are starting their education pathway. These are fundamental aspects from a social viewpoint, because of they can be linked to a better quality of life, time spent for individual knowledge, and to prevent child labour [139]. Nevertheless, the Education Index, in its present form, can not supply information on the student's individual problem-solving skills, and technical or scientific knowledge, which represent the key levers for improvements in technologies and to achieve more sustainable global conditions.

Furthermore, societies' advantages from education, including its link with the economic growth, were demonstrated to be more strictly related with learning [193], while other education proprieties resulted to be related to schooling years [18]. Thus, these two aspects of education (quantity and quality) should be considered at the same time, being representative of different results of education itself. Indeed, enhancing the quality of education presents positive consequences if a wide number of pupils attend school for a longer period, and programs that increase schooling years lead to more knowledge if the considered education system is of a higher quality.

Hence, the resulting outcome is that all these aspects must be considered within the EI index, in order to perform the assessment of a country's education level, and of its potential contribution in the context of sustainable development. As concerns the students' education outcomes, since 2000, the PISA project has been proposed to monitor the education systems results in different countries. It constitutes a worldwide analysis, organized by the Organisation for Economic Co-operation and Development (OECD) in member and non-member countries, with the aim to obtain an evaluation of the education systems outcomes, by verifying 15-year-old school pupils' performances in three different areas: Reading, Mathematics, and Sciences. The PISA assessment represents a powerful tool to get a unified information on students' capabilities in different countries, because it actually constitutes the broadest dataset of schooling performances collection available at global scale [505].

As concerns the education process, what should be considered is that it involves, among others:

- A lifelong process, which aim is to provide an as long-lasting as possible progress of students' personal abilities, knowledge and skills;
- A social aim, with the final goal of improving the individual potential, in order to allow each individual to be an aware and productive member of the future society;
- A personal aim, that means allowing any individual to become a respected person in the social context based on his/her cooperation to improve society, by providing to he/she opportune knowledge and skills;
- A cultural aim, by giving to the pupil the bases in order to improve his/her sense of to be a part of a society, but also improving its art, morals, laws, etc. knowledge;
- The personal behaviour of any individual, with the improvement of some principles such as honesty, truthfulness, justice, goodness, etc.;
- An intellectual aim, with the final goal of improving the methodological skills of problem understanding and solving.

However, mostly of these aspects are not considered or only partially and implicitly included within the actual Education Index. Indeed, *EI* takes into account a given country's educational attainment by means of schooling years, with the introduction of the average adult years of schooling and expected years of schooling for students, which are fundamental aspects from a social viewpoint, related to a better quality of life [492], as previously argued. Nevertheless, this index fails in providing information about the student's individual problem-solving skills, and technical or scientific knowledge, which are central aspects for a sustainable development. Consequently, all these requests must be considered when the assessment of a country's education and knowledge system is performed. Thus, in order to take into account all the features previously commented on education and knowledge, I have considered to introduce into the traditional UNs Education Index a component related to the OECD's Programme for International Student Assessment (PISA) results, which can be used both in HDI and $THDI$.

To achieve this aim, an indicator has been here developed, considering for each country, the normalised OECD's PISA scores [345] for Maths and Sciences, by using their arithmetic mean, as follows:

$$OP = \frac{Mth + Sci}{2} \tag{3.54}$$

where OP stands for the OECD's PISA Index, which has been here introduced, based on the normalised values of the PISA scores in Mathematics (Mth) and Sciences (Sci). These represent the outcomes of the sample of pupils, who have performed the test. In this way, we can obtain a new Education Index, able to weight in an equivalent manner both the social aspects referred to education, just considered in the EI, and the student's skills, which can give information on the abilities acquired to be able to face the present and the future challenges:

$$EI_p = \sqrt{EI \cdot OP} \tag{3.55}$$

where the subscript p stands for *more professional oriented*.

Consequently, a Thermodynamic Human Development Index professional oriented, able to consider the pupil's competences, can be obtained as follows:

$$THDI_p = \left(\frac{LEI \cdot EI_p}{I_T} \right)^{1/3} \tag{3.56}$$

This result is an index useful for the development of a more deep analysis of a country in relation to its sustainability level, pointing out features related to human well-being: society, economy and environment. In fact, $THDI_p$ takes into consideration the following aspects:

- The social one, related to lead long and healthy lives, accounted by the Life Expectancy Index (LEI), which is linked to expectancy of life and to the possibility to access to social services;

- The knowledge one, related to education, Education Index professional oriented (EI_p), which gives information both on the schooling years and on the acquired knowledge level;
- The quantity related both to economic well-being and thermodynamics, I_T, that contains information on:
  - The technological level, accounted by the environmental impact through the entropy generation;
  - The economic well-being, accounted by the Income Index, II.

Now, in order to show the relation between level skills in the educational system and the sustainable development, I introduce for simplicity the subsequent hypotheses:

- The *LEI* index is assumed to be constant, because it isn't directly linked to education;
- The UNs *EI* index is assumed to be constant, because it depends from education policies - and for the following considerations - the interest is associated to the acquired knowledge skills, and not strictly associated with the time period spent in school.

Under these assumptions, in relation to the definition of $THDI_p$, a system is considered sustainable if the $THDI_p$ index increases with time, i.e.:

$$d(THDI_p) \geq 0 \tag{3.57}$$

from which it follows that:

$$dI_T \leq \frac{I_T}{6\,OP} d(OP) \tag{3.58}$$

So, some considerations can be introduced related to this analytical result:

- Sustainability from an environmental viewpoint entails $dI_T < 0$: if the mathematical and scientific skills grow, then $d(OP) > 0$, and the condition of sustainability (3.58) results always verified;

- If $dI_T > 0$, the condition of sustainability (3.58) results verified only if:

$$\begin{cases} d(OP) > 0 \\ \\ \dfrac{d\dot{m}_{\text{CO}_2}}{\dot{m}_{\text{CO}_2}} \leq \dfrac{1}{6} OP \cdot d(OP) + \ln 750 \cdot d(II) \end{cases} \tag{3.59}$$

  which entails that an environmental impact is acceptable only in relation to a progress of the educational and socio-economic condition of a nation, which is in accordance with the approach of the UNs for the developing countries.

OECD's Programme for International Student Assessment is a triennial assessment, that gives information on some central schooling subjects, including Mathematics and Sciences, focusing on the students' extrapolation capability from what they have learnt and from what they know, by applying this knowledge to unfamiliar settings in several competence areas [342]. Following the same approach used for the other indicators, to obtain the related index, a normalisation on the Mathematics and Sciences PISA scores for each country has been carried out, by taking into account the initial average score, referred to the year 2000, for all the subjects (which was equal to 500, data retrieved in Ref. [342]) and the related standard deviation (which was equal to 100, data retrieved in Ref. [342]). Thus, in order to manage the normalisation for all scores of each country, the minimum value for the Mathematics and Sciences results has been fixed to 1.5 times the standard deviation below the average score (350), and its maximum value has been fixed to 1.5 times the standard deviation above the average score (650). Normalisation has been obtained with the same normalisation formula proposed by the United Nations Technical Report on *HDI* [492], with the previous introduced goalpost values:

$$Q = \frac{q_{actual} - q_{min}}{q_{max} - q_{min}} = \frac{q_{actual} - 350}{650 - 350} \tag{3.60}$$

where Q is the normalised quantity (Mth or Sci scores), q_{actual} the current value of the considered quantity, q_{min} and q_{max} represent the minimum and maximum goalposts, respectively, which have been set for the quantity q itself (respectively: below 1.5 times standard deviation in 2000, above 1.5 times standard deviation in 2000).

In Figure 3.2 **a)** the results of the arithmetic average of the normalised Mathematics (Mth) score and Sciences (Sci) score are shown. They have been evaluated by using Equation (3.54), and are referred to the following countries: Australia, Austria, Belgium, Brazil, Canada, Denmark, Finland, France, Germany, Greece, Italy, Japan, Mexico, Netherlands, Norway, Portugal, Russian Federation, Spain, Sweden, U.K., U.S.A. They are referred to the years on that the new OECD's PISA surveys have been carried out in their actual form: 2006, 2009, 2012, 2015, and 2018.

It is possible to highlight that, for all the analysed countries, the results of the year 2018 demonstrate a descending trend, in relation to the ones of the previous years. In particular, in 2018, the *OP* of each country has diminished with respect of the country maximum value itself, which can be quantified as reported in Table 3.2.

Table 3.2 *OP* variation for the analysed countries with respect to their maximum value during the period 2006-2018.

Country	*OP* Variation [%]
Australia	−15
Austria	−9
Belgium	−7
Brazil	−3
Canada	−9
Denmark	−4
Finland	−20
France	−2
Germany	−10
Greece	−14
Italy	−9
Japan	−7
Mexico	−5
Netherlands	−10
Norway	−3
Portugal	−3
Russian Federation	−8
Spain	−6
Sweden	−1
United Kingdom	−1
United States of America	−3

It is possible to point out that since the year 2018, PISA data are available also for China, that ranks at the top of all scores of the assessment. Nevertheless, in this

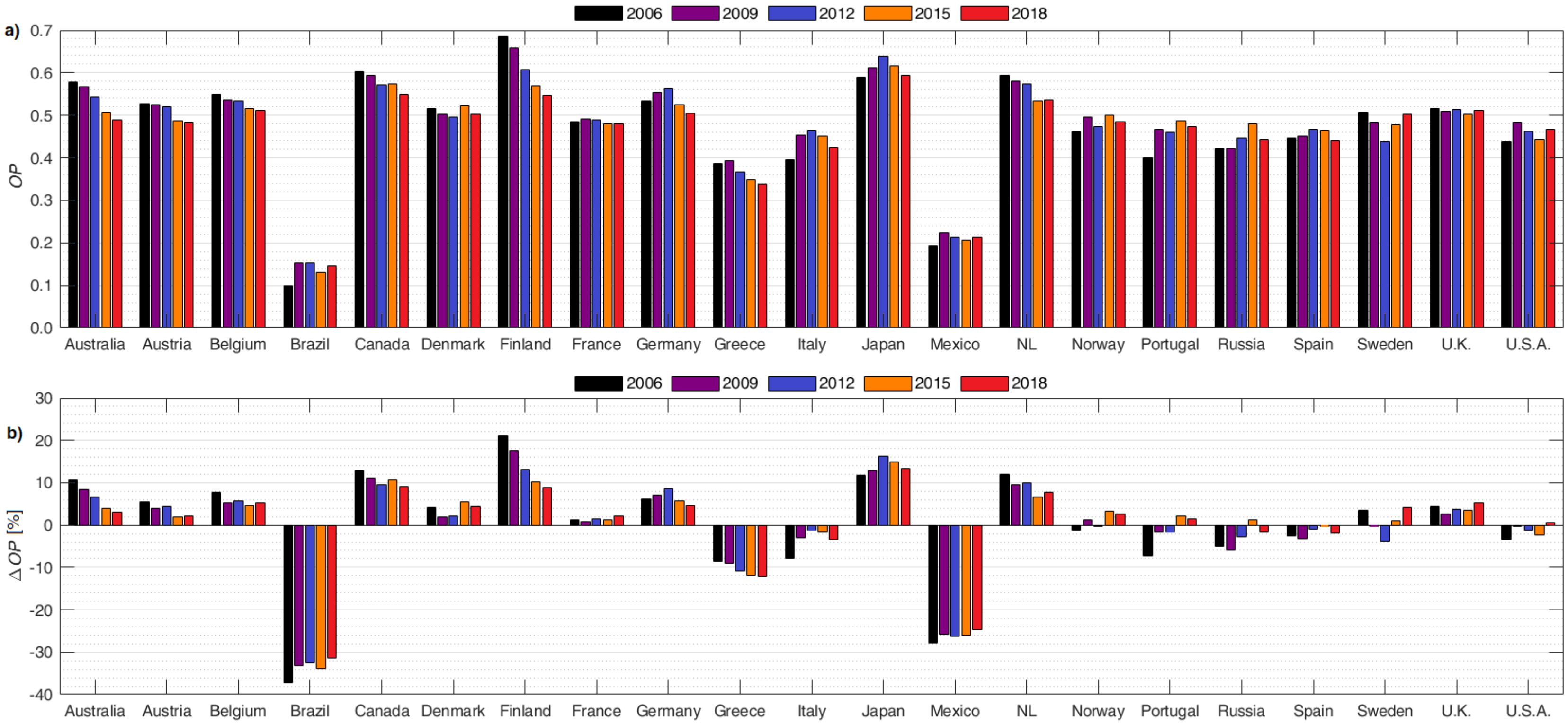

Figure 3.2 **a)** Normalised *OP* average values, relative to Mathematics and Sciences OECD's PISA results during the time period (2006-2018). Their raw scores data have been taken from the OECD's Database [345]. **b)** Percentage variation for each surveys' assessment year available and for each considered country, from the annual *OP* average value within the considered countries. So, it is dependent from the considered sample.

context China participation is different from the other countries because it considers only the Beijing, Shanghai, Jiangsu and Zhejiang regions, that are considered the wealthiest and most economically developed ones of the entire China [80].

In Figure 3.2 **b)** are represented the percentage variations of the normalised OECD's PISA values from the average annual value within the countries considered, for each country, for each OECD's PISA reference year. The mean average value for the i-th year, has been evaluated as follows:

$$\overline{OP}_i = \frac{1}{N} \sum_{j=1}^{N} OP_{ij} \tag{3.61}$$

where: j is the j-th country considered, and N is the total number of them.

Figures 3.2 **a)** and **b)** point out the need of an improvement in teaching scientific disciplines, in order to allow pupils to obtain better bases for the growth of their technical abilities. In fact, considering the continuous increase in technologies use in the productive systems, these children will achieve a job in a more technological context (their future), and the well-being in that work environment will depend on their technical abilities. So, policy-makers should pay particular attention in performing the present choices in the educational context, with the aim of better designing a future sustainable society.

In Figure 3.3 **a)** are shown the UN's Education Index values, EI, for each considered country (in 2006, 2009, 2012, 2015, and 2018). It is possible to highlight that for the majority of the considered countries, an increasing trend of their EI has occurred, presenting the maximum value in the year 2018. Only three of them presented a different tendency: Australia, Denmark and Portugal reached their EI maximum value respectively in 2012, 2012, and 2015. Furthermore, their trend is increasing again, moving towards their previous maximum values. As concerns China,it has raised its EI from 2006 ($EI = 0.551$) to 2018 ($EI = 0.649$), and the four Chinese regions previously cited (Beijing, Shanghai, Jiangsu and Zhejiang) have marked in 2018 the top scores in Mathematics and Sciences, which results in a OP equal to 0.802; thus, they exhibit high levels of teaching in mathematical, physical, biological, and engineering topics, as described in Ref. [280].

The UN's EI, which is closer related to social aspects than to the pupil's knowledge and skills, shows a positive trend for all countries. After having obtained normalised indexes which evaluate the overall education (EI and OP), it is possible to calculate their geometric mean, EI_p, by using the Equation (3.55), and the Thermodynamic Human Development Index - professional oriented, $THDI_p$, including EI_p into Equation (3.56). Then, Figure 3.3 **b)** shows the ratio between the $THDI_p$ and $THDI$, useful to point out the effects of considering also the students' abilities, or the features related to scientific reasoning, and problem-solving skills, which will help in preparing young people to face both current and future global challenges, with greater awareness and knowledge. Figures 3.3 **a)** and **b)**, point out that the indicator $THDI_p$ improves information on a country, developing a deeper analysis of the context, maintaining its characteristics as concerns I_T and LEI.

Moreover, the ratio between $THDI_p$ and $THDI$ presents, for all countries, values lower than 1, and an overall diminishing tendency for all of them. This is because of within EI_p different aspects of education are considered: the social one, in relation to the years of schooling (included into EI), and the student's gain of knowledge in scientific and reasoning features (included into OP). In fact, even thought the EI had an increasing trend during the 2006-2018 period, the OECD's PISA results during the same period on Mathematics and Sciences have affected the overall EI_p results, and consequently the related $THDI_p$ values. Particularly, new policies are needed to achieve sustainable societies. With this aim, a great level of scientific knowledge and problem-solving skills will be a requisite.

It is possible to point out that, the consequences of the decreasing trend in EI_p will have effects in the next decades, when the 15-years old students – today under test in these PISA analysis - will be the future workers and they will play central roles in the future societies.

The $THDI$ and $THDI_p$ values, for the countries under considerations as example of analysis, have grown in the 2006-2018 time range; consequently, the overall countries' well-being and their environmental impact are improving. Nevertheless, it should be considered that the rebound effect related to the 15 years pupils' diminished performances, in problem-solving and scientific knowledge, could have consequences on the global achievements in the next future. Moreover, a positive relationship exists between national estimates of cognitive skills and product sophistication [264], that affects country's innovation outputs, intellectual property position, and its long-term global economic competitiveness, too.

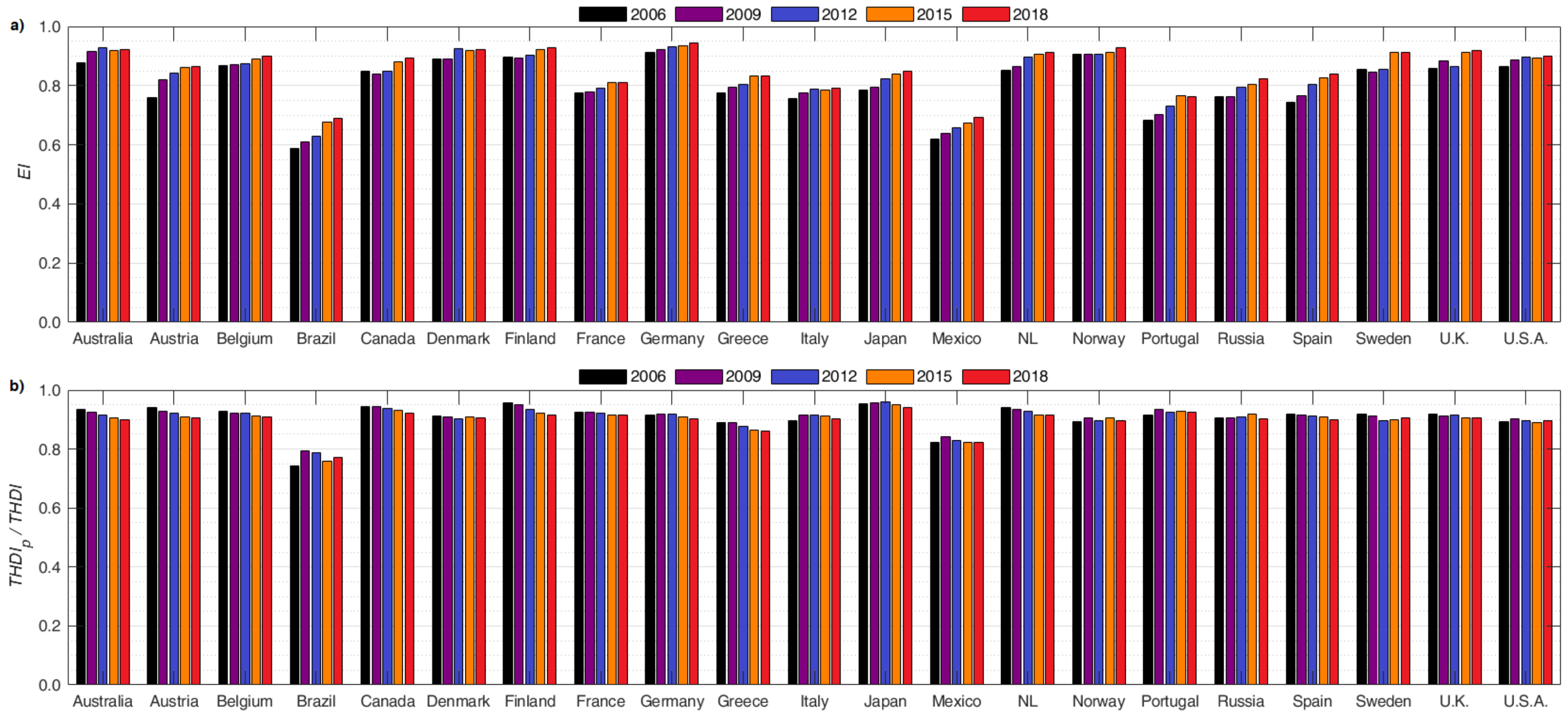

Figure 3.3 **a)** UNs EI values for the years on which the OECD PISA has been carried out, data have been collected from the United Nations Development Programme - Human Development Report database [482]. **b)** Ratio between the Thermodynamic Human Development Index professional oriented, $THDI_p$, and the original one, $THDI$, of the same countries in the same years. Data to perform their evaluation have been retrieved in the following datasets [482, 494, 495, 532, 530, 347, 346, 534, 496]

Today, PISA data can mostly be available for countries classified by the Uns as high and middle-income. But, the OECD is promoting the PISA-D project initiative (PISA for its Development), with the aim of enlarging the assessment, making it more accessible and suited to a higher range of countries, by enhancing the data collections and analysis also to out-of-school children, aged between 16-18, and to the students' parents, in order to obtain also information on the countries' education system and their citizens' knowledge level.

In this context, the Thermodynamic Human Development Index, $THDI$, represents a thermodynamic improvement of the HDI towards environmental considerations, with particular regards to the technological level of a country, and to its sustainable development level, by introducing the Gouy-Stodola theorem to evaluate the losses due to irreversibility. However, in relation to education, these indexes present the above mentioned limit of taking into consideration only the schooling years, in the EI, without any other information on the professional skills achieved during the education time. From a socio-economic point of view, the education level plays a more central role on behalf of the amount of schooling years. In order to introduce an appropriate improvement of the $THDI$, the OECD-PISA results have here been incorporated. Thus, EI has been modified by introducing the professional measure, EI_p, by introducing the normalized OECD-PISA scores for Mathematics and Sciences, as expressed in Equation (3.55). In fact, the OP index is related to the acquired skills and abilities of students. The ratio $THDI_p/THDI$ shows a negative tendency for almost all countries, in the time range on which PISA data are available (2006-2018). This evidence cannot be ignored by policy-makers because of its relevance in the competences acquisition of future generations and, by doing so, laying the groundwork to develop more sustainable, equitable societies, introducing features able to fuel creativity for new approaches and methodologies in education, in order to achieve higher performances in Mathematics and Sciences, with the aim of building the dynamic knowledge needed for the complexity of the sustainable development [206].

These results point out that sustainable development is founded on technological development and its proper use, both related to the use of mathematics and technical sciences, that require the acquisition of relevant knowledge during the education time. So, the educational component of some indexes of sustainability (EI), has been improved by introducing the OECD-PISA evaluations into the Education Index, with a consequent improvement of both the $THDI$ and HDI indexes, which, now, consider also the capabilities of students in relation to Mathematics and Sciences, in addition to the value of schooling years.

Now, in order to show the use of the introduced indicators, a case study is developed, in relation to the indicators evaluated for the European Union countries (EU27).

3.7.1 Case study: the EI_p in the 27 EU countries

This case study develops the evaluation of the indicators for all the countries in the European Union. In Figure 3.4 are shown all the EU 27 countries, with their average expenditure on primary and secondary education in the time period from 2006 and 2018, that corresponds to the years in which the OECD PISA data are available. The data here considered are in constant US$, at purchasing power parity. The countries have been subdivided in quartiles, and the colours of the bars are representative of this subdivision. The first group of countries, or the green ones depicted in the graph, present an expenditure per student above 11779 $\$_{\text{PPP}}$ student^{-1}, the countries belonging to the second group (the yellow one) have an expenditure in the range 9189 – 11779 $\$_{\text{PPP}}$ student^{-1}, the third group encompasses expenditures in the range 6261 – 9189 $\$_{\text{PPP}}$ student^{-1}, while the last group (depicted in brown) present values lower than 6261 $\$_{\text{PPP}}$ student^{-1}. These quantity present a positive trend, or the percentage variation considering a linear regression is positive for almost all countries. However, it must be highlighted that this data are affected by the almost decreasing trend in the number of students during the period considered.

Another splitting, which may be more interesting, because it weights also the size of the population, is the average amount of government expenditures on primary and secondary education in relation to *GDP* and to the primary and secondary students number. So, the EU27 members have been set into four groups, depending on their education spendings. The expenditures evaluation is rooted on the percentage of *GDP* allocated for primary and secondary education per student. This analysis has been carried out by considering the average of the quantity, on the time period from in the seven previous years to 2006 (first year on which PISA tests have been completely performed in the actual form). The result of this analysis is shown in Table 3.3, together with its relative variation among the time period considered. As can be observed, almost all the European countries present a negative trend in the time

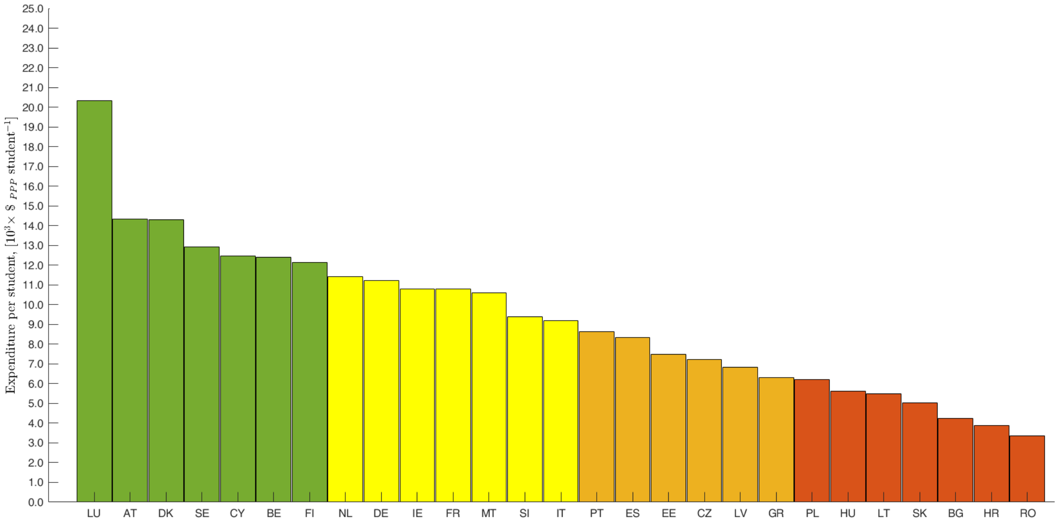

Figure 3.4 European Union (EU27) countries subdivided by government expenditures on education per student (average value referred to 1999-2005), raw data are available in Refs.[489, 490].

period considered. Furthermore, any spending has been weighted in relation to the country size, by considering the amount of the GDP allocated for primary and lower secondary education per student, data elaborated from [533, 489, 490]. So, in order to consider the expenditure fluctuations between one year and another, an average value has been adopted. This value has been calculated, for each country, by averaging the expenditure of the last seven years preceding the first complete available PISA survey (2006). The values reported in Figure 3.5 refer to these averages. The four groups in which the EU27 countries have been subdivided have been represented with different colours, each colour is associated to a group, as follows: EU1 green, EU2 red, EU3 magenta, and EU4 blue. It should be noted that the first group contains almost small countries (population in the range of $(0.4-2.8)\cdot 10^6$ people), which in some cases present quite differences in their historical framework (i.e. Malta, Cyprus, Estonia, Latvia, Lithuania, Slovenia are members of the EU only from 2004).

Being the UNs Education Index related to the student's mean years of schooling it may be correlated to the government expenditures on education. Therefore, usually an increase of the years of schooling (associated to the UNs *EI* index) determines an increase on education expenditures, as partially shown in Figure 3.7. Indeed, the EU2 group, presents an higher *EI* value, rather than EU1, with a greater variation of its value in the time period 2006-2018.

Table 3.3 Average European expenditures on primary and secondary education in relation to *GDP* and their percentage variation, considering the seven years before the time period 2006-2018.

Group	Country	Expenditure per *GDP* [%]	Variation [%]	Expenditure per *GDP* per student [%]	Variation [%]
EU2	Austria	3.25	-14.71	$3.07 \cdot 10^{-6}$	-5.41
EU3	Belgium	4.22	-5.32	$2.12 \cdot 10^{-6}$	-6.73
EU2	Bulgaria	2.36	-5.58	$2.92 \cdot 10^{-6}$	17.41
n.a.	Croatia	n.a.	n.a.	n.a.	n.a.
EU1	Cyprus	4.66	-6.39	$4.00 \cdot 10^{-5}$	4.86
EU3	Czechia	2.50	7.86	$1.88 \cdot 10^{-6}$	13.28
EU2	Denmark	4.54	-20.88	$4.75 \cdot 10^{-6}$	-30.39
EU1	Estonia	3.05	-2.97	$1.82 \cdot 10^{-5}$	7.18
EU2	Finland	3.88	-1.74	$4.67 \cdot 10^{-6}$	-13.62
EU4	France	3.49	-0.85	$3.36 \cdot 10^{-7}$	-1.26
EU4	Germany	2.71	0.13	$2.64 \cdot 10^{-7}$	12.30
EU3	Greece	2.63	-0.04	$2.01 \cdot 10^{-6}$	-0.41
EU3	Hungary	2.64	-25.95	$2.08 \cdot 10^{-6}$	-14.53
EU2	Ireland	3.37	-28.54	$3.94 \cdot 10^{-6}$	-47.55
EU4	Italy	2.89	-6.83	$3.91 \cdot 10^{-7}$	-9.06
EU1	Latvia	3.36	-16.38	$1.30 \cdot 10^{-5}$	17.99
EU1	Lithuania	2.73	-33.00	$6.28 \cdot 10^{-6}$	7.49
EU1	Luxembourg	2.86	-0.79	$3.58 \cdot 10^{-5}$	-14.42
EU1	Malta	3.92	-30.78	$6.77 \cdot 10^{-5}$	-18.85
EU3	Netherlands	3.33	-2.30	$1.18 \cdot 10^{-6}$	-1.81
EU4	Poland	3.17	-23.52	$6.28 \cdot 10^{-7}$	-3.06
EU3	Portugal	3.62	-0.43	$2.52 \cdot 10^{-6}$	1.25
EU4	Romania	1.84	-30.04	$6.98 \cdot 10^{-7}$	-14.19
EU2	Slovakia	2.51	10.68	$3.45 \cdot 10^{-6}$	44.33
EU1	Slovenia	3.28	-14.35	$1.28 \cdot 10^{-5}$	-23.93
EU4	Spain	2.81	-1.69	$4.67 \cdot 10^{-7}$	-14.29
EU2	Sweden	3.93	1.94	$2.68 \cdot 10^{-6}$	-23.19

Now, for the EU 27 countries, it is possible to calculate the normalised indexes, which are useful to evaluate the Education Index more professional oriented, EI_p. In Table 3.4 are shown the results, calculated by means of Equation (3.60) of the average normalised indexes related to the OECD PISA scores, in relation to the time interval 2006-2018. I_{Sci} stands for normalised index related to *Sci*, and I_{Mth} stands for normalised index related to Mth (Mathematics), while *OP* has been calculated by using Equation (3.54). Their relative variation during the time period 2006-2018 has been evaluated by considering a linear regression on the same time interval. In

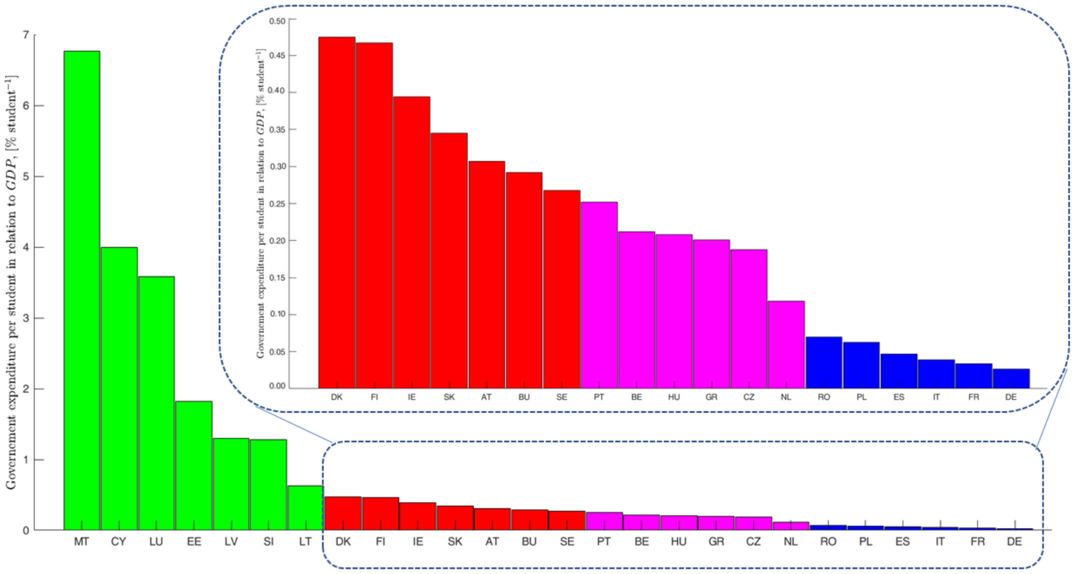

Figure 3.5 European Union countries divided by government expenditures on education. The spendings are referred to the percentage of GDP for primary and lower secondary education, divided by the number of students involved in that level of education (the values reported in the graph are multiplied by 10^{-5}), raw data are available in Refs. [533, 489, 490].

Figure 3.6 are shown the behaviours of these quantities in relation to the previous grouping category. It is possible to observe that the countries that present a higher expenditure in education relatively to GDP per student, tend to have better results in their OECD PISA scores. However, this result can not be generalised. Indeed, in the four groups belong countries which singularly present slightly different scores within their own group.

Once the OP is known, it is possible to evaluate the Education Index more professional oriented, by means of Equation (3.55). The UNs EI and the EI_p for each country are presented in Table 3.5. As can be observed, all countries present a lower value for the EI_p, compared to the EI. In Figure 3.7 the mean value of EI and EI_p along the years 2006-2018 is shown for the four groups EU1, EU2, EU3 and EU4. The advantage of using EI_p is that it contains information also on the students knowledge which will be needed to the next generation citizens and which has been decreasing during the last seven years. With EI_p the improved Thermodynamic Human Development Index ($THDI_p$) may be calculated by using the Equation (3.56).

Table 3.4 Average normalised values for Sciences (I_{Sci}) and Mathematics (I_{Mth}) and *OP* for the EU 27 countries, and their relative variation on time, considering the time period 2006-2018

Group	Country	I_{Sci}	Variation [%]	I_{Mth}	Variation [%]	*OP*	Variation [%]
EU2	Austria	0.497	-13.09	0.668	-3.49	0.582	-7.70
EU3	Belgium	0.515	-7.23	0.713	-6.07	0.614	-6.55
EU2	Bulgaria	0.293	-11.90	0.415	23.66	0.354	7.83
n.a.	Croatia	0.446	-14.55	0.539	-2.04	0.492	-7.88
EU1	Cyprus	0.288	1.52	0.455	9.02	0.372	6.05
EU3	Czechia	0.508	-9.87	0.661	-5.42	0.584	-7.36
EU2	Denmark	0.492	-2.23	0.693	-1.86	0.592	-2.01
EU1	Estonia	0.610	-0.71	0.732	4.50	0.671	2.12
EU2	Finland	0.644	-19.43	0.758	-17.82	0.701	-18.55
EU4	France	0.487	-1.54	0.648	-0.07	0.567	-0.70
EU4	Germany	0.548	-7.64	0.692	-2.02	0.620	-4.54
EU3	Greece	0.378	-17.62	0.507	-5.54	0.443	-10.90
EU3	Hungary	0.472	-14.95	0.604	-5.70	0.538	-9.84
EU2	Ireland	0.525	-7.72	0.661	-1.00	0.593	-3.96
EU4	Italy	0.438	-5.89	0.597	17.32	0.517	7.04
EU1	Latvia	0.475	-1.64	0.620	5.92	0.548	2.66
EU1	Lithuania	0.455	-4.27	0.594	-3.10	0.524	-3.60
EU1	Luxembourg	0.447	-7.01	0.620	-3.82	0.534	-5.16
EU1	Malta	0.369	-7.14	0.575	-4.31	0.472	-5.42
EU3	Netherlands	0.554	-12.28	0.747	-5.37	0.650	-8.33
EU4	Poland	0.529	8.95	0.686	11.39	0.608	10.34
EU3	Portugal	0.466	13.97	0.610	17.76	0.538	16.12
EU4	Romania	0.264	10.78	0.417	15.61	0.341	13.72
EU2	Slovakia	0.416	-17.62	0.616	-3.41	0.516	-9.38
EU1	Slovenia	0.543	-7.00	0.685	2.38	0.614	-1.86
EU4	Spain	0.466	-3.74	0.604	0.89	0.535	-1.14
EU2	Sweden	0.484	-2.54	0.645	0.02	0.564	-1.08

Last, in Table 3.6 the average Total Primary Energy Supply per capita, $TPES_{pc}$, related to each EU27 country (time period 2006-2018) is reported with its relative variation on the same period, together with the carbon dioxide equivalent emissions, $CO_{2e,pc}$, and their relative variation. So, the measures of primary energy needs and of the related environmental impact in terms of GHGs emissions. As concerns $TPES_{pc}$ reduction in the considered period, Greece, Malta, Denmark (as Italy) and Romania have obtained a decrease of approximately -25%, -19%, -17% and -16% respectively. Only few countries present an increasing trend (Poland, Estonia

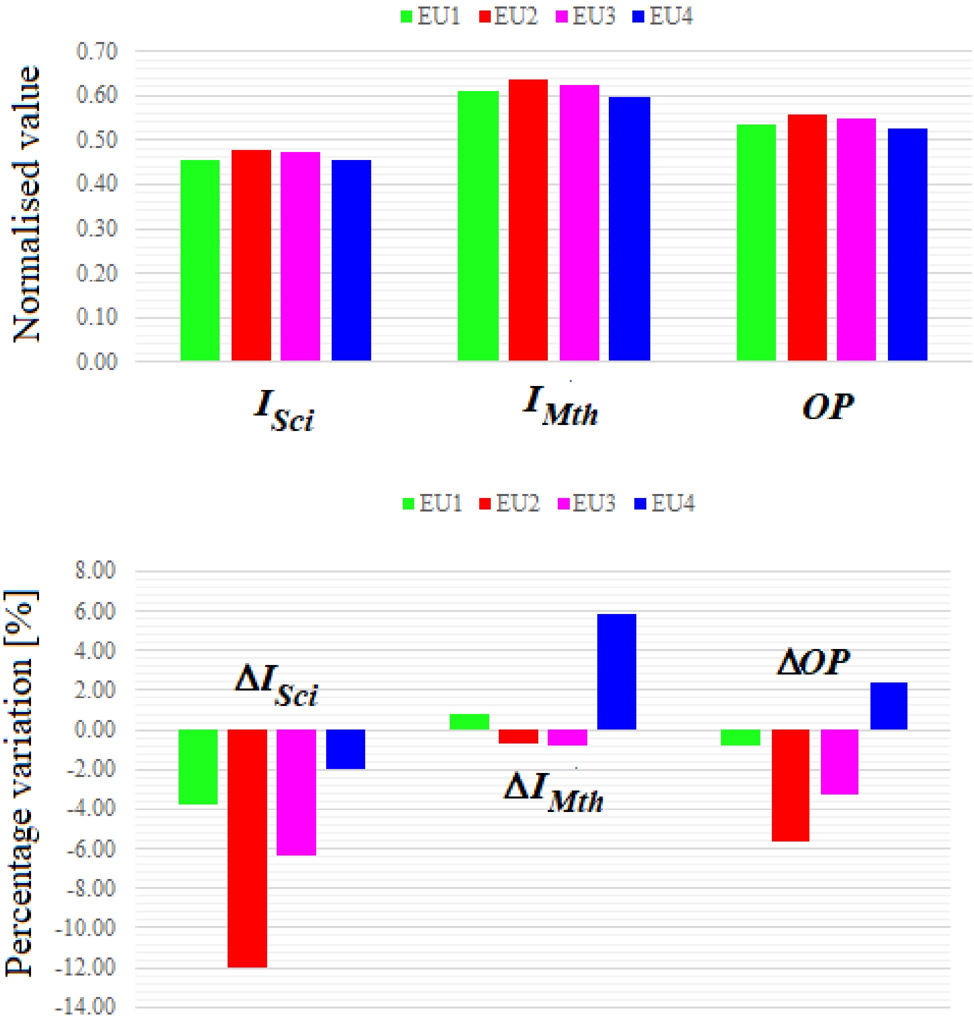

Figure 3.6 Normalised OECD PISA [345, 344] Indexes (calculated by Equation (3.60)): I_{Sci} is the normalised score in Sciences, I_{Mth} is the normalised score in Mathematics. OP is the normalised indicator which considers scientific and technical skills, calculated by means of Equation (3.54). The data here shown are the mean values on the time period 2006-2018 for the four groups EU1, EU2, EU3, EU4.

and Sweden). Unfortunately, regards the reduction of GHGs emissions, the highest decrease does not correspond to the countries that emit more per capita, and the Baltic Republics have increased their per capita GHGs emissions during the period (2006-2018).

As previously, in Figure 3.8 the overall EU1, EU2, EU3, and EU4 trends are shown. It can be noticed that the highest average Total Primary Energy Supply per

Table 3.5 Average normalised values for Sciences (I_{Sci}) and Mathematics (I_{Mth}) and *OP* for the EU 27 countries, and their relative variation on time, considering the time period 2006-2018

Group	Country	*EI*	Variation [%]	EI_p	Variation [%]
EU2	Austria	0.830	14.76	0.695	2.92
EU3	Belgium	0.879	2.76	0.735	-2.01
EU2	Bulgaria	0.769	11.65	0.522	9.72
n.a.	Croatia	0.769	9.64	0.615	0.50
EU1	Cyprus	0.782	9.59	0.544	5.21
EU3	Czechia	0.863	8.65	0.710	0.33
EU2	Denmark	0.909	3.37	0.734	0.64
EU1	Estonia	0.870	3.40	0.764	2.76
EU2	Finland	0.894	4.21	0.790	-7.87
EU4	France	0.793	4.78	0.671	2.00
EU4	Germany	0.931	3.84	0.760	-0.44
EU3	Greece	0.808	7.48	0.598	-2.14
EU3	Hungary	0.815	2.64	0.662	-3.80
EU2	Ireland	0.848	39.09	0.708	15.58
EU4	Italy	0.780	4.76	0.635	5.89
EU1	Latvia	0.855	3.08	0.684	2.87
EU1	Lithuania	0.868	3.25	0.675	-0.24
EU1	Luxembourg	0.780	5.67	0.645	0.11
EU1	Malta	0.776	12.21	0.620	-2.27
EU3	Netherlands	0.884	6.46	0.758	-1.21
EU4	Poland	0.834	7.18	0.712	8.75
EU3	Portugal	0.727	11.45	0.626	13.76
EU4	Romania	0.762	3.96	0.509	8.73
EU2	Slovakia	0.806	7.71	0.644	-1.20
EU1	Slovenia	0.872	3.60	0.732	0.83
EU4	Spain	0.790	10.75	0.650	4.64
EU2	Sweden	0.876	7.03	0.703	2.89

capita results that of the EU2 group, and than decreases for EU3, EU1 and EU4. The highest reduction in $TPES_{pc}$ (-10%) has occurred for the group EU3, followed by EU4 (-8.5%), while EU1 and EU2 present nearly the same value (approximately -7%).

Nevertheless, the GHGs emissions per capita result the highest for the EU1 group, while both EU2 and EU3 group present an approximately the same average value of 10 t capita^{-1}, meaning that within the EU2 group there are countries particularly

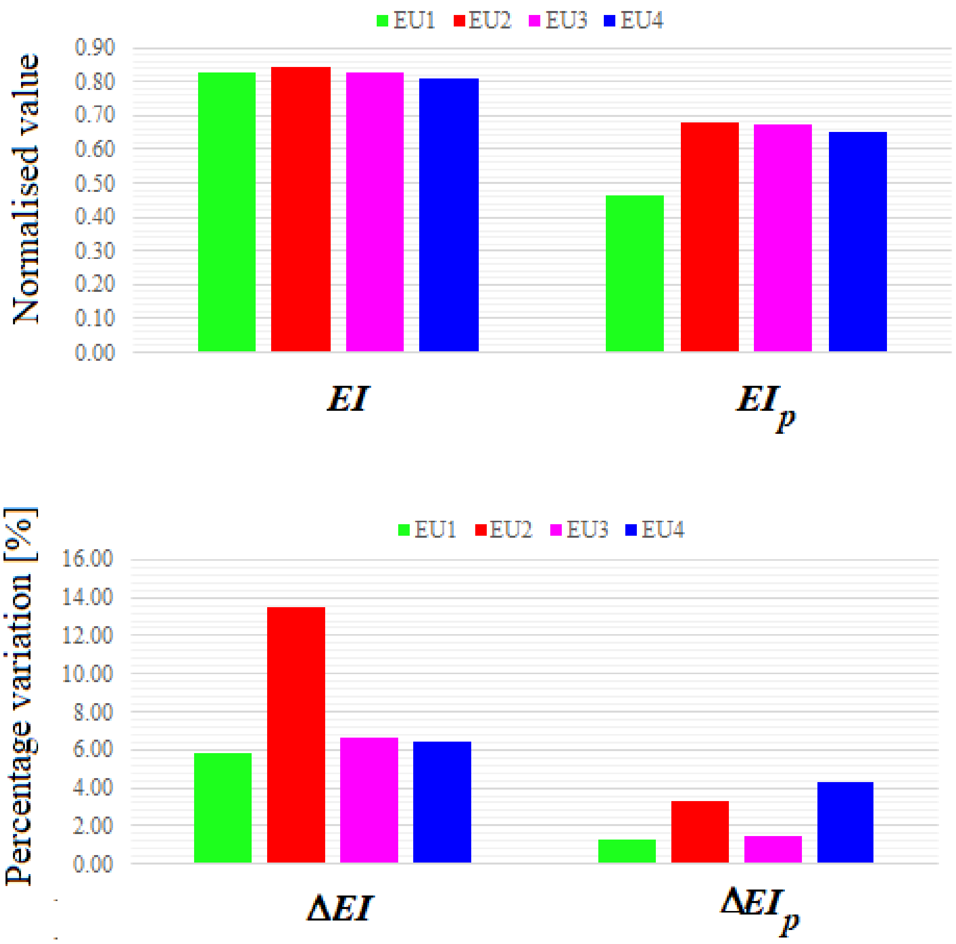

Figure 3.7 Both the UNs Education Index EI, and the Education Index more professional oriented, EI_p (calculated by means of Equation (3.55)) are here shown for the four groups EU1, EU2, EU3, EU4.

advanced in the reduction of their GHGs emissions per capita (variation of -22%). The EU3 and EU4 groups reduction results similar (-17.5%), thus within the EU4 group there are countries which have made big efforts to abate GHGs emissions.

Table 3.6 Average European Total Primary Energy Supply per capita ($TPES_{pc}$) and average carbon equivalent dioxide emissions for the EU27 countries, and their percentage variation (with a linear regression), considering the time period 2006-2018

Group	Country	$TPES_{pc}$ [GJ capita^{-1}]	Variation [%]	$CO2_{pc}$ [$t_{CO_{2,e}}$ capita^{-1}]	Variation [%]
EU2	Austria	156.78	-2.47	9.90	-17.12
EU3	Belgium	201.18	-7.64	11.79	-22.30
EU2	Bulgaria	110.34	-8.60	8.38	-1.19
n.a.	Croatia	90.45	-12.34	6.33	-15.71
EU1	Cyprus	80.95	-1.00	11.96	-17.52
EU3	Czechia	170.86	-6.49	13.15	-16.89
EU2	Denmark	131.01	-17.14	10.82	-38.03
EU1	Estonia	175.64	4.65	15.34	10.79
EU2	Finland	260.75	-8.90	12.51	-31.85
EU4	France	166.05	-7.18	7.72	-21.59
EU4	Germany	161.11	-12.65	11.65	-13.71
EU3	Greece	104.12	-24.75	10.43	-26.83
EU3	Hungary	111.22	-5.40	6.63	-11.84
EU2	Ireland	120.93	-6.25	14.15	-20.59
EU4	Italy	113.58	-17.10	8.35	-27.72
EU1	Latvia	96.82	-1.25	5.56	17.31
EU2	Lithuania	117.14	-12.62	7.12	2.82
EU1	Luxembourg	276.96	-9.95	24.12	-31.31
EU1	Malta	74.17	-18.62	7.15	-36.59
EU3	Netherlands	187.48	-7.41	12.48	-14.18
EU4	Poland	109.18	12.22	10.75	-1.80
EU3	Portugal	94.74	-10.54	6.98	-12.66
EU4	Romania	74.62	-16.24	6.24	-14.08
EU2	Slovakia	130.85	-8.12	8.18	-17.02
EU1	Slovenia	141.97	-9.12	9.25	-17.48
EU4	Spain	113.76	-10.97	8.17	-25.74
EU2	Sweden	204.49	1.37	6.35	-28.00

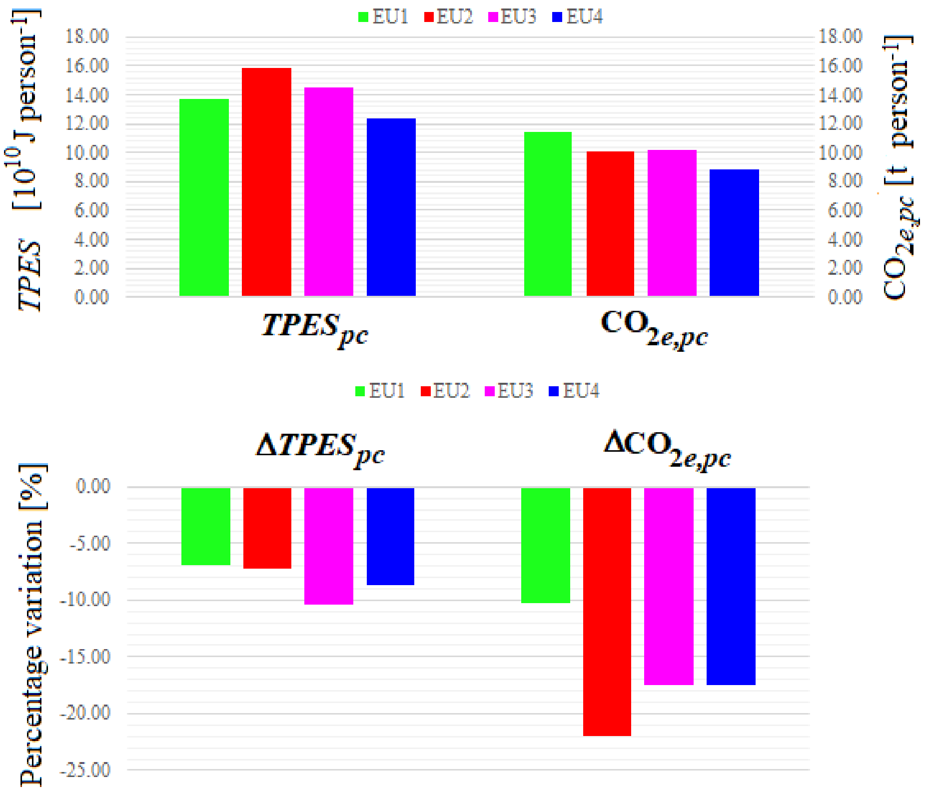

Figure 3.8 Total primary energy supply per capita and carbon dioxide equivalent per capita considering the time period (2006-2018), and their relative variation on the same period. The data here shown are the mean values on the time period 2006-2018 for the four groups EU1, EU2, EU3, EU4.

3.7.2 Considerations

The UN's Education Index, *EI*, takes more into consideration the social aspects than the pupil's knowledge and skills ones. On the contrary, sustainable development is usually based on the introduction of new technologies and on their use, with a related requirement of new workers' abilities. Thus, the central role of technical skills and of the ability of adaptation of the workers emerge in relation to new approaches to work, particularly related to the propensity for innovation, and the individual worker's contribution. But, the UN's *HDI* does not collect any information on these skills. Consequently, UN's *HDI* must be improved in order to take into consideration the measurement of these new workers' skills, too. In order to improve this index, the OECD PISA scores have been included, because of PISA is a comprehensive and accurate international assessment of students' learning outcomes [342], and it was designed just to extrapolate the students' abilities related to their knowledge. Therefore, it results a comprehensive test, where students' abilities can be exploited *at work*, in relation to their knowledge and skills for any specific issue. This represents the main requirement to the citizens of next future. Furthermore, PISA results allow policy-makers to get information on both the quality, and equity of learning outcomes reached by the 15-years old pupils [343]. Indeed, it was pointed out that the personal body of knowledge must be based on [46]:

> *Teaching and learning are the mental activity of grasping a new subject as something familiar.*

Furthermore, higher education has been pointed out to have to include training in sustainability disciplines [140], and, in this context, Mathematics plays a key role in the achievement of the Sustainable Development Goals [6, 507, 260].

The OECD PISA assessment presents data on the students' skills in Reading, Mathematics, and Sciences, and develops their analysis based on the following approach:

- Reading represents the ability of students in order to make any text intelligible;
- Mathematics represents the ability of students in order to carry out a logical attempt to any problem towards the problem solving ability;

- Science represents the ability of students in order to achieve the essential background for technical knowledge and applications.

All these items are all fundamental aspects for the present and future generations to build sustainable societies, in which all citizens have the possibility to give a personal contribution [75]. Indeed, new solutions and technologies are required, not only for the mitigation of the anthropic impacts on the environment, but also for finding solutions on the adaptation to the consequences of the human activities. So, knowledge, problem solving, understanding of sciences, mathematical skills are abilities crucial in order to support actions for more sustainable societies [353, 365, 391]. These abilities will be increasingly required in the next future, together with trans-disciplinary knowledge and soft skills [444, 129]. In this context, it must be pointed out that even if PISA project does not consider all the characteristics of the human growth driven by education, e.g. creativity, critical thinking, ethics, freedom, etc. [88], to the aim of this PhD Thesis is to obtain a tool for quantitative evaluation in relation to the sustainable development and not to study any possible improvement of the education system. With this aim in mind, even if PISA summarizes only few topics of education, its result represents a useful topic to obtain a unified approach to improve the sustainable index for a large number of countries. So, this result represents the tool useful to develop the PhD Thesis analysis, although all the PISA project limits.

As occurs for the International Large-Scale Assessments (ILSAs), also PISA presents some limitations [394], that can be summarised as follows:

- It is a cross-sectional study, that gives a measurement of the educational outcomes at a time for a specific population;
- Its design reflects the educational outcomes and relationships with a related background information within the education systems;
- Its content areas can not be considered exhaustive, but it allows us to take into consideration the fundamental aspects of the education system related to the abilities of students required in the technological growth of the sustainable development.

Therefore, some criticisms on the methodology of the PISA assessment have emerged e.g. sampling participants, achievement estimation model, measuring trends, and commercial interests [554, 399, 451, 205, 452]. Moreover, the OECD's choices related to the methods, in relation to the creation of data have been highlighted to be neither explicit nor clear [450, 22], and some criticisms have been noticed on the scaling model for the final scores [253]. So, PISA project methodology could be improved by making all rough data and procedures to be open source and clearly stated.

Nonetheless, at present, PISA represents the largest available international educational test, which is also considered unique, due to its focus on the student's capabilities related to the use of their knowledge in every day life context [213]. Furthermore, the ilk assessment is carried out in 79 countries, belonging to all continents, with the possibility to use and compare them. Moreover, the implementation of this project is occurring also for low and middle income countries with the PISA for Development (PISA-D). So, taking into account all its limits and the criticisms pointed out, at present, it results a useful tool, in the context of international education assessment.

Here, some other considerations have emerged; in particular:

- The Education spending and the Expected Years of Schooling time are not directly correlated;
- In all the considered cases, a spending threshold can be pointed out in relation to the PISA scores: below this threshold, the PISA grades reduce sharply;
- The $THDI_p$ maintains the same information of $THDI$, but it considers also the outcomes of the pupil's education path, specially in Mathematics and Sciences, disciplines considered in the PISA assessment. $THDI_p$ presents lower values than the $THDI$, because the new improved Education Index, EI_p, presents lower values than the UN's EI, due to its information on pupil's outcomes;
- The increase in education spending isn't strictly correlated to higher $THDI_p$ values.
- Countries with higher education spending present higher greenhouse gases emissions.

In relation to these outcomes, some future developments can be outlined:

- OECD PISA points out the results of 15-years old pupils, but also the subsequent school cycles deserve to be monitored, both in terms of education spending and student results;
- The share of this spending for each country should be more detailed, e.g., number of teachers and their salaries, faculty refresher courses, ICT equipment, school infrastructures, etc.;
- The temporal effect should be deeply further evaluated: any change in education spending determines long-term effects, as well as its time trend and one average mean cycle (7 years) may be not sufficient for this analysis. However, within the considered sample, the data related to some of the countries which have entered into EU from 2000 and after are not available.

In summary, the results obtained in this Section point out that sustainable development needs technical abilities for future workers, due to the more advanced technologies introduced in any sustainable activity. Therefore, these abilities can be achieved by a broad background, that can be built only dedicating long time in discussions, reflections, and reasoning. This can be realised in a stimulating, multidisciplinary, creative and collaborative environment, as just the time spent in school may represent. In fact, during this period, children can grow as a person, human being, increasing their relationship skills, their creative thinking, their emotional management, etc. in a continuous learning-teaching process through the different disciplines. In this context, Mathematics and Sciences are a resource for pupils future job placement, in relation to sustainable development, but also in the context of the problem solving approach of teaching. This will allow pupils to realize themselves in their future work life, that is a facet of a person life. So, to develop some analysis on this topic, a measurement tool useful to compare the greatest number of countries is needed, and OECD PISA results just interesting for the analysis here developed, taking into account its limits. Indeed, the PISA assessment is carried out every three years and the publication of the results is a long process.

3.8 Mutualism as optimisation approach to biofuels production

Nowadays, the attention in reducing the greenhouse gases emissions is continuously growing towards an energy transition from the deep dependence upon fossil fuels as sources to other alternative fuels. An example is represented by the land-based transport, that requires a gradually abandoning of liquid fossil hydrocarbons and actual internal combustion engines towards the introduction of electrical power, even if, today, in relation to aviation transport and shipping, no viable alternatives have yet been found. Thus, this new sensibility on the reduction of carbon dioxide emissions is driving the present energy production systems to the development of new liquid biofuels. Although since the ’70s the production of biodiesel and bioethanol has rapidly increased, at $30-40\%$ per annum, the total energy production of bioethanol and biodiesel remains only of the order of 10^6 TJ with respect to the total global energy amount, which is of the order of 10^8 TJ [266].

Consequently, this Section of the PhD Thesis develops the introduction of the previous results into the analysis of the production of the third generation of biofuels. In order to develop this aim, some considerations on biosystems must be introduced.

For maintaining their life, living organisms must interact with their environment, by exchanging matter and energy flows; so, living systems can be studied as thermodynamic open systems, by introducing the First and the Second Law of Thermodynamics [124]. Life could not exist without any interaction with the environment; consequently, this interaction must be taken into account as the key factor of life, including any other possible interaction, also with other living species in the environment.

When more species co-exist in the same ambient, a natural phenomenon, called symbiosis, can occur. The term *symbiosis* has first been introduced in 1879 by Heinrich Anton de Bary[11], in relation to different species of organisms, which live and interact together [351]. Symbiosis constitutes a fundamental component in Earth’s life due to its relation to the evolution of the living organisms, as Stanley highlighted [455]. Thus, symbiosis is considered as the association between at least two different species of living organisms [357], that persists on time for an undefined

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[11] Heinrich Anton de Bary, Frankfurt am Main, January 26th, 1831 – Strasbourg, January 19th, 1888

duration or for a finite time and that can vary its effects along the same time range, in relation to the environment conditions in which the interaction occurs [67].

The interaction between living organisms can lead to an advantage for at least one of the symbionts or to a disadvantage or to nothing at all, and these different kinds of symbiosis have been categorised, on the base of the effects of the association between the organisms considered [528]:

- Mutualism, that implies an obligatory interaction with a reciprocal benefit for both species;
- Cooperation, that implies a non-obligatory interaction with a reciprocal benefit for both species;
- Commensalism, that implies a positive relationship between the species, where one of them takes an advantage and the other is neutral to the interaction, e.g., the waste of one organism represents a resource for the other, which uses it as nutrient;
- Predation, that is a negative form of symbiosis, one organism is attacked and preyed by the other one;
- Parasitism, that is a complex interaction in which an organism (parasite) gains a benefit and the other one is damaged (host);
- Amensalism, that is an unidirectional interaction and implies the production by one organism of a compound that has a negative effect on the other one;
- Competition, that overcomes when both species need the same resource (nutrient) to live, the organisms can co-exist at lower levels or one organism can overwhelm the other one.

All these subcategories are useful from a theoretical biology point od view in order to define and to classify all kinds of interaction. Therefore, it has experimentally pointed out that it is very difficult to distinguish which is the category of symbiosis for each single case analysed [528]; indeed, they can also switch from one form to another one, during the life of the living organisms [297]. Furthermore, all types of symbiosis and mutualism declinations are not universally recognised and defined [297, 361, 64, 130, 301, 322]. Thus, in accordance to Paracer and Ahmadjian [357], here, the term mutualism is used for the association in which each symbiont gets a benefit. Furthermore, in Refs. [134, 171, 133] it is possible to find other definitions in relation to the cooperative interactions between species/organisms; for example:

- Detritivory, that is categorised as a particular kind of commensalism, in which one specie gets a benefit from the other one, that is no more alive (thus, resulting neutral);
- Facilitation, that consists in any unidirectional benefit for one of the involved species [134];
- Protocooperation, in which both organisms get conditional benefits, although they are able to continue their life independently from the other [171];
- Synergism, that is considered the general non obligatory relationship, in which the two organisms get benefit one from another [133];
- Syntrophy, that is a kind of mutualism and synergism, in which the metabolisms of the two species are complementary among them [133];

A complete review of the terminology on symbiosis is summarised and discussed in the Ref. [297].

When the two species of microorganisms (i.e. bacteria, bacteria/alga, alga/alga, yeast/alga, yeast/bacteria) are living together, they absorb exergy Ex_{in} in different forms (heat, metabolites, etc.), and they can release products useful for biofuels, bioplastics or other useful bioproducts production, as their wastes, a schematic example has been drawn in Figure 3.9). Thus, the entropy generation can be evaluated by considering the photosynthetic contribution of each species, and of the results of their interaction among them. This last contribution is the more difficult to be evaluated. Thus, for photosynthetic micro-organisms the evaluation of the efficiency of the symbiosis can be evaluated by taking into consideration of the useful effect required; in relation to the aim of this PhD Thesis, it is the lipid mass production. In fact, in order to obtain biodiesel from photosynthetic microorganisms, the fundamental parameters are the biomass productivity and the amount of lipids stored inside their cells. Thus, if the two species live separately they release the mass of products m_1 and m_2 respectively, that holds the energy releases $m_1 h_f$ and $m_2 h_f$ respectively, where h_f represents the formation enthalpy of the product. On the contrary, when

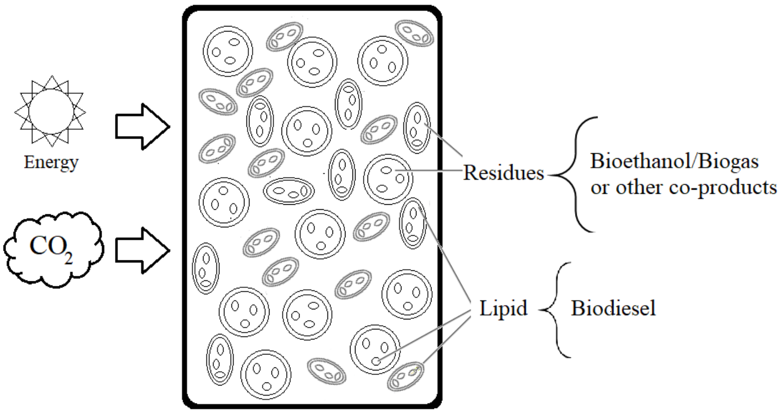

Figure 3.9 Schematic drawn of the co-cultivation of two different species, where the lipid content is useful for the biodiesel production and the remaining fraction of the biomass can be used for other applications.

the species live together, they release $(m_1 + m_2)h_f$, while in the case of mutualism they release $(m_1 + m_2 + \Delta m)h_f$.

So, introducing the hypothesis that the total working hour for mutualistic and non-mutualistic cases are constant, the indicator (3.45) results:

$$I = \frac{T_0 S_g}{W} = \frac{Ex_{in} - m h_f}{m h_f} \tag{3.62}$$

where T_0 is the absolute environmental temperature, Ex_{in} is the inflow exergy, m is the lipid mass formed, and h_f is the specific enthalpy of formation. Thus, the indicator for the two different processes results:

- non-mutualistic process:

$$I = \frac{Ex_{in} - \left(m_1 + m_2\right) h_f}{W} = \frac{Ex_{in} - \left(m_1 + m_2\right) h_f}{\left(m_1 + m_2\right) h_f} \tag{3.63}$$

- mutualistic process:

$$I_m = \frac{Ex_{in} - \left(m_1 + m_2 + \Delta m\right) h_f}{W} = \frac{Ex_{in} - \left(m_1 + m_2 + \Delta m\right) h_f}{(m_1 + m_2 + \Delta m) h_f} \tag{3.64}$$

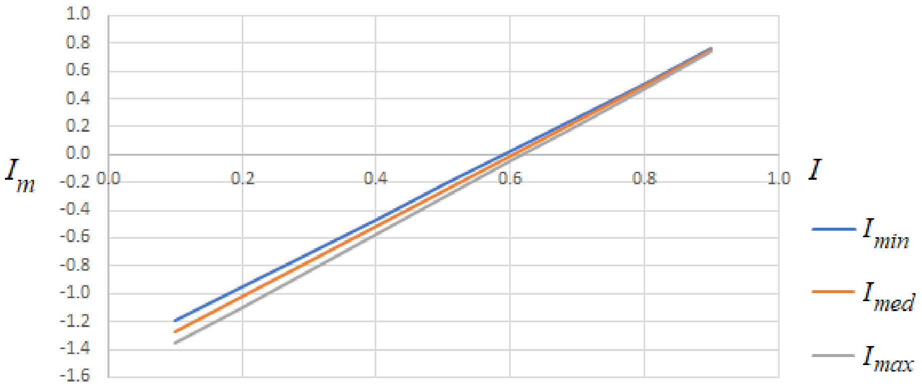

Figure 3.10 Mutualistic indicator vs non-mutualistic one in relation to the better and worst condition of growth in non-mutualistic conditions for *Chlorella* and *Monoraphidium*, and calculated by using the data collected in Ref. [383].

Now, considering the process as a thermodynamic regenerative process, it follows:

$$I_m = \frac{m_1 + m_2}{m_1 + m_2 + \Delta m} I - \frac{\Delta m}{m_1 + m_2 + \Delta m} < I \qquad \text{always} \tag{3.65}$$

which points out that the mutualistic process results more sustainable; indeed, the related indicator results lower than the non-mutualistic process one.

Now, in order to show an experimental proof for the result obtained, two different examples of co-cultivation are considered. In each case, two different photosynthetic microorganisms have been cultivated together, in order to study their lipid and biomass productivity for biodiesel production (and eventually other useful co-products from their biomass residues [412], left after the process of lipid extraction, as shown in Figure 3.9).

Starting from the data summarised in Refs. [383] and [553], two different examples in relation to the comparison of the mutualistic and non-mutualistic cultivation can be carried out:

- Case 1. Co-production of *Ettlia sp.* and *Chlorella sp.* [383], which data are summarised in Table 3.7;
- Case 2. Co-production of *Chlorella sp.* and *Monoraphidium sp.* [553], which data are summarised in Table 3.8.

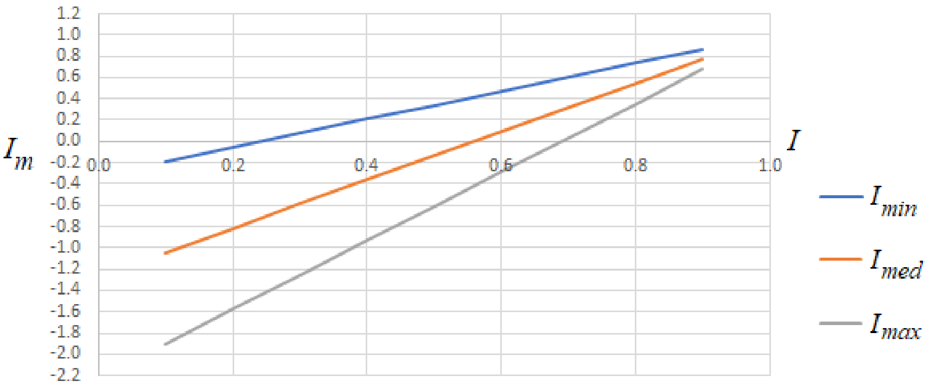

Figure 3.11 Mutualistic indicator vs non-mutualistic one in relation to the better and worst condition of growth in non-mutualistic conditions for *Ettlia* and *Chlorella*, and calculated by using the data collected in Ref. [553].

Table 3.7 Case 1. Lipid biomass formation per unit of volume in mono-cultivation of *Ettlia sp.* (1) and *Chlorella sp.* (2) vs their mutualistic co-cultivation

Lipid biomass formation	Mono-cultivation (1) m_1 [mg L^{-1}]	Mono-cultivation (2) m_2 [mg L^{-1}]	Mutualistic cultivation $m_1 + m_2 + \Delta m$ [mg L^{-1}]
Case 1.	30.3 ± 4.7	201.7 ± 8.2	353.7 ± 6.0

Table 3.8 Case 2. Lipid biomass formation per unit of volume in mono-cultivation of *Chlorella sp.* (1) and *Monoraphidium sp.* (2) vs their mutualistic co-cultivation

Lipid biomass formation	Mono-cultivation (1) m_1 [mg L^{-1}]	Mono-cultivation (2) m_2 [mg L^{-1}]	Mutualistic cultivation $m_1 + m_2 + \Delta m$ [mg L^{-1}]
Case 2.	370.6 ± 177.3	95.6 ± 26.7	592.6 ± 184.6

The results based on these data [383, 553], confirm the result previously obtained, as shown in Figure 3.10 and in Figure 3.11, respectively. The indicator for the mutualistic condition results always lower than the indicator for non-mutualistic condition, highlighting a more sustainable result for the mutualistic condition. So, the mutualist condition represents an optimisation approach for the lipid production, showing an efficiency of production of (1.53 ± 0.09) and of (1.27 ± 0.95), respectively, with respect to the efficiency of the single species culture. Thus, the mutualistic interactions represent a spontaneous condition for the improvement of the biodiesel production.

The sustainable use of the Earth limited resources represents a key factor for the efficient use of the resources. Indeed, natural resources (metals, minerals, fuels, water and land, etc.) are fundamental for the economy, due to their role of vital inputs for all the economic processes. The request and use of resource materials is continuously growing [13]. In this context, at least two kinds of risks can be highlighted [500]:

- The supply risk, that considers the political-economic stability of the producing countries, the concentration level of production, the potential for substitution and the recycling rate;
- The environmental country risk, that considers the risks for the countries with weak environmental performance, to protect the environment.

So, in this PhD Thesis, an indicator has been introduced with the aim of quantification of the sustainable resources usage with respect to their economic and environmental role. The entropy generation in relation to the carbon dioxide emissions, weighted by the useful results of the considered process, is the key quantity of the analysis, leading to the exergetic consideration of the processes. Moreover, the unite of measurement of the entropy generation can be the kWh; consequently, it is possible to introduce a link to a reference energetic cost, e.g., the cost of the electric energy, enabling the comparison among different processes in relation to the desired product obtained.

Furthermore, the expression of the thermodynamic indicator, here introduced, evaluates the sustainability of the considered process, because the entropy generated is weighted by the desired product, with the consequence that lower is the value of the indicator higher is the sustainability of the process.

Last, using this indicator in the analysis of micro-organisms for biofuel production points out that a natural optimisation, for the biofuel production process itself, constituted by the exploitation of a natural behaviour that can occur between two different species of interacting living organisms. Thus, mutualism represents a natural improvement of the lipid production, useful for biodiesel production. So, a simplified approach is obtained in order to evaluate the efficiency of mutualism, and to quantify the optimisation of the process, with respect to the same biochemical process, developed by any species. The mutualistic efficiency, for the lipid production, results 1.53 times the efficiency of the lipid production of any single species.

3.9 Conclusions

Today, the human history is in front of a crossroad, and has been driven mainly by social and economic deepening, which has led to complex dynamics and to a difficulty in managing the socio-economic systems. Consequently, both the socio-economic degradation and the environmental problems are continuously growing [197]. Concurrently, new opportunities for improvements are coming from scientific and technological advances in fields such as healthcare and to the growing of consciousness of environmental issues.

Economy as a physical system [102, 178, 191, 240, 271] can be analysed by Laws of Thermodynamics, by introducing the system boundary with respect to producers and consumers of goods and services, but also to the intermediate inputs and final outputs. Furthermore, the environment must be taken into account; indeed, environment is the set of all the natural resources and the sinks, but also the place to which the wastes of all human activities are discharged. Energy represents the fundamental physical quantity for all the transformations and transitions within the system [153, 156]. During the social and economic development, people must increase their knowledge on the technologies involved for obtaining the useful processes. Then, following the Second Law of Thermodynamics, high-quality energy suffers a degradation into the work transformation.

Spreng considered the evaluation of the economic activities in relation to the importance of their output, by measuring their efficiency and information.

Here, the choice among alternative technologies has been shown to be based on entropy, being entropy the physical quantity related both to information and to efficiency.

Since the 1980s, optimization of energy processes has been reconsidered [118], and Bejan introduced a new standpoint of maximization of power with heat engine models associated to heat transfer irreversibility, proving that the maximum power corresponds to minimum entropy generation rate [37], then proved in agreement with the maximum entropy generation approach, that agrees with the Gouy-Stodola theorem [288, 287]. Thus, entropy generation analysis has been highlighted to represent a design tool to obtain system improvements, and, consequently, also a measure of sustainability. The process with the lower entropy generation rate is more sustainable than others, due to its ability to realize the energy conversion in a more efficient way [251, 202]. Furthermore, in the last decades, the key role of the thermodynamic analysis has emerged in relation to fluxes and irreversibility, in biology, economy, ecology and more in general in physics, chemistry, bioeconomy, complex systems, and engineering, with particular interest in optimization, design and control on systems behaviour [284, 387, 100, 47, 289].

Thus, in this PhD Thesis, a thermodynamic indicator has been built in order to approach the cooperative effect of the link among technological, economic and social requirements, in relation to sustainability. An indicator has been obtain to consider:

- The effect of the human activities on the environment, by evaluating the thermodynamic waste, by the evaluation of the entropy generation;
- The effect on economy and society, by considering the total hour of labour, with the consequence that the *GDP* disappears, providing a concrete answer both to the request of the Nobel laureate Joseph E. Stiglitz who highlighted [458] the inadequacy of the *GDP* in relation to sustainability assessments, and also to the European Commissions initiative “Beyond GDP” [176].

So, with respect to the resource consumption, the fundamental role of the exergy flows has been pointed out, showing how evaluate the entropy generation for the processes.

Last, in relation to biofuels, it s important to develop some considerations on the the different applications on the plants, that are examples usually discussed in literature [52]. Thus, with respect to the lipid production for biodiesel from microorganisms, two mutualistic species have been shown to be able to improve the lipid production, with higher efficiency. The measure of the mutualistic consequence on the lipid production has been carried out by introducing a simplified analytical model. Its limit is that nature is complex and non-linear, so this model represents a simplified approach to obtain quantitative results, but without any analysis of the biophysical processes at cellular level.

Moreover, biotechnology has historically utilized organisms for a variety of purposes. Recently, a directed modifications of organisms for chemical production has been developed [223]. In fact, changes in available information present in the microorganisms DNA may be useful to improve the biofuels production [170, 174]. But, the synthetic biological improvement can be considered more effective if constrained by a well defined aim, which can be highlighted by a deep analysis of the natural behaviours of the microorganisms themselves [101]. A natural optimisation of the lipid production have been pointed out to consist in the co-cultivation of the microorganisms, and a driven approach for any synthetic biological manipulation can consist in the improvement of this natural behaviour, with a related amplification of the spontaneous behaviour of the microorganisms. Symbiosis improves some favourable aspects of the biofuel production; indeed:

- In relation to ethics, symbiosis improves the productivity of the algae and bacteria, with the consequence of a reduction of surface required for their cultivation;
- In relation to technology, symbiosis increases the optimisation of nutrients and water used with the related decreasing in the request of molecules and energy required for the cultivation of the algae and bacteria; consequently, it generates a reduction in local pollution;
- In relation to economics, symbiosis increases the profit because it increases the productivity with a decrease of the requests in energy and nutrients.

Chapter 4

Valorisation of a field residue for energy purposes: The rice straw biomethanation

Summary. In this Chapter, the thermodynamic index, previously obtained, is used to approach the valorisation of a field residue, the rice straw. Indeed, at present, rice straw is usually abandoned in the field or burned there, without any second use. So, it is considered a waste, without any value. But, here, by using the anaerobic digestion, the bio-methane production from rice straw is evaluated, and, consequently, by introducing the thermodynamic index, the rice straw is shown to represent a possible new energetic resource. First, a particular case, the Novara district, is considered, then the analysis is extended to Italy, and, last, to countries in different continents.

4.1 Introduction

Nowadays, there is an urgent need to find alternative solutions to the conventional fossil fuels use, reducing the dependence of each country upon external energy sources. In this context, the use of wastes from other supply chains results really interesting both for biofuels and bio-products production, within the frameworks of circular economy and energy communities, too. Thus, in this Chapter the use of an agricultural waste to produce biofuels, which can be performed combined with other useful bio-products will be analysed. In particular, rice straw will be considered as the potential feedstock to supply this value chain. The choice of this feedstock has been elaborate on due to the actually harmful common practices of its disposal, with the related negative impacts. In order to avoid this issues, the scientific community and entrepreneurs must develop alternative sustainable solutions to turn rice straw into a commodity, in order to build value chains around this agricultural waste.

The waste-to-energy conversion routes of agricultural residues into renewable energy sources can contribute in reducing global greenhouse gases emissions (specially methane ones), without compromising valuable land resources for food production [324]. In fact, being agricultural residues a second generation biofuel feedstock, they do not compete with agricultural lands as opposed to first generation ones. Unused agricultural wastes can be one of the most stable energy sources, and can represent key-elements to support national long-term energy strategies: playing a crucial role in mitigating the growing energy demand, with a sustainable approach [324, 413]. Thus, biomass from field residues could become a resource in the energy sector, but also in other bio-products production chains.

In Table 4.1, the total production (P) in 10^6 t, the production-area ratio (P/A) in t ha $^{-1}$, and the estimated mean dry residual biomass availability (P_w) in 10^6 t, related to four main crops in different world regions, are summarised. In particular, the data related to barely, maize, rice and wheat are reported. The average availability of the residual biomass has been calculated by introducing the following considerations:

- An average composition in terms of moisture content for barely, maize, rice, and wheat respectively of [241]: 13.8%, 11.3%, 11.4%, and 10.9%;
- The residue to product ratio for barely straw, corn stover, rice straw and wheat straw respectively of [241]: 1.30, 1.00, 1.35, and 1.30. These coefficients are referred to dry mass of residue and dry mass of product ($\mathrm{kg}_w\ \mathrm{kg}_P^{-1}$);
- The fact that, in most of the cases, not all the produced residues can be used without causing issues like the soil erosion and the decrease of soil organic matter. The residues availability depends on many factors such as climate of the considered geographic area, land conditions, location of the crop, harvesting conditions, etc. For instance, the US Department of Agriculture [352] uses for its estimates that conservation tillage practices for crop residue removal require

> that at least 30% of the soil surface should be covered with crop residues after planting, in order to lower soil erosion due to water, and 1:1 t ha^{-1} for small grain residues to lower the soil erosion due to winds. The results shown in Table 4.1 consider the hypothesis, introduced also in Ref. [241], of 60% of ground cover, in order to consider uncertainties of local situations. Thus, the average 60% of ground cover coefficients for the different crops are the following ones [241]: 1.3 t$_{dry,w}$ ha^{-1} for barely straw, 2.7 t$_{dry,w}$ ha^{-1} for corn stover, and 1.7 t$_{dry,w}$ ha^{-1} for wheat straw. The advantage of rice straw is that no rice straw on the field is required to prevent soil erosion.

As can be observed, rice straw represents the most abundant field residue among major crops, and that makes it an eligible candidate to be further investigated as a potential source in the circular economic context; in particular, for energy purposes due to its chemical and physical properties.

4.2 Rice straw

The rice plant is botanically named *Oryza* and it is a monocotyledon plant. There are two main cultivated families of *Oryza*: the one which origins are from Asia *Oryza sativa*, and the one originated from Africa *Oryza glaberrima*. Actually, the latter is cultivated only in the West Africa region. Indeed, it has a lower yield and milling quality than *Oryza sativa*. The rice plant is a semi-aquatic plant. However, it can be cultivated also in dry land or in deep water (up to 5 m), but with lower yields. A general scheme of *Oryza* is shown in Figure 4.1.

Rice straw composes all the non-edible vegetative parts of the rice plant (*Oryza*), cut at grain harvest or after, and it is considered a field (or crop) residue. In general terms, the crop residues (or agricultural residues) are all the non-edible parts of the plant, which remain on the fields after harvesting [262]. However, technically, there is a difference between field residue and process residue: a field residue is what remains after the crop harvesting, while a process residue is the waste left when the crop is processed into a usable product [319]. So, rice straw is the residual by-product of the rice production at harvest. Here, the term field residue will be used for both these aspects, due to the rice processing chain. It is important to highlight that flooded rice (lowland rice) fields are responsible for $(10-15)\%$ of the global

Table 4.1 Production (P) [154], Production-crop area (P/A) [154], crop residue availability for different purposes (P_w) related to barely, maize, rice, and wheat crops, related to the year 2020.

Region	Barely			Corn			Rice			Wheat		
	P [Mt]	P/A [t ha^{-1}]	P_w [Mt]	P [Mt]	P/A [t ha^{-1}]	P_w [Mt]	P [Mt]	P/A [t ha^{-1}]	P_w [Mt]	P [Mt]	P/A [t ha^{-1}]	P_w [Mt]
Africa	5.53	1.29	n.a.	90.53	2.10	n.a.	37.89	2.21	45.32	25.23	2.53	12.28
Northern America	14.34	3.91	9.83	373.81	10.75	237.66	10.32	8.54	12.35	84.87	3.41	56.00
Central America	0.86	2.94	0.47	31.49	3.47	3.43	1.44	4.91	1.72	2.99	5.30	2.50
South America	5.94	3.75	3.96	176.29	6.02	77.33	24.97	6.12	29.86	29.96	2.88	16.99
Central Asia	4.50	1.43	n.a.	2.37	6.28	1.08	1.14	3.69	1.37	23.21	1.58	1.85
Eastern Asia	1.28	3.08	0.73	263.18	6.28	120.34	230.14	6.97	275.27	135.72	5.65	116.40
Southern Asia	5.53	1.95	1.36	47.50	3.61	6.64	254.80	4.05	304.76	156.24	3.04	93.50
South-eastern Asia	0.16	2.36	0.06	44.27	4.66	13.64	189.07	4.29	226.15	0.11	1.86	0.03
Western Asia	14.05	2.21	4.95	7.98	7.83	4.33	1.45	6.32	1.74	32.64	2.87	18.47
Europe	94.37	3.96	65.21	123.94	6.38	57.51	4.07	6.38	4.87	255.02	4.14	190.59
Oceania	10.46	2.06	3.08	0.48	8.21	0.27	0.06	6.69	0.07	14.93	1.51	0.45
World	157.03	3.04	88.25	1162.35	5.75	485.65	756.74	4.61	905.14	760.93	3.47	509.07

n.a.: the hypothesis of reincorporation on the soil (60% of ground cover), provides values that do not allow to recover wastes from the fields.

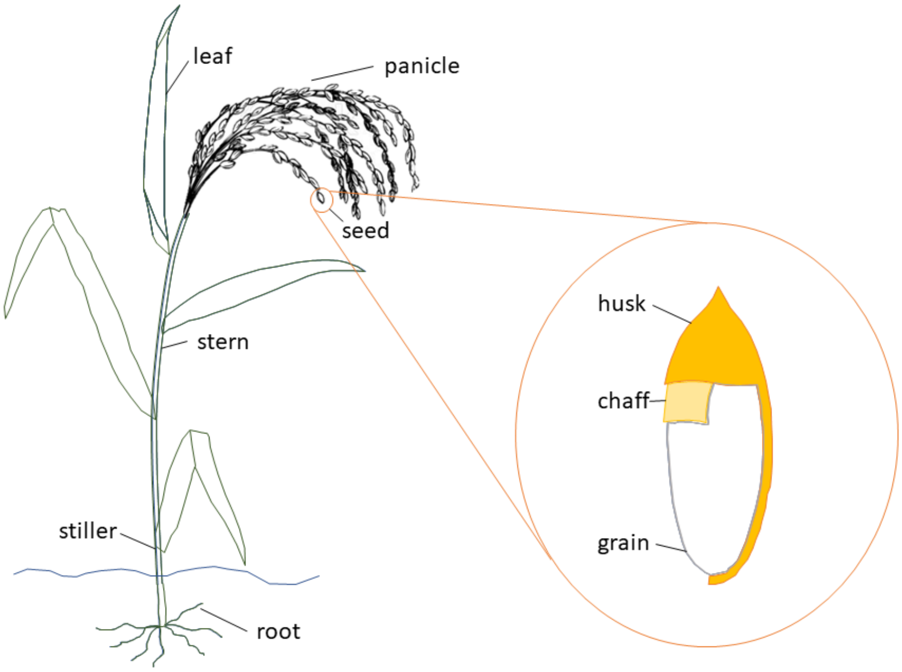

Figure 4.1 Main components of the *Oryza sativa* plant and of the rice seed (husk, chaff and grain are highlighted).

methane (CH_4, $GWP = 28$) emissions caused by anthropic activities, or 10% of the global GHG emissions from agriculture, and rice straw is the major contributor [324]. Indeed, rice is one of the largest sources of methane, nitrous oxide (N_2O, $GWP = 265$), and carbon dioxide (not accounted by the IPCC guidelines) [11].

Rice cultivation, without considering the harvesting process, presents some polluting consequences alone, linked to the irrigation methods, to the fertilising techniques, etc. When the plant growths, amounts of methane and nitrous oxide are emitted into the atmosphere [397, 546]. Indeed, effects of methanogenesis can occur as the result of the bacterial transformation of soil organic carbon, under anaerobic conditions. Furthermore, pollutants are realised during fertilisation [278]. Another cause of pollution is represented by the irrigation technique employed[502].

As concerns the rice production chain, the paddy harvesting steps include: reaping, staking, handling, threshing, cleaning and hauling. The rice combine harvesters are usually employed for the harvesting process, and they can combine all operations: cutting, handling, threshing, and cleaning. The combined harvesters leave loose rice straw into the ground. So, the rice straw collection and transportation are not simple and free of costs [29]. These are also the reasons that push farmers to continue rice straw burning practice, neglecting the consequent hazardous health issues. In Figure 4.2, the post-process to have the polished rice are summarised, with the related by-products.

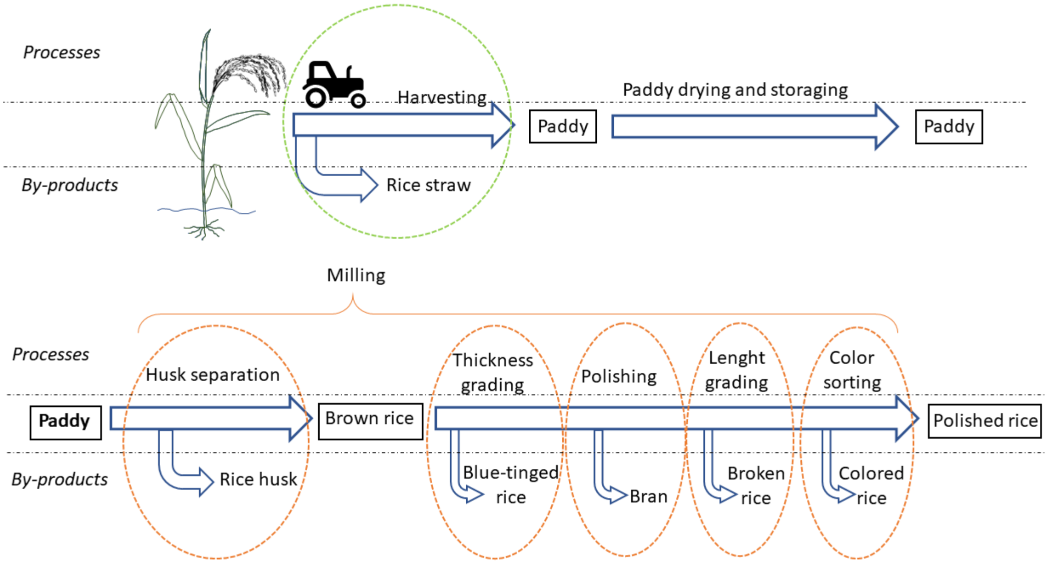

Figure 4.2 Common processes adopted to obtain the polished rice and related by-products of the post-processes, figure adapted from [389, 388].

After the rice harvest, besides the rice grains, it is possible to obtain other by-products, such as straw, husk and chaff. Their production depends strongly on the rice variety and on its management (growth, harvest, and post-processing methods), and it can be estimated as follows [209, 415, 256]:

- Rice straw: $(0.70 - 1.50)$ kg per kg of rice grain;
- Husk (or hull): the major co-product of the rice milling, it represents $0.16 - 0.28$ times the weight of the milled white rice and contains approximately 20% silica in amorphous form. Moreover, it consists of $(60 - 65)\%$ of volatile matter, $(10 - 15)\%$ of fixed carbon, and $(17 - 23)\%$ of ash;
- Chaff (or bran): it constitutes approximately $0.05 - 0.10$ times the weight of the paddy rice, its composition strongly depends on the milling process, however it contains high nutritive values.

However, husk and chaff have yet a second life, with a related economic value, in various industrial sectors, such as the energy, pharmaceutical, and nutritional ones. The rice straw, instead, is poorly used, except in little productions for pulp and paper industries [237], mushrooms production [506], and for building materials (such as insulation and construction panels [377]; researches are also ongoing for straw cement-based building materials [91]). But, most of these productions require particular attention during the harvesting, such as for the pulp and paper production, it results more suitable the rice straw collection without machineries [415]. Consequently, rice straw is still considered a field waste. Moreover, the rice straw presents a high silica content (SiO_2), which constitutes about the 13% by weight of rice straw. This characteristic makes rice straw unsuitable for feeding grazing animals, as occurs for other straws, because it causes wear in their teeth [25]. Furthermore, the high silica and lignin contents of rice straw make this feed poor of nutrient and low digestible by animals, if not properly pretreated [19]. It should be highlighted that in some World regions, despite the poor nutrient content and the issues related to the silica content, rice straw is sometimes used as feeding for grazing animals.

Thus, the farmers still employ two common disposal practices for rice straw directly on the field, which are responsible of high amounts of anthropogenic greenhouse gases emissions:

1. *Open field burning*: it has been estimated that more than a half of the total quantity of rice straw is burned worldwide, releasing into the atmosphere during the combustion, both pollutant and ~ 11 t ha^{-1} yr^{-1} of carbon dioxide equivalent [414]. This disposal method, specially in the developing countries, is responsible of the Atmospheric Brown Clouds (ABC) phoenomena, which represents a source of human health diseases [182];
2. *Incorporation of straw into the soil*: this procedure increases soil organic carbon (SOC) sequestration and reintroduces elementary substances (such as Carbon, Potassium, Phosphorous, Nitrogen, etc.) into the lithosphere. Nevertheless, the benefits due to the reincorporation of carbon in the soil can be outweighed by the increase in GHG due to the rice straw decomposition emissions, specially in flooded areas. Indeed, in order to reincorporate rice straw on the field, adequate time is required having a low degradation rate: its half-life has been estimated to be of two years, and around the $(80-90)\%$ of it is decomposed during the first year [324]. Thus, this technique is not suitable for intensive cropping areas. As concerns greenhouse gases emissions, soil incorporation can be two times higher than rice straw collection activities,

accounting for approximately $(3.5 - 4.5)$ t ha^{-1} of $\mathrm{CO}_{2,eq}$ [396]. Moreover, the rice straw removal from flooded rice fields has been shown not to reduce the levels of soil organic matter [442].

Some researches have suggested that rice straw incorporation on the wet soil results in higher GHG emissions by 98% than the rice straw burning [11]. This result has been obtained without considering carbon dioxide emissions derived from the combustion (considering the hypothesis of carbon neutrality of photosynthetic elements). If they are accounted too, the two processes are almost equivalent in terms of GHG emissions [286].

4.2.1 Paddy rice demand and rice straw availability

Rice is the third major food crop commodity harvested in the world, after wheat and corn. It is crucial to global food security, and socio-economic stability [548]. Moreover, it represents the most important aliment crop of the developing countries, as it is the staple food of more than half of the global population, and approximately one fifth of the total population, relies on rice cultivation for livelihoods [155]. The paddy rice demand has increased worldwide during the last 20 years by 26.4%, as can be observed in Figure 4.3. This increase grows up to $\sim 250\%$ if the 1961 data are compared with the ones of 2020. The World's gross grain rice production in 2020, that actually represents the last available data, was 756.7 Mt, with an harvested area of $\sim$ 164.2 Mha. In Table 4.2, the gross grain rice production and the harvested land data, related to the main world regions, are reported for completeness.

Consequently, rice straw, or the unused part of the rice at harvesting, is available in large quantities, in most world regions. So, its management represents a challenge, specially where the rice cultivation constitutes the main source of food, such as in Asia [502], considering that the most common practice for rice straw is its open field burning. The rice straw burnt in open field causes dangerous levels of air pollutants locally, with the related health issues to the inhabitants, and greenhouse gases emissions. Thus, new solutions to manage and exploit the potential of rice straw should be adopted.

The rice straw availability amount depends on several factors as the rice variety, the plant height, the nutrient and soil conditions and management during the harvest-

Table 4.2 Annual rice production (P) [t yr^{-1}] and crop area (A) [ha yr^{-1}] for the main world regions in 2000, 2005, 2015, 2020; data from [154].

	Year									
Region	2000		2005		2010		2015		2020	
	P $\times 10^6$ [t]	A $\times 10^5$ [ha]	P $\times 10^6$ [t]	A $\times 10^5$ [ha]	P $\times 10^6$ [t]	A $\times 10^5$ [ha]	P $\times 10^6$ [t]	A $\times 10^5$ [ha]	P $\times 10^6$ [t]	A $\times 10^5$ [ha]
Africa	17.5	75.6	20.3	89.5	26.0	112.7	29.8	132.1	37.9	171.7
Northern America	8.7	12.3	10.1	13.6	11.0	14.6	8.7	10.4	10.3	12.1
Central America	1.3	3.7	1.2	3.3	1.3	3.4	1.2	2.8	1.4	2.9
South America	20.5	56.6	23.8	60.7	22.7	50.1	25.9	45.5	25.0	40.8
Central Asia	0.5	2.2	0.7	2.2	0.8	2.0	1.1	3.1	1.1	3.1
Eastern Asia	210.6	336.8	202.4	323.9	216.1	332.2	232.4	338.9	230.1	330.0
Southern Asia	181.6	609.7	196.6	600.8	212.8	600.9	231.0	608.9	254.8	628.6
South-eastern Asia	152.1	430.3	173.4	447.2	196.7	479.3	194.4	448.3	189.1	440.6
Western Asia	0.4	1.6	0.9	1.9	1.0	1.5	1.0	1.4	1.5	2.3
Europe	3.2	6.1	3.4	5.8	4.3	7.1	4.2	6.5	4.1	6.4
Oceania	1.1	1.4	0.4	0.6	0.2	0.2	0.7	0.7	0.1	0.1
World	598.7	1540.0	634.2	1552.7	694.5	1608.3	732.0	1602.1	756.7	1641.9

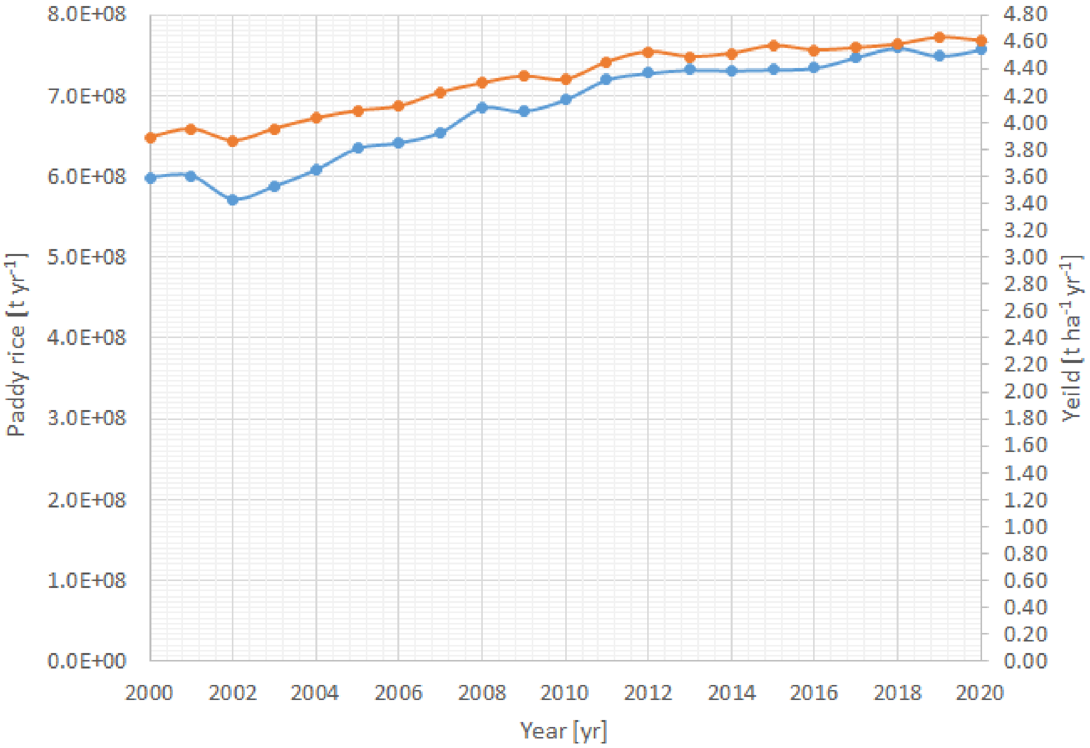

Figure 4.3 World paddy rice production [t] (blue line) and yield [t ha^{-1}] (orange line) from year 2000 to 2020, data have been retrieved from FAO database [154].

ing [502]. In Table 4.3, are summarised the plant height, the gross grain production, and the rice yield (ratio between gross grain production and harvested land).

Table 4.3 Average rice plant height, annual gross grain production and yield in different countries, related to year 2020 [154, 415, 403, 375, 364, 473].

Country	Plant height [m]	Gross grain production [Mt]	Yield [t ha^{-1}]
India	0.900-1.300	178.20	3.96
Indonesia	0.701-0.998	54.69	5.13
China	0.362-0.483	213.59	7.04
Japan	1.020-1.170	9.69	6.64
Malaysia	∼0.630	2.34	3.60
Thailand	1.000-6.000	30.26	2.91
Vietnam	0.900-1.750	42.74	5.92
United States	0.950-1.880	10.33	8.54

Rice straw production can be quantified into 0.70-1.50 times the quantity of harvested rice [324, 121]: being 1.35 times the rice grain production, the usual common mean value adopted as reference in technical studies [230, 282, 334, 393].

4.3 Rice straw properties and its characterisation

In order to utilise rice straw for energy purposes, it is fundamental its characterisation. So, an overview of rice straw properties is given in this section. In particular the rice straw chemical, physical, and thermal properties will be summarised.

4.3.1 Chemical properties

The chemical properties of the biomass are fundamental to understand its potential and suitability for applications. From these characteristics it is possible to estimate also the thermal properties, which are fundamental for the conversion of the biomass into energy. Here, the biochemical composition, the proximate, and the ultimate analysis are reported. The main difference between proximate and ultimate analysis is that proximate analysis analyses the compounds which constitute a mixture (moisture content, ash content and fixed carbon), whereas the ultimate analysis analyses the single elements present in a compound.

Biochemical characterisation

Rice straw has the prevailing composition of an agricultural lignocellulosic residue. Its main biochemical composition can be summed up as follows [413, 256]:

- Cellulose, average chemical formula ($C_6xH_{10x+2}O_5x+1$, x-degree of glucose polymerization): which is the major component ($29-80\%$) of a lignocellulosic biomass. Cellulose is a polysaccharide, with a linear chain of D-glucose bind to each other by β bonds. The cellulose strains form cellulose fibrils, that are linked by intra–molecular and inter-molecular hydrogen bonds. Cellulose results non soluble in water and in most organic solvents. During the anaerobic digestion, its amorphous form is easier to degrade than the crystalline form;

- Hemicellulose, average chemical formula $(C_5H_8O_4)_m$ $(10-45\%)$: light heterogeneous branched biopolymers, easily to be hydrolysed (amorphous structure, lower molecular weight, lower degree of polymerization, lower crystalline structure), with a short lateral chain. The main components in rice straw consists mostly in sugars with 5, 6 or 7 carbon atoms;

- Lignin, average chemical formula $[C_9H_{10}O_3(OCH_3)_{0.9-1.7}]_n$ $(5-25\%)$: an aromatic hydrophobic complex polymer, collection of heterogeneous lignols. This polymer gives to the plant structural strength and protection from biotic and abiotic stresses. Thus, it is resistant to degradation, and pretreatments are required to exploit rice straw for energy purposes. Moreover, the lignin content is inversely proportional to the methane yield during anaerobic digestion.

Table 4.4 Biochemical composition on dry basis values of rice straw, data from literature.

Biochemical composition [%]			
Cellulose	Hemicellulose	Lignin	Reference
30.2	35.0	22.0	[168]
39.2	21.4	19.6	[272]
38.0	18.3	21.6	[479]
32.0	35.7	22.3	[521]
34.3	25.1	18.6	[184]
36.0	24.0	15.6	[335]
38.0	25.0	12.0	[502]
50.84	22.19	3.33	[468]
36.29	20.67	9.42	[54]
32.0 – 38.6	19.7 – 35.7	13.5 – 22.3	[175]
30.0 – 45.0	20.0 – 25.0	15.0 – 20.0	[335]

Proximate analysis and ultimate analysis

The main elements of the proximate analysis and the terms usually adopted are reported in Figure 4.4. The biomass moisture content influences the choice of the available technology to convert it into energy. For values higher than 60% by weight, the calorific value of the biomass itself is too low for the combustion processes. Indeed, usually, biomass contains a large quantity of moisture, which changes quickly if exposed to air. For this reason, the meaningful values of chemical composition are always expressed on dry weight basis. So, the total solids of the biomass are obtained after heating the biomass sample at 105°C, when the moisture content is evaporated (moisture-free).

The biomass behaviour at its heating can be provided by the proximate analysis, determining how much of the feedstock becomes vapour and how much remains as fixed carbon. Thus, it provides the amounts of volatile matter, fixed carbon and ashes. Indeed, the total solids are constituted both by the volatile solids and by the non volatile solids. The latter can be further split into fixed carbon (carbon left when the volatiles are driven off) and ashes (non combustible fraction of the biomass). The volatile solids are the amount of the total solids in the biomass, which are lost when the dry biomass is combusted at 550°C in the presence of excess air. The volatile matter is important for the thermal conversion routes, since higher volatile matter implies higher amount of realised combustible gases. Rice straw has a large quantity of volatile matter, which can represent an advantage for its combustion, due to an easier ignition and combustion rate. However, the resulting quick combustion can lead to difficulties to control the combustion itself. Fixed carbon is the amount of the biomass realised heating the volatile matter free biomass at 575°C for 4 h. Some proximate and ultimate analysis of rice straw, collected from literature, are reported in Table 4.5 and Table 4.6, respectively. The citations that are followed by a letter are referred to the same article cited in the paper of Van Hung *et al.* [502]. The rice straw ash content encompasses all the non combustible residues of the biomass, thus a high content of these elements causes a decreasing heating value. One of the fundamental aspects of the rice straw ashes is the high silica content (SiO_2 constitutes approximately $67.78 - 82.60\%$ of ash in dry basis [502]), which can lead to issues during the post-processing activities.

4.3.2 Thermal properties

In energy terms, the fundamental property of a biomass is it calorific value. The energy efficiency of a biomass can be evaluated in first approximation by dividing the energy output by its calorific value. The higher heating value of rice straw, which encloses the latent heat of water, based on literature data, is reported in Table 4.7: it ranges from 12.30 to 18.82 MJ kg^{-1}.

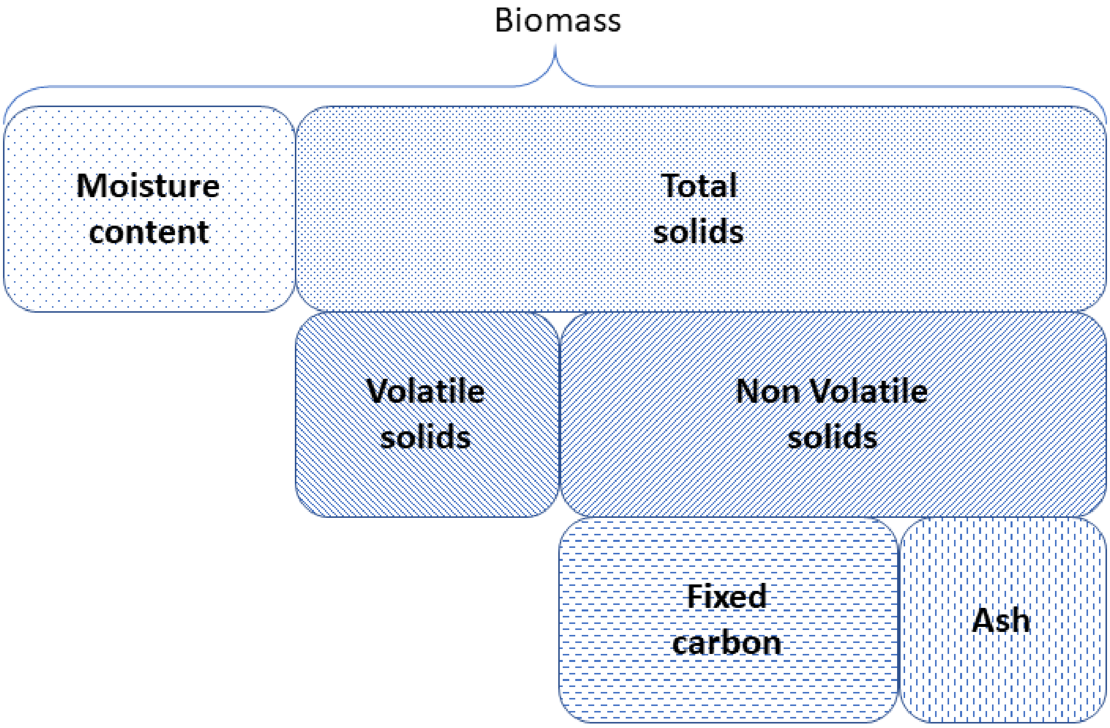

Figure 4.4 Main elements constituting the biomass proximate analysis.

Table 4.5 Proximate analysis of rice straw, data retrieved from literature.

		[%]		
Moisture	Volatile matter	Fixed carbon	Ash	Reference
10.80	66.89	14.57	7.56	[384]
8.53	70.20	14.37	6.9	[402]
6.43	72.61	10.64	10.41	[499]
0.00	72.7	9.3	17.9	[218]
6.43	61.95	29.25	11.22	[254]
11.13	67.27	13.05	8.55	[329]
11.69	78.07	6.93	15.00	[56]
n.d.	74.7	15.2	10.1	[521]
n.d.	65.47	15.86	18.67	[502]a
n.d.	69.70	11.10	19.20	[502]b
n.d.	64.24	16.75	22.70	[502]e
n.d.	60.55	16.75	22.70	[502]f

Table 4.6 Ultimate analysis of rice straw, data retrieved from literature.

		[%]			
C	H	N	O	S	Reference
33.70	4.00	1.71	n.d.	0.16	[502]d
35.35	3.91	0.71	37.35	0.03	[502]f
35.94	n.d.	1.18	n.d.	n.d.	[502]c
36.02	6.63	1.12	55.85	0.38	[35]
36.07	5.20	0.64	57.83	0.26	[56]
38.24	5.20	0.87	36.26	0.18	[502]a
39.98	2.45	4.43	52.61	0.53	[384]
44.40	7.40	1.13	47.07	n.d.	[502]e
45.20	6.50	0.80	47.50	n.d.	[521]
45.20	6.45	1.30	46.55	n.d.	[218]
45.30	6.93	0.92	46.71	0.14	[254]
45.69	4.65	n.d.	50.32	n.d.	[329]
48.70	5.92	1.05	44.20	n.d.	[335]

Table 4.7 Higher Heating Value (HHV) of rice straw, data retrieved from literature.

HHV MJ kg^{-1}	Reference
12.30	[402]
14.08	[502]d
14.21	[329]
14.39	[502]f
14.57	[502]c
14.87	[56]
15.03	[502]e
15.04	[35]
15.30	[234]
15.86	[502]a
17.80	[283]
18.82	[335]
12.30 – 18.82	Range

4.3.3 Physical properties

The rice straw bulk density depends on the method used to collect the rice straw itself, and results fundamental for the rice straw transport and post-processes (with the relative transporting and handling costs). For the same reason, it results fundamental the moisture content of the rice straw when it is collected. Indeed, the rice straw biomass storage system should be properly designed, in order to avoid its decomposition and self-heating to its ignition point. Thus, the moisture content should be lower than 30% on dry basis [385]. Moreover, in order to reduce te rice straw volume effectively by compression, its moisture content should be in the range $(12-17)\%$ [502].

Table 4.8 Densities of different forms of processed rice straw on dry basis, data taken from literature.

Form	Density [kg m^{-3}]	Note	Ref.
Loose	$13-18$	Collected from the field	[502]
	$20-40$		[415]
Chopped	$50-120$	Lenght 2-10 mm	[96, 282]
	$40-80$		[415]
Hammer milled	$40-100$		[415]
Round baled	$60-90$	Lenght 0.7 m, radious 0.25 m	[330]
Moduled	$96-128$		[415]
Baled	$110-200$		[415]
Cubed	$320-640$		[415]
Briquetted	$350-450$	Thickness 7-15 mm, radious 45 mm	[502]
Pelletted	$560-720$		[415]

4.4 Rice straw energy routes

Being rice straw a biomass, it can be converted in different energy forms, i.e. heat, power, or biofuels. Biofuels can be obtained both *via* thermochemical, and biochemical routes. Usually, thermo-chemical processes of wasted biomasses are believed more reliable and efficient than biochemical ones [362, 309, 26], presenting a higher conversion efficiency and a shorter reaction time [449]. These processes bring to the decomposition of the biomass in several components, in various forms (gaseous, solid or liquid) by exposing it to heat. The products of the thermo-chemical processes depend mainly on the temperature, pressure, time, and oxygen supply during the process itself. When the biomass is heated, the hydrogen and oxygen contents are volatilized or distilled from the biomass, increasing the carbon content of the non-volatilised matter. The main thermo-chemical biomass conversion processes and characteristics (summarised in Table 4.9), and explored for the rice straw conversion have been the following ones:

- Gasification;
- Pyrolysis;
- Direct combustion.

Table 4.9 General thermochemical routes for biomass conversion, with some key average characteristics: temperature, average reaction time, oxygen supply ratio, and their relative products. Adapted from [292].

Process	Oxygen supply ratio, λ [-]	Temperature [°C]	Time order of	Product Solid/ Liquid	Product Gaseous
Combustion	≥ 1	≥ 700	seconds	Ash	CO_2, H_2O, CO, C_xH_y, NO_x,SO_x
Gasification	$0.2-0.5$	> 600	seconds to minutes	Ash Char[a]	CO, CO_2, H_2, H_2O, CH_4, C_xH_y, NH_y, NO_x, H_2S, tar[b]
Pyrolysis	0.0	$300-650$	seconds (fast) to days (slow)	$C_mH_nO_k$, Ash, char, Pyrolysis oils[c]	CO, CH_4, C_xH_y, CO_2, H_2O,

[a] char is the char-coal like carbon rich residue, usually made by more than 50% of carbon (dry basis), with 75% of it as fixed carbon.

[b] tar are the organics (largely aromatic), produced under thermal or partial-oxidation regimes (gasification) of any organic material.

[c] with oil-like properties, usually need an upgrade due to their high contents of sulphur/nitrogen compounds.

The latter is the widely adopted method of thermal energy conversion to process rice straw. It consist on the exposure of the rice straw to high temperatures, usually above 700°C, in presence of an excess of air, compared to the stoichiometric one ($\lambda = O_2/O_{2,stoic}$ higher than 1). The combustion produces hot gases, with their associated thermal energy. The produced gases are mainly CO_2, H_2O, N_2 and in lower amounts CO, C_xH_y, NO_x, SO_x.

4.4.1 Gasification

The biomass gasification process consists in a thermo-chemical conversion of the organic matter into a synthesis gas (syngas), in the presence of a gasifying agent (air or oxygen, steam, carbon dioxide, or their mixtures), at temperatures usually greater than 600°C, with the oxygen supply constituting only a fraction of the stoichiometric one. The syngas produced can be in turn used for the heat production and electricity generation, ammonia and biofuels production, etc.

Syngas constitutes a mixture of primary and secondary components, in the gaseous form, with a solid carbonaceous residue (char). Its main primary components are: carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), while water vapour (H_2O), hydrogen sulphide (H_2S), ammonia (NH_3), tar are the most diffused secondary components. The syngas production depends on the feedstock sample, on the operating conditions, and on the gasification technology [404, 408]. Moreover, also syngas composition strictly depends on feedstock, technology, and operating parameters. In particular, in relation to particulate matter, condensible hydrocarbons, alkaline metals, nitrogen, sulphur, and halides, purity of syngas for second-generation biofuels production has been highlighted. Some treatments are performed to the syngas in order to increase the combustible components, and to remove water and non combustible gases. Syngas cleaning requirements depend on downstream processes, operating conditions, catalysts, and main reaction mechanisms [200]. Alchools and diesel can be obtained by performing a Fischer-Tropsch process from the syngas.

The four main steps which constitute the gasification process are the following ones [449, 409]:

1. Heating of the biomass (drying, until 200°C), in order to reduce its moisture content (optimal level: lower than 15%);
2. Decomposition of the biomass (pyrolysis, temperature from 220°C): from hemicellulose, cellulose, and lignin to volatile compounds and solid residues;

3. Oxidation - if the oxidation agent is oxygen (partial combustion, over 700°C): the process in which the volatile compounds are oxidised mainly into carbon monoxide, carbon dioxide, and water;
4. Reduction - if the oxidation agent are CO_2 and steam, or others (gasification, over 800°C): the process in which volatile compounds are transformed into carbon monoxide, methane and hydrogen.

The main reactions that occur during gasification and the relative specific enthalpies are summarised in Table 4.10.

Table 4.10 Main reactions that occur during the gasification process, and their relative standard molar enthalpies [292].

Chemical reaction	Δh° [kJ mol^{-1}]
Partial oxidation reaction	
$2\,C + O_2 \leftrightarrow CO_2$	-268
Complete oxidation reaction	
$C + O_2 \leftrightarrow CO$	-406
Water gas reaction	
$C + H_2O \leftrightarrow CO + H_2$	118
Water gas shift reaction	
$CO + H_2O \leftrightarrow CO_2 + H_2$	-42
Steam methane reforming reaction	
$CH_4 + H_2O \leftrightarrow CO + 3\,H_2$	88
Hydrocarbon reactions	
$C_nH_m + n\,H_2O \leftrightarrow n\,CO + (n + \frac{m}{2})\,H_2$	> 0

After the gasification process, the biomass inorganic materials remain in the form of solid agglomerates (rock-like), which are named vitrified slag (or ash).

The three widely diffused types of biomass gasifiers have been derived from the fossil coal gasification technologies, their use depends on the upstream processes that the biomass requires, on the gasifying agent and on the final product requirements; they are [449, 522]:

- Fixed bed (or moving bed) gasifier;
- Fluidized bed gasifier;
- Entrained flow gasifier.

4.4.2 Pyrolysis

Pyrolysis (or destructive distillation) is the thermal biomass conversion which occurs in absence of oxygen (inert atmosphere), with the degradation of the biomass, starting at temperatures higher than $(150-200)°C$. Usually the pyrolysis process is realised at temperatures in the range $(300-600)°C$. The products which can be obtained have a higher energy density components than the biomass; the main products are: gaseous products (syngas), bio-oil and bio-char. The process can occur also if the biomass is surrounded by oxygen, it does not take part to the combustion process because of the pyrolysis gases do not allow oxygen to reach the biomass itself [366]. When the temperature increases, and oxygen (less of the stoichiometric one) is introduced, the pyrolysis process shifts into the gasification one, while if the stoichiometric oxygen is introduced it becomes a combustion process. In general terms, if the pyrolysis process occurs in a long time (slow pyrolysis, characterised by a vapour residence time of the order of few seconds), the carbon content of the feedstock increases, producing almost char. On the other hand, fast pyrolysis (characterised by a vapour residence time of the order of minutes up to days) generates gaseous products, such as carbon dioxide and water vapour. The bio-oil produced, contains aliphatics, alchools, acids, esters, amines, nitriles, etc.; however, this product must be upgraded both physically and chemically, due to its moisture content and acidity to be used as a fuel. On the other hand, char presents similar properties to fossil coal. The syngas produced is usually returned to the pyrolysis plant to supply the heat power needed to the process itself. Indeed, usually the pyrolysis plants are composed by facilities to pretreat the biomass (drying and particle size reduction), hopper and feeder, reactor (in which the pyrolysis reaction takes place), char separation system, quencher to separate the condensible gases (which become bio-oil) from the non condensible ones (syngas).

In the following bullet list, some findings available from literature, related to rice straw pyrolysis, are summarised. It should be noted that this studies are more focused on the bio-char and bio-oil production from rice straw pyrolysis:

- Park *et al.* [358] have carried out the slow pyrolysis of rice straw in the range temperature between $(300-700)$°C, characterising the composition and yields of the pyrolysis products (bio-char, bio-oil and non-condensible gases). In particular, their analysis is focused on the produced bio-char. For higher temperatures than 500°C, the organic fraction mass yield obtained was 25%, with bio-char as mainly pyrolysis product, with energy content of 40%, and 45% of the carbon of the biomass. So, bio-oil and gas yield in terms of energy was approximately 60%.

- Biswas *et al.* [56] have performed an analysis on the slow pyrolysis of different agricultural wastes, including rice straw, by using a lab-scale fixed bed reactor, at different temperatures (range $(300-450)$°C) under nitrogen atmosphere. Before the pyrolysis process, the biomass has been pretreated by drying, crushing and sieving it, obtaining a feedstock with a small particle size (0.5-2.0 mm). The authors have analysed the bio-oil yield and composition in relation to the different temperatures, which presents a threshold temperature, from which the bio-oil yields start to decrease. The rice straw bio-oil yield has been higher at 400°C, resulting in 28% by dry weight, being the lowest if compared to corn cob, wheat straw and rice husks (47.3%, 36.7%, and 38.1% respectively). However, at 450°C, the total rice straw conversion (sum of bio-oil and bio-gas yields by weight) has been higher than the rice husks one (66.9% vs 65.0%).

- Kongkaew *et al.* [248] have performed an analysis on the kinetics of slow rice straw pyrolysis, and the chemical analysis of the produced bio-char in nitrogen gasifying agent, with a temperature ranging from 25°C to 700°C, and three different heating rates. The main pyrolytic processes result in the range $(180-470)$°C.

- Shoaib *et al.* [437] have designed a free-fall lab-scale pyrolysis reactor to overcome issues of lacking parts, feeding it with rice straw, and performing a fast pyrolysis process ($(450-700)$°C). They have investigated the design and use of this kind of reactor for biomass wastes to obtain bio-oil. The maximum bio-oil yield registered has been of 46% by weight, at 500°C. They have characterised also the produced gases, obtaining mostly methane, hydrogen, carbon monoxide, carbon dioxide, ethylene and ethane.

- The investigation of Chandra and Bhattacharya [87] regards the effects of some fundamental parameters, such as temperature and residence time, on the yields and characteristics of the resulting bio-char. They have performed a slow pyrolysis process in a heating chamber, connected to a gas absorbing cum exhaust chamber. The rice straw was pretreated by cutting it with a length of 5-10 mm. The authors have found that when the temperature increase from 400°C to 700°C determines that the biochar yield in weight drops from 45.04% to 33.45%. Moreover, the bio-char properties result more influenced by temperature if compared to heating time.

- Cao *et al.* [81] have investigated and characterised the rice straw pyrolysis using various kinds of catalysts (salts, metal basic oxides, acid metals, zeolites), at different temperatures (range $(350-500)$°C) and with different catalysts amounts ($(5-20)\%$ by weight). The highest bio-oil yield without catalysts (38.5%) has been obtained at the temperature of 450°C, while with Y-zeolite catalyst, at the same temperature, it has been 55.2%, with a higher boiling point range. Moreover, the authors observed a higher heating value of zeolite catalytic bio-oil of 36.7 MJ kg^{-1}.

- Sakhya *et al.* [406] have studied the slow pyrolysis of rice straw, in a fixed bed reactor, with the main result of a decreased bio-char yield at increasing temperatures from 300°C to 600°C, with an increased higher heating value (from 17630 kJ kg^{-1} to 20130 kJ kg^{-1}). Moreover, the highest bio-oil yield has been registered at a temperature of 500°C, while the energy and exergy efficiency have increased with increasing temperature from 0.842 to 0.896, and from 0.744 to 0.874 respectively. Furthermore, the optimal temperature from a thermodynamic viewpoint individuated in their study was 600°C.

4.4.3 Anaerobic digestion

The main biological way to convert the rice straw energy potential is the anaerobic digestion process, that is a natural process to which biomasses are subjected when are exposed to a free-oxygen environment, in presence of micro-organisms. Indeed, micro-organisms degrade the organic matter of the biomass, producing biogas as main product, that can be upgraded to bio-methane, or renewable natural gas. This natural phenomenon is exploited in the anaerobic digesters, and it is considered one of the most promising conversion processes for rice straw. In fact, some authors [256] have analysed that it constitutes the most favourable energy conversion route to better exploit the energy potential of this agricultural residue.

During the anaerobic digestion process, a certain amount of biogas is produced. Biogas is a mixture of gases, primarily composed by methane (CH_4, $50-65\%$) and by carbon dioxide (CO_2, $35-40\%$), with a balance of nitrogen (N_2), and trace amounts of hydrogen sulphide (H_2S) and water vapour (H_2O).

The anaerobic (oxygen-free environment) digestion process, can be divided into four main phases in a simplified description (Figure 4.5), which depend on the interactions among the micro-organisms [62]:

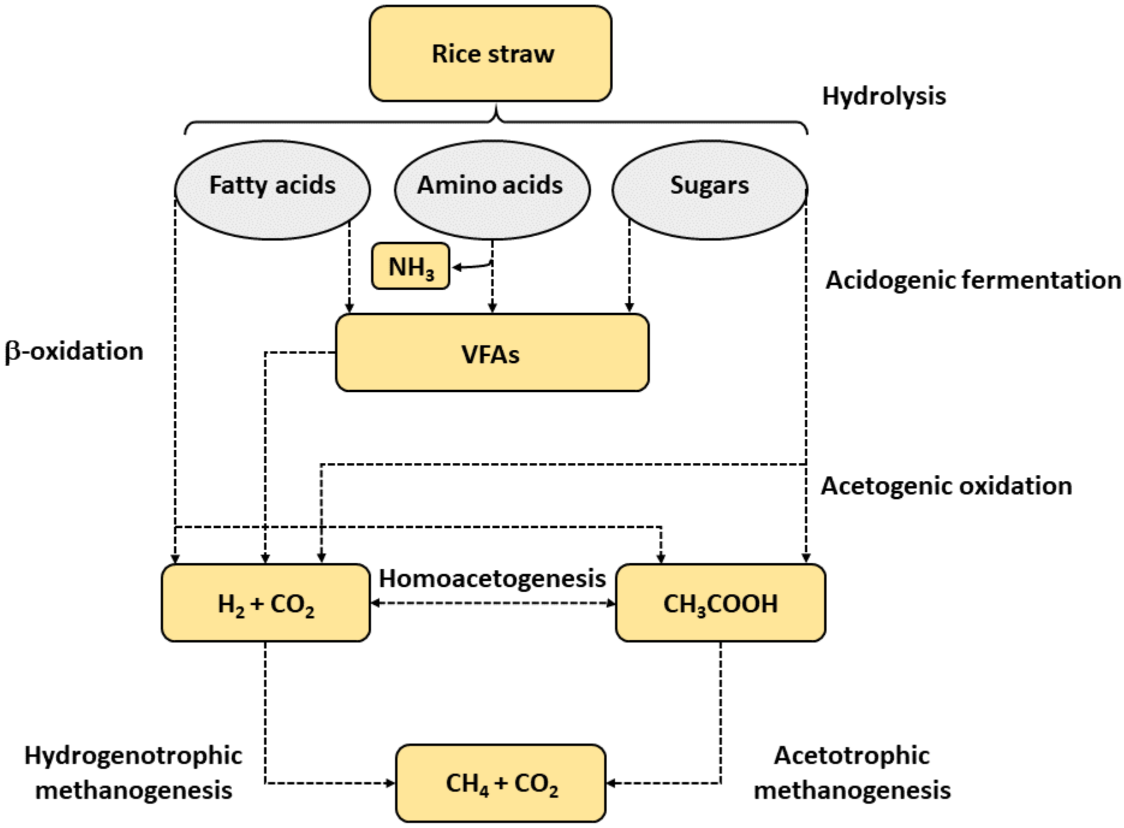

Figure 4.5 Main steps of the anaerobic digestion process, adapted from [184].

1. *Hydrolysis stage*: in which the hydrolase enzymes (produced by micro-organisms) and the anaerobic bacteria, start to decompose non-soluble compounds of the biomass, which include mainly cellulose and other carbohy-

drates, fats, proteins, etc. The hydrolysis rate depends mainly on the size of the biomass particles, pH, production of hydrolytic enzymes and their distribution on the reactor, adsorption of biocatalysts on the biomass particles [443]. As a result of this brake-down process, products with smaller chains are produced: sugars, amino acids, fatty acids and alchools, respectively. The product formation from carbohydrates results faster (few hours) than protein and lipid hydrolysis (up to days). The products formed in this phase are required as raw materials for the second phase. Lignocellulosic compounds have a long and incomplete decomposition time. This phase is considered the critical limiting-step for the beginning of the anaerobic digestion process. Lastly, the hydrolysis reaction can be written as follows:

$$(C_6H_{10}O_5)_x + x\,H_2O \rightarrow x\,C_6H_{12}O_6 \ + \ x\,H_2$$

2. *Acidogenic stage*: in which the short chain compounds of the first phase are absorbed by acidogenic bacteria, and transformed into volatile fatty acids (VFAs): acetates, and larger organic acids as propionate and butyrate. During this phase, the concentration of H^+ ions varies and can influence the products of the fermentation. Indeed, if the pH decreases (increase of the H^+ ion concentration), the following formation of acetate is reduced. However, this second phase (short) implies a fermentation of the first phase products into organic acids, alchools, CO_2, H_2. The products of the acidogenic phase constitute the substrate for the bacteria involved in the acetogenic phase. Moreover, it must be highlighted that during this phase, the ammonia production from deamination (during the amino acid brake down) occurs. The NH_3 formation inhibits the anaerobic digestion. Lastly, the acidogenesis reactions can be written as follows:

$$C_6H_{12}O_6 \leftrightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

$$C_6H_{12}O_6 + \ 2\ H_2 \leftrightarrow 2\ CH_3CH_2COOH + 2\ H_2O$$

$$C_6H_{12}O_6 \rightarrow 3\ CH_3COOH$$

3. *Acetogenic stage*: in which the higher VFAs and intermediates are transformed into acetate, with H_2, CO_2 formation, too. During the acetogenic phase, fats undergo to a acetogenesis transformation through acidogenesis (acetate from

glycerol) and β-oxydation (acetate from long chain fatty acids). Lastly, the acetogenesis reactions can be summarised as follows:

$$CH_3CH_2COO^- + 3\,H_2O \leftrightarrow CH_3COO^- + H^+HCO_3^- + 3\,H_2$$

$$C_6H_{12}O_6 + 2\,H_2O \leftrightarrow 2\,CH_3COOH + 2\,CO_2 + 4\,H_2$$

$$CH_3CH_2OH + 2\,H_2O \leftrightarrow 3\,CH_3COO^- + 3\,H_2 + H^+$$

4. *Methanogenesis stage*: in which the methanogenic micro-organisms consume the accessible intermediates in anaerobic conditions, forming CH_4 via an exothermic reaction. Two main CH_4 formation processes can be highlighted: (i) reduction of acetate (CH_3COO^-) performed by acetotrophic mathanogens, and accounting for approximately 77% of the methane production; (ii) conversion of H_2 and CO_2, performed by hydrogenotrophic methanogens, and accounting for approximately 33% of the methane production. The methanogenic bacteria tend to require higher pH if compared to the previous phases, and a lower redox potential. This process can take approximately from 5 to 17 days, even if some hydrogenotrophic species present a doubling time of only few hours. The end of this phase occurs when the biogas production stops. Lastly, the methanogenesis reactions can be summarised as follows:

$$CH_3COOH \rightarrow CH_4 + CO_2$$

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$$

$$2\,CH_3CH_2OH + CO_2O \rightarrow CH_4 + 2\,CH_3COOH$$

Approximately the 80% of the methane obtained from rice straw derives from the acetic acid conversion, while approximately the 20% of the methane derives from the hydrogen and carbon dioxide conversion [324]. The limiting step for lignocellulosic biomasses is the cellulose hydrolysis. For temperatures higher than 45°C, the limiting step is the conversion from acetate to methane, performed by acetoclastic methanogens, which present a slow metabolism and growing rate. So, a higher buffering capacity of the system is needed to avoid an over-production of acetic acid. Some of the fundamental parameters to analyse the anaerobic digestion process can be summarised as follows:

- Biochemical Oxygen Demand (*BOD*): it is a metric of biodegradable organics present in a sludge, which is a synonym of effectiveness of an anaerobic digester. This quantity can be used to understand the microbial metabolism of dissolved oxygen in a defined time period (5 d), or to quantify the amount per unit of volume of biodegradable organics in the sludge;

- Chemical Oxygen Demand (*COD*): it is a metric of the oxygen contained within the sludge, which can react in presence of oxidising agents. Thus, it can be used in quantifying the amount of organics contained in the sludge. Its decreasing value can be used to quantify the amount of degradation which is occurring in the anaerobic digester. Measuring all the organics, its value is higher than *BOD*;

- The C/N ratio of the substrate: it characterises the nutrients available for the anaerobic digestion process. The elements that produce nitrogen during their degradation are mostly the proteins. In order to obtain biogas with a high quality, the microbial community in the digester must correctly grow. In order to allow so, the optimal C/N ratio should be in the range 20-30:1, due to the bacteria carbon uptake results 20-30 times higher than the nitrogen one. With a higher C/N ratio than the optimal one, the degradation process results slower. On the other hand, with values less than the optimal ones, the ammonia accumulation may occur, inhibiting the bacteria activity;

- Total Solids (TS) and Volatile Solids (VS): the TS are a measure of the amount of dry matter, organic or inorganic, contented within the biomass (moisture-free). In relation to the amount of TS, anaerobic digestion can occur in wet (TS concentration <15%), semi-dry TS in the range 15-20%) or dry (TS concentration greater than 20%) conditions [324]. The VS, on the contrary, is a measure of the organic fraction of total solids, or better, the amount of the biomass TS that are realised during the biomass combustion process;

- Hydraulic Retention Time (HRT): as a measure of the time of residence of the substrates within the reactor, or the time needed for micro-organisms to their metabolic activity to synthesize the substrate. It depends mainly on the feedstock, varying in the range 30-60 d (10-20 d for materials with high decomposition rate);

- Loading rate: it is the amount of organics fed to a digester per day (in continuous digesters); it can be evaluated by the COD per unit of volume per day (or by volatile solids per unit of volume per day), and by the mixture Hydraulic Retention Time (HRT). Higher the loading rate is, higher accumulation of fatty acids will occur during the acetogenic stage, which means lower yield of methane;

- Temperature: the anaerobic digesters are characterised by a temperature, which depends on the micro-organisms used to perform it, being one of the most influencing parameters for methanogenic bacteria. There are three main kinds of anaerobic digestion processes, based on the reactors temperature:

  - Psychrophilic anaerobic digestion, characterised by a temperature lower than 20°C;
  - Mesophilic anaerobic digestion, characterised by a temperature in the range $(20-40)$°C;
  - Thermophilic anaerobic digestion, characterised by a temperature in the range $(45-60)$°C.

  Usually, highest the temperature is, highest the biogas yield is. However, if the temperature is too high (above 40°C), the biogas production drops down, because of it results an unfavourable condition for mesophilic and termophilic bacteria. For temperatures above 65°C the biogas production stops. The favourable range to produce biomethane results $(35-40)$°C. Even a difference of 1°C inside the reactor may affect the methanogenic bacterial activity [256]. Thus, the methane production efficiency and the economic input depend on temperature.

- pH: the microbial communities need of a certain environment condition to perform their activities (to live), and the pH is one of the most influencing factors for this scope. In 1964, the optimal anaerobic digestion environment pH was determined in the range $6.6-7.6$ [304]. More recently, the optimum pH range in the anaerobic digester has been suggested to be in the range $6.8-7.2$. Nevertheless, the process can tolerate values in the range $6.5-8.0$ [99]. Studies on anaerobic digestion of rice straw have identified the same optimal pH range for anaerobic digestion [324]. When pH drops to 5.5, the methanogenic bacteria are inhibited, while the acidogenic bacteria can continue their activity; when the amount of VFAs during the acidogenesis phase, the pH drops to values lower than 6.6. On the other hand, for values higher than 9.0, the methanogenesis process stops.

- Redox potential: is a metric of the ability of oxidase (or reduce); in anaerobic reactors, biogas production occurs with a redox potential lower than -150 mV (it always results lower than -100 mV in absence of oxygen in the environment). The redox potential varies depending on the substrate, moreover this quantity is useful to forecast the variations on pH within the reactor. To obtain methane from CO_2 and H_2 the redox potential results < -250 mV, while the formation of H_2O and H_2S requires values < -150 mV;
- Salt concentration: if this quantity is high, jointly with high ammonium concentration, the anaerobic digestion results negatively affected, due to the osmotic pressure that is generated, and which acts on the bacteria membrane. However, small concentrations of these salts enhance methane yield.

Anaerobic digestion systems are mainly designed in two possible configurations [324]: (i) Batch reactors, in which all the substrate/inocula mixture is added at the beginning: these are simpler and 40% less expensive, but with larger volume requirements and a related larger area footprint for the reactors is required; (ii) Continuously-fed reactors, in which the substrate/inocula mixture is added incrementally over time.

As concerns the rice straw anaerobic digestion process, the main issues are related to its composition. Indeed, the lignocellulosic shield, the high silica content and C/N ratio (or low nitrogen content), make the anaerobic process more difficult for the micro-organisms. In particular, the lower biodegradability is caused by [445]:

1. The lignocellulosic structure, which reduces the accessibility of micro-organisms to the carbohydrates (cellulose and hemicellulose) that are enclosed within the shield;
2. The high silica content, which reduces the adherence of micro-organisms to the biomass;
3. The high C/N ratio, which reduces the microbial activity and growth due to the scarcity of some nutrients, increasing the HRT and decreasing the biogas production.

Thus, rice straw biomass requires pretreatments in order to be effective. In fact, its use as a single substrate brings to lower biogas yields (rice straw C/N ratio is above 40:1, which results too high compared to the optimum range 20-30:1). Indeed, the micro-organisms use the biomass carbon as an energy source during the hydrolysis step, turning the environment acid (lowering the pH) and inhibiting the methanogenic process. So, the accumulation of VFAs can lead to the reduction of the pH inside the anaerobic digester with a consequent acidification. The issue of acidification, due to VFAs accumulation, is usually outflanked by using multiple complementary digestion substrates. So, the acidification issue is overcome by co-digestion with animal manure or other natural nitrogen-rich wastes (i.e. sewage sludge, food wastes, industries effluents, etc.), adoption of specific micro-organisms and the addition of trace elements into the digester. As regards the latter method, in order to generate the enzymes necessary for the degradation of VFAs (mainly formic acid, lactic acid, acetic acid, and propionic acid) and to improve their conversion efficiency, trace elements such as: Fe, Co, Ni, Mo, Mn, Cu, Se, and Zn, are needed [281, 311]. Cai *et al.* [76] have studied the consequences of trace elements in rice straw anaerobic digestion by considering the introduction of low, medium and high concentrations of trace elements within the digester substrate. In particular, they have found that the addition of Fe, Mo, Se and Mn causes a reduction of VFAs, increasing the bio-methane yield; on the contrary, Co and Ni do not affect the methane yield. The role of the addition of trace elements is to change the metabolism and structure of the micro-organisms colonies within the anaerobic digester.

Pretreatment

As previously highlighted, the anaerobic mono-digestion of rice straw is difficult and inefficient, like other lignocellulosic biomasses. In Table 4.11, the bio-methane yields (in terms of volatile solids) of different agricultural residues have been reported, to overview the potential of different kind of biomasses.

In order to make effective the rice straw anaerobic digestion, three different types of pretreatments can be performed, combining them too:

1. *Physical pretreatment*, which consists mainly in the biomass particle size reduction, increasing the surface area accessible to micro-organisms, improving the lignocellulosic biomass digestibility, and reducing the degree of polymer-

Table 4.11 Methane yields of different kinds of agricultural pretreated biomasses and residues, values are expressed in terms of volatile solids (VS).

Biomass	Methane yield [L kg_{VS}^{-1}]	Ref.
Barley Stalks	239*, 230	[324, 207]
Coffee husks	300	[207]
Corn stove	225	[445]
Cotton stalks	145.69	[142]
Grass cut	300	[268]
Maize	340, 390	[207, 15]
Maize stalks	229.46	[142]
Oat straw	246, 320	[445, 268]
Rye	290*	[324]
Sugar beat leaves	210	[15]
Sugar beat (top)	340	[268]
Sunflower	135, 200, 300	[445, 324, 15]
Water hyacinth	244.07	[142]
Wheat straw	200, 290*, 300	[445, 324, 207]

* value referred to total solids (TS)

ization and crystallinity of the biomass carbohydrates. Some of the main physical pretreatments adopted are the following ones: cutting, chipping, milling, grinding, extrusion, steam explosion, hot water, irradiation, and ultrasonic pretreatments. Reducing the size of rice straw brings to an increase of the hydrolysis yield in the anaerobic digestion, with a higher methane yield and reduced digestion time. However, the inclusion of a milling phase implies higher costs caused by the energy required for this pretreatment. Moreover, excessive size reduction can cause an excessive acidification. When the rice straw particles have dimensions above 2 mm, the heat and mass transfer are slowed during the hydrolysis step. Nevertheless, increased biomethane production has been verified also with rice straw particles up to 10 mm [256]. The bio-methane yield is enhanced to 50.95 – 83.7% with particles dimensions between 1.000 mm and 0.075 mm compared to 20.000 mm [119]. Milling and extrusion bring to at least a twice higher bulk density, improving water holding capacity, specific porosity and surface area, improving methane yield by approximately 30% and 72% respectively [92]. Hydrothermally pretreated rice straw has been effectively proven by many authors [256]. However, for temperatures higher than 200°C the methane yield strongly decreases (more than 30% of reduction), due to the furfural formation [518]. In Ref. [291], the hydrothermal optimal temperature has been identified in a lower range $(90-130)$°C, with a methane yield of 127.6 L kg_{TS}^{-1} ($+22.8\%$ compared to the untreated rice straw) at 100°C. Moreover, combining hydrothermal pretreatment (80°C, 6 h) with the chemical one (adding 5% of $Ca(OH)_2$) brings to a methane yield of 411.1 L kg_{VS}^{-1} [137], but to be economically feasible the process must be performed at maximum 2% of $Ca(OH)_2$. In Ref. [232], a study on microwave pretreatment has been developed, investigating the maximum methane yield over different pretreatment conditions; the maximum methane yield obtained has been 325.76 L kg_{VS}^{-1}, at 190°C for 4 min. Usually physical and thermal pretreatments are always combined in order to increase their yield. In Table 4.12, are summarised some methane yields obtained from physical pretreatments, with the related optimal conditions and anaerobic digestion parameters.

2. *Chemical pretreatment*, which enhances the biodegradability of the biomass by adding chemicals. These treatments are less energy-intensive than the physical ones. The main frequent chemical pretreatments are the acid (e.g. diluted H_2SO_4, HCl, HNO_3), the alkali (e.g. NaOH, $Ca(OH)_2$, KOH), and ionic ones H_2O_2. The acid and alkali pretreatment role is to break lignin bonds, in order to make cellulose accessible by micro-organisms. The alkali pretreatment brakes down ester and glucoside side chains which increase the substrate porosity and reduces acetyl and other uronic acid substitutes, which are inhibitors for sugar degradation. Many studies on alkali pretreatment have been performed by using NaOH. In Ref. [198] its effect on rice straw, at different loading rates has been investigated, with the highest biogas yield of 520 L kg_{VS}^{-1} at 6% NaOH, with an organic loading rate of $50 \cdot 10^{-3}$ kg_{TS} L^{-1}. Yang et al. [540], have investigated and compared different rice straw alkaline pretreatments for biogas production, and the most effective has resulted 10% alkali (NaOH) loading at 20°C for 24 h, with a biogas yield of 600 L kg_{VS}^{-1}. In Ref. [401] the maximum methane yield of 498 L kg_{VS}^{-1} has been obtained with 1.5% w/v of NaOH, for a duration of 3 h. The loads of NaOH should not be too high in order to avoid the dissociation of Na^{+}, which increases the osmotic pressure in the digester, which inhibits the methanogenic bacteria activity. Furthermore, an issue to be consider when alkali pretreatments are adopted is the formation

of irrecoverable salts during the pretreatments itself [256]. In Table 4.13, are summarised some methane yields obtained from chemical (and combined) pretreatments, with the related optimal conditions and anaerobic digestion parameters retrieved from literature.

3. *Biological pretreatment*, which is preformed by using biological agents (micro-organisms) with the substrates, in order to degrade cellulose, hemicellulose and lignin. Usually, brown rot fungi, white rot fungi and soft rot fungi are used. The brown ones are specialised in attacking cellulose, while the white ones attack both celluloses and lignin. Kainthola et al. [232], have investigated the 5 weeks pretreatment influence with different fungal species (*Pleurotus ostreatus*, *Phanerochaete chrysosposrium*, *Ganoderma lucidum*) on the rice straw methane yield, obtaining respectively 269.99, 339.31, 295.91 L kg_{VS}^{-1}. In Table 4.14, are summarised some methane yields obtained from biological (and combined) pretreatments, with the related optimal conditions and anaerobic digestion parameters retrieved from literature.

In Figure 4.6, a scheme related to rice straw pretreatments, and possible nitrogen-rich co-digestion elements, is summarised. It should be observed that different kinds of pretreatments can be combined together in order to obtain higher yields.

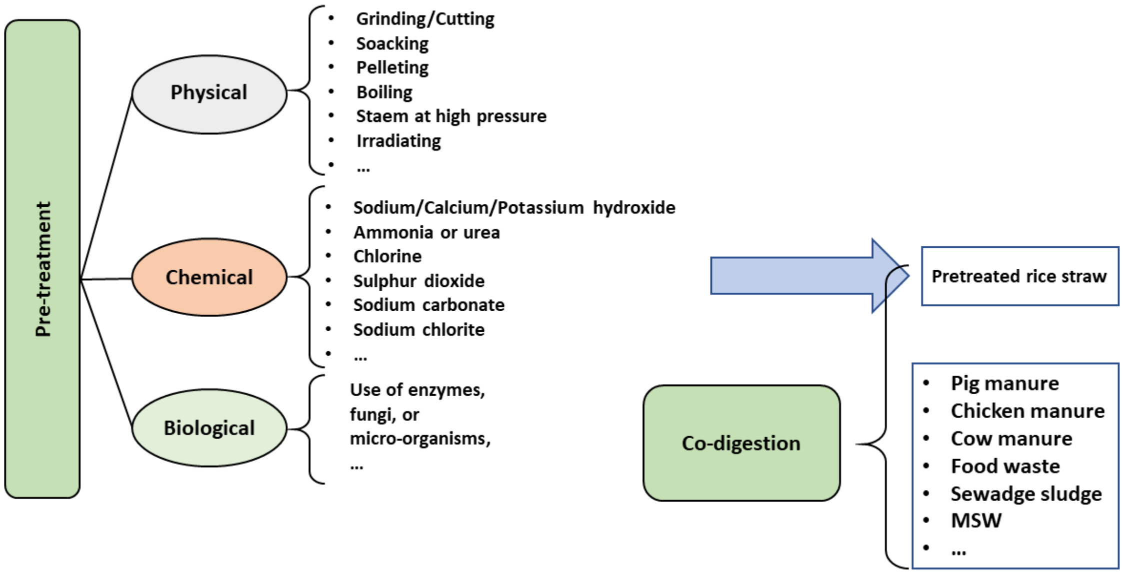

Figure 4.6 Scheme of the main pretreatments performed on rice straw for the anaerobic digestion and main elements used for co-digestion.

Table 4.12 Methane yields of rice straw, in terms of volatile solids (VS), related to physical pretreatment. Data collected from literature.

Pretreatment	Methane yield [L kg_{VS}^{-1}]	Note	Ref.
Hydrothermal (100°C, 150 min)	128	Glass bottle, time: 32 d Temperature: 35°C	[291]
Cut (50 – 100 mm)	195	Glass digester, digested slurry Time: 40 d, pH: 8.14, Temperature: 40°C	[132]
Cut (0.075 mm)	197	Bottle Time: 25 d, pH: 7.0, Temperature: 37°C	[119]
Dry & pulverized	215	Batch, cattle dung (total 8% TS) Temperature: 35°C, time: 120 d	[142]
Cut & pre-digestion biogas sludge (46 h)	273	Dry-batch, pig manure Temperature: 27°C, time: 146 d	[89]
Cut (3 – 5 mm)	280	Batch, acclimated sludge Moisture: 10.2%, time: 120 d, temperature: 22°C, pH: 7.2 – 5.8	[269]
Cut (<10 mm) & Microwave (190°C, 4 min)	326	Glass bottle, cow manure pH: 7.0, time: 40 d, Temperature: (30 – 35)°C	[232]
Hydrothermal (80°C, 6 h) & 5% $Ca(OH)_2$	411*	Glass bottle, pretreated straw & raw rice straw, pH: 7.5, Temperature: 37°C, time: 30 d	[137]

* Value referred only to biogas yield

Thus, the bio-methane yield from rice straw strongly depends on the pretreatment method adopted and on the substrate used in the co-digestion. An overview of quantitative bio-methane yields related to anaerobic digestion of rice straw, inocula, with the relative pretreatments available in literature is given in Tables 4.12, 4.13, 4.14.

Table 4.13 Methane yields of rice straw, in terms of volatile solids (VS), related to chemical pretreatment. Data collected from literature.

Pretreatment	Methane yield [L kg_{VS}^{-1}]	Note	Ref.
Grind (25 mm) & NH_3 (2%) & heat (110°C)	245	APS system Temperature: 35°C, time: 24 d	[550]
Cut (20 – 30 mm) & NaOH (6%)	264	Bottle, municipal wastewater sludge, pH: 7.37 – 7.79 Temperature: 37°C, time: 36 d	[536]
Cut (< 4 mm) & NaOH (1.6%), 30°C, 24 h	318	Bottle, paper mill wastewater treatment, time: 40 d, Temperature: 37°C	[295]
Cut (5 mm) & NH_3 (4%)	397*	Bottle, anaerobic sludge Moisture: 70%, pH: 7.2 – 7.5, T_{90}: 30 d	[545]
Cut (1 mm) & photocatalytic pretr. TiO_2 (0.25 g L^{-1})	397	Bottle, pretreated cow manure, time: 45 d, Temperature: 37°C	[401]
Cut (3 mm) & NaOH (2%)	409	Bottle, pretreated cow manure, time: 45 d, Temperature: 37°C	[229]
Cut (1 mm) & NaOH (1.5% w/v), 3 h	498	Batch, cow manure & anaerobic sludge Temperature: 37°C, pH: 7.0	[401]
Cut (5 – 10 mm) & NaOH (6%)	520	Batch, wastewater & NH_4Cl, OLR: 50 mg_{VS} L^{-1}, C/N: 25, Temperature: 35°C	[198]
Cut (< 10 mm) & NaOH (10%), 20°C, 24 h	600*	Batch, wastewater, time: 23 d, Temperature: 35°C	[540]
Cut (1 mm) & NaOH (1.5% w/v), 320-330 nm, TiO_2 (0.25 g L^{-1})	645	Batch, wastewater, time: 45 d, Temperature: 37°C	[401]

APS: anaerobic phased solid digester system; * value referred to total solids (TS); Technical digestion time (T_{90}) is the time needed to produce 90% of the digester's maximum gas production;

Table 4.14 Methane yields of rice straw, in terms of volatile solids (VS), related to biological pretreatments. Data collected from literature.

Pretreatment	Methane yield [L kg_{VS}^{-1}]	Note	Ref.
Milled & white rot fungi	92	Bottle & Pilot, leachate Temperature: 25°C, time: 59 d	[274]
Milled & white rot fungi	124	Bottle & Pilot, leachate Temperature: 35°C, time: 59 d	[274]
Cut & delignified	224*	Batch, slurry Temperature: 30°C, time: 63 d	[169]
Cut (30 mesh) & rumen fluid (39°C, 24 h)	285	Bottle Temperature: 35°C, C/N: 25, time: 30 d, pH: 7.2	[549]
Cut & white rot fungi	240	Bottle & Pilot, leachate Temperature: 18 – 27°C, time: 89 d	[274]
Cut (5-10 mm) & *Ganoderma lucidum* (30 d, 30°C)	296	Batch Temperature: 30°C, time: 35 d	[232]
Cut & delignified & brown rot fungi	296*	Batch, slurry Temperature: 30°C, time: 63 d	[169]
Cut & delignified & white rot fungi	328*	Batch, slurry Temperature: 30°C, time: 63 d	[169]
Cut (5-10 mm) & *Phanerochaete chrysosposrium* (30 d, 30°C)	339	Batch Temperature: 30°C, time: 35 d	[232]

* value referred to total solids (TS)

4.5 Bio-methane from Rice Straw

4.5.1 The context

Energy is one of the principal resources of the industrial and contemporary society, and, consequently, one of the principal topic of investigation related to sustainability. The continuously growth in the world population and the consequent request of increasing the economic activities causes a growth in the energy demand, with related consequences on the Earth's environment [308]. In fact, the energy demand is registered to be in continuous growth, with related actual problems with respect climate change, energy crises, and food security [197]. Technical and socio-economic answers are needs in relation to these challenges, providing sustainable solutions from the environment viewpoint and cost-effectiveness for large-scale applications. Thus, waste-to-energy conversion of agricultural residues into renewable energy represents a possible solution for the reduction of global methane emissions, and for the preservation of valuable land resources for food production [324]. So, unused agricultural waste could represent a possible stable sources of energy in order to support countries to achieve a long-term energy strategy [324]: wheat straw and rice straw could play an important role in the sustainable production of energy in relation to this growing demand [413]; consequently, biomass, when considered a field residue can become a new resource in the sustainable approach in energy sector. Indeed, field residues are defined as what remain after crop harvesting, while process residues are the waste of the crop after its harvesting [319].

The aim of this Section of the PhD Thesis is a focus on the rice straw, that is considered just a field residue, because it isn't usually used in industry or agriculture. The production of rice straw is evaluated in about 0.70–1.50 kg of rice straw [324, 121] per kg of harvested rice produces: usually, 1.35 kg of rice straw per kg of rice grain is accepted as the mean reference value in technical analyses [230, 282, 334, 393]. Lignocellulosic biomass can represent an economical and renewable substrate to process biofuels [319], with particular regards to biogas and biomethane, because these ones can be produced by anaerobic digestion of lignocellulosic substrates from microorganism [369]. Thus, bioenergy production could represent an efficient approach to reduce waste generation [163]. Furthermore, the consequent digestate can also find application as an organic fertiliser, because of its phosphorus and nitrogen content [93].

So, valorisation of rice straw is proposed as a possible solution in relation to the atmospheric pollution with respect to its disposal, by means of its possible use for the production of second-generation biofuels and/or biodegradable plastics [175], with particular interest to microbial polyesters, which at present represents the biodegradable bio-based plastics, most attractive for replacing fossil-fuel-based plastics [539, 411, 474].

4.5.2 Rice as an Agricultural Commodity

Rice represents the third most popular agricultural crop in the world, after wheat and corn. In 2020, its total cultivated area accounted for 164.2 Mha and its gross grain yield production was around 756.7 Mt yr^{-1} [155, 154]. In Figure 4.7, the total global rice production is represented in the time range 2000-2020. During the 21st century, the rice production is continuously growing, estimated in around the 26% in the same time range, with a related increase of around 250% since 1961 up to 2020.

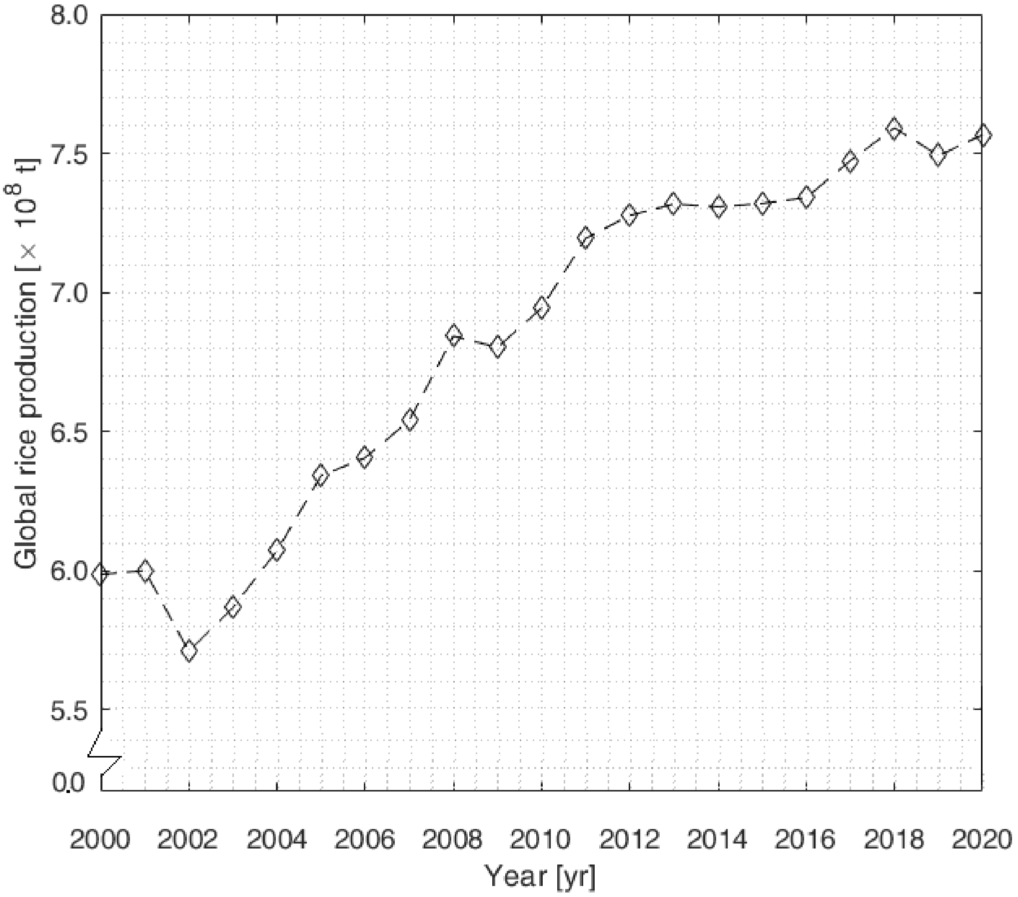

Figure 4.7 Global rice production [t] from 2000–2020 based on FAO data [154].

Table 4.15 summarises the area, plant height, and rice yield in different regions in order to show some information on the global rice production. In Table 4.16, rice production for the year 2020 is reported with respect to continent. In Table 4.17, rice production of some of the largest rice-producing countries for different continents is summarised in the time range 2000-2020. In 2017, dry lignocellulosic biomass in relation to rice production has been evaluated around 905 Mt yr^{-1} [413, 55].

Table 4.15 Area, plant height, and rice yield by region [154, 415, 403, 375, 364, 473] for the year 2020. Rice yield is the ratio of overall rice grain production to harvested area.

Country	**Area [Mha]**	**Plant Height [mm]**	**Yield [t ha^{-1}]**
China	30.34	362–483	7.04
India	45.00	900–1300	3.96
Indonesia	10.66	701–998	5.13
Japan	1.46	1020–1170	6.64
Malaysia	0.65	631	3.60
Thailand	10.40	1000–6000	2.91
United States	1.21	950–1880	8.54
Vietnam	7.22	900–1750	5.92
World	164.19	n.d.	4.61

Table 4.16 Rice production by macro-area for the year 2020 [154].

Continent	**Rice Production [Mt yr^{-1}]**
Africa	37.9
Asia	676.6
Australia	0.1
Central America	1.4
Europe	4.1
Northern America	10.3
Russian Federation	1.1
South America	25.0
World	756.5

4.5.3 Rice Straw: From Residual Waste of Rice Production to a Potential Energy Source

Rice represents a fundamental food crop for the global food security, but also for the socio-economic stability[548]. Therefore, rice cultivation causes pollution because of the related irrigation and fertilization methods. In fact, during the growth

Table 4.17 Rice production by some of the leading countries on different continents; data from Ref. [154].

					Rice Production					
Year	**Bangladesh [$\times 10^7$ t]**	**Brazil [$\times 10^7$ t]**	**China [$\times 10^8$ t]**	**India [$\times 10^8$ t]**	**Italy [$\times 10^6$ t]**	**Pakistan [$\times 10^6$ t]**	**Spain [$\times 10^5$ t]**	**Thailand [$\times 10^7$ t]**	**USA [$\times 10^7$ t]**	**Vietnam [$\times 10^7$ t]**
2000	3.76	1.11	1.90	1.27	1.23	7.20	8.27	2.58	0.87	3.25
2005	3.98	1.32	1.82	1.38	1.41	8.32	8.24	3.06	1.01	3.58
2010	5.01	1.12	1.97	1.44	1.52	7.23	9.28	3.57	1.10	4.00
2015	5.18	1.23	2.14	1.57	1.52	1.02	8.47	2.77	0.87	4.51
2020	5.49	1.11	2.14	1.78	1.51	8.42	7.39	3.02	1.03	4.28

phase of the rice plant, relevant amounts of CH_4 and N_2O are emitted into the atmosphere [397, 546]: methanogenesis is the result of the bacterial transformation of soil organic carbon under anaerobic conditions. Furthermore, fertilisation plays a role in relation to the air pollution [278] due the interaction between the fertilizer and the soil.

As the result of rice cultivation, husk, chaff, and rice straw are produced in relation to the variety of rice, as summarised as follows:

- Husk: 20% by weight of the rice;
- Chaff: 10% by weight of the rice;
- Rice straw: 700–1500 kg for every ton of rice grain.

While husk and chaff present an economic value related to their use in some industrial sectors, such as energy, food, and pharmaceutics, only the 20% of the rice straw is used as a raw material for the pulp and paper industry, particularly when it is harvested, without any machinery [415]. So, rice straw is a field residue, with a high content in silica (SiO_2) (the 13% by weight). Commonly, two disposal methods are used for rice straw, evaluated to cause pollution for around 10–15% of worldwide anthropogenic emissions [324]:

- Open-field burning: at least 50% of total rice straw is globally burned [415], generating atmospheric pollution equivalent to around 11 t ha^{-1} yr^{-1} of CO_2 [414];
- Incorporation by the soil: up to 12 t ha^{-1} yr^{-1} with a related increase of CH_4 and N_2O emissions [282].

But, these disposal methods allow the reintroduction of elementary substances into the lithosphere (C, K, N, P, etc.) and eliminate weeds from the soil, with the favourable result of avoiding compromising the quality of the next harvest [502]. Nevertheless, rice straw removal from flooded rice fields has been proved to not decrease the level of soil organic matter [442].

Now, some considerations on the carbon dioxide emissions related to the open-field burning of the biomass can be developed. In fact, biomass is always assumed to be carbon neutral [211, 224], in relation to the biospheric carbon cycle; indeed, the carbon released during combustion is just the same that the plant has sequestered from atmosphere, during its life cycle. But, in accordance with the exergetic analysis, a resource (energy included) has a quality [249, 14], that can be also represented by the number of its uses before becoming a waste. So, open-field burning of rice straw causes loss of unused heat, atmospheric pollution, and CO_2 emissions, which are directly outflow into the environment [221]. Heat, pollution, and CO_2 emissions represent exergetic losses. However, if the rice straw is converted into biofuels (or other useful by-products), it becomes a resource, useful to generate work; so, even if an equivalent amount of CO_2 emissions and heat are released, the production of useful work can be obtained. In this last process, the rice straw presents a higher quality (i.e., exergy) due to the production of useful work in addition to the carbon dioxide and heat.

In relation to the energy content, the heating value, summarised in Table 4.18, represents one of the most important properties of biomass: it is strictly related to its composition. So, it is possible to outline the average of rice straw calorific values depending on the World region of provenance of the biomass. There are also empirical formulae to calculate this property based on proximate analysis, ultimate analysis or chemical composition. It is possible to calculate an average heating value in Italy, by considering the experimental values, referred to a sample of rice straw coming from North Italy (Ref. [34]) and the empirical formula for the higher heating value (HHV) by Jimennez et al. [222]:

$$HHV = \left(1 - \frac{A}{100 - A}\right) \cdot \left(0.1739\, Ce + 0.2663\, L + 0.3219\, E\right) \tag{4.1}$$

where A is the ash content in wet basis, Ce is the biomass weight percent of cellulose (including hemicellulose), L is the biomass weight percent of lignin and E is the biomass weight percent of other extractives. The result obtained for the Italian case is of approximately $HHV = 16.8$ MJ kg^{-1}.

Table 4.18 Calorific values of rice straw from different countries [415].

Country	**Calorific Value $[10^6$ J kg$^{-1}]$**
China	18.0
India	12.3–28.5
Malaysia	15.1
Thailand	11.7–16.3
United States	11.5–15.3

The bioenergy production from crop residues can be developed by [308]:

- thermal conversion, such as combustion, pyrolysis, and gasification;
- biochemical conversion, such as anaerobic digestion or co-digestion, fermentation, and transesterification.

In particular, the organic substrate can be degraded into biogas and digestate by developing the anaerobic digestion [62]. In this context, rice straw could represent a low-cost choice for the bio-based economy; indeed, as a field residue of rice cultivation, it would otherwise be burned or left in the soil, without any economic value. So, its possible energy use could represent a new use as resource, along with techniques for its collection and baling [65].

Anaerobic digestion of rice straw is considered the best route to exploit its energy potential [256]. As previously analysed, in relation to the rice straw composition, lignin results not easy to be digested by micro-organisms [520], and, with the aim of overcoming this problem, lignocellulosic residues are mechanically, thermally, biologically, and chemically pretreated [555]. In particular, mechanical pretreatments reduce the biomass into particles, increasing porosity, that allows the degradation by anaerobic bacteria [11]. Table 4.19 shows the densities of different forms of processed rice straw [415], which is a reduction of Table 4.8.

Nevertheless, high lignin content slows anaerobic digestion of lignocellulosic biomass waste, increasing the time required for its degradation. So, the efficiency of the process has to be improved for decreasing the costs of biomasses use. Cellulose, hemicellulose, and lignin are the fundamental components of rice straw, and their

Table 4.19 Densities of different forms of processed rice straw [415].

Form	**Density [kg m^{-3}]**
Baled	110–200
Chopped	40–80
Cubed	320–640
Hammer milled	40–100
Loose	20–40
Pelleted	560–720

proportions affect the rate of degradation of the substrate [319]: in aerobic decomposition, cellulose is depolymerized to produce glucose, that is then oxidized into CO_2 and H_2O. Thus, the biomass is reduced over time: rice straw in the soil presents a half-life of two years, and around the 80–90% is decomposed during the first year [324].

So, following the results obtained in a recent analysis of the Novara district [65], when the authors (members of the Department of Energy of the Politecnico di Torino) have introduced the concept of rice straw barrel, i.e., a cylindrical bale of rice straw considered as a metric unit for the use of rice straw for energy [65], in analogy with the oil straw barrel. The barrel of rice straw was proposed based on having the same energy potential as a barrel of oil.

In this context, it is important to remember that rice straw composition of polysaccharides and lignin, makes it easily degradable; indeed, at the end of the season around 80–90% of the added rice straw disappears [328] in a natural degradation. Consequently, a difficulty emerges in the introduction of the rice straw barrel as energy storage, making it suitable only for local and quick use. In fact, the energy and density of rice straw is lower than the on of the fossil fuels, with the consequence that more biomass is needed to obtain the same amount of energy. So, the economic feasibility of solid biomass transport limits rice straw use to distances within 200 km of the source [454].

Nowadays, great interest is paid to the anaerobic conversion of lignocellulosic biomass into bio-methane, with particular attention to the kinetic characteristics of the digestion process, in relation to the lag phase, hydrolysis rate, methane production rate, and methane yield [308]. Thus, fertilizer can also results as by-product [90] of this process.

So, in this PhD Thesis, in order to evaluate the potential biomethane production, and all the fundamental quantities to assess the sustainability of biomethanation from anaerobic digestion, it is fundamental the evaluation of the number of rice straw barrels needed.

With this aim in mind, first, the amount of rice straw available is evaluated in relation to its energy use, by quantifying it in relation to the number of rice straw barrels. Nevertheless, in this evaluation it must be considered that the 20% of the total amount of rice straw is usually used for other purposes, such as the pulp and paper industry [415]; so, only the 80% of the total amount of rice straw is considered available for energy use.

Then, after having evaluated the average number of available rice straw barrels, the amount of biomethane obtained from anaerobic digestion can be estimated. The flow of the approach used is represented in Figure 4.8.

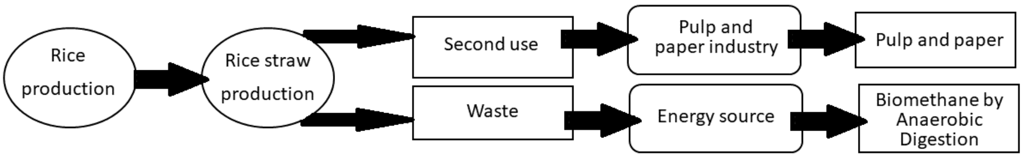

Figure 4.8 Schematic assumptions used in this analysis, considering the milled rice production: an average evaluation of the related rice straw production is carried out, of which 20% by weight is considered to be potentially used in other sectors (different from the energy one) such as the pulp and paper industry. So, the remaining part is the one considered available for energy purposes (for which the available *RSB* are evaluated), and their biomethane potential is evaluated by considering anaerobic digestion.

Last, a comparison is developed on the effects between the use of at least 50% of the total available amount of rice straw for anaerobic digestion and the current practice of open-field burning, by using the indicator of sustainability, $THDI$, defined in the previous Chapter 3.

The total amount, m_{rs}, of rice straw available on fields before bailing, is proportional to the amount of milled rice, m_r, produced:

$$m_{rs} = k\, m_r \tag{4.2}$$

where m is the mass, and the subscripts rs and r denote the rice straw and the rice, respectively, while k represents an empirical coefficient that gives the amount of rice straw related to the amount of rice.

Following Giaretto, Campagnoli and Bressan [65], the concept of rice straw barrels is used with the aim of evaluating the potential use of rice straw for the production of by-products such as methane and the related digestate. To do so, first the analysis of the rice straw barrel is carried out, starting from its definition as introduced in Ref. [65], and then an improvement is developed to evaluate its effective use in the energy context for the bio-methane production.

The rice straw barrel has first been introduced in Ref. [65], in the context of the analysis of rice production in the Novara district, Italy. Novara district presents an area of 134025 ha, with a temperate climate characterised by cold winters (minimum temperatures often below 0 °C between December and February) and quite hot summers (frequently 30 °C). Mean rainfall amounts to approximately 1000 mm yr^{-1}, characterised by two maximums (148.9 mm in November and 110.7 mm in May) and two minimums (52.5 mm in July and 56.5 mm in January). Winter averages approximately 35 cm of snow. Referring to Torrion Quartara Geophysical Observatory data [350], i.e., meteorological archive dating back to August 1999, the average annual temperature during the 21st century is 13.9°C [3]. In Novara district, the rice variety mostly cultivated is *Baldo*, a variety characterised by round, thick, hard grains. Its cultivation season is from January to October, carrying out by submersion and high levels of agricultural mechanization [65]: all agricultural processes occurs by using medium-power tractors and specific equipment, and the fields are flooded by water irrigation canals [65].

The rice straw barrel are made by the rice straw, removed from the field when its moisture content has dropped from 50% to below 20%, in order to prevent fermentation [65]: it is removed 3-4 days after harvest, in relation to the local climate [230]. When the biomass remains in the field, it decomposes, decreasing the available biomass. This reduction in biomass is taken into account by the empirical relation [519]:

$$m(t) = m_r + m_d \cdot e^{-kt} \tag{4.3}$$

where $m(t)$ represents the mass of the rice straw over time, m_r represents the remaining mass after time t, m_d represents the difference between the initial mass $m_0 = m_r + m_d$ and the remaining one m_r, t is the time in month, and k represents the decomposition rate (month^{-1}). Table 4.20 summarises these quantities for the Baldo variety in Novara district. So, referring to Equation (4.3), considering that in Novara district rice straw is removed after 4 days or 1 month, it follows that the available biomass results:

$$m = m_r + 0.024\, m_d$$

- 5765.4 kg ha^{-1}, after 4 days;
- 4177.3 kg ha^{-1}, after 1 month.

Table 4.20 Numerical values of the coefficients in Equation (4.3) for Novara area during rice harvesting [65].

Quantity	**Value**	**Unit of Measurement**
m_r	1828.8	kg ha^{-1}
m_d	4262.2	kg ha^{-1}
k	0.596	month^{-1}

The barrel considered is a cylinder of 1.8 m in diameter and 1.2 m in height, wrapped in a nylon film, with a mass of 430 kg and having a density of 141 kg m^{-3}, which is in agreement with the values reported in Table 4.19: its energy content is around 6020 MJ.

In Northern Italy, the major environmental impact from cultivation has been estimated to be related to field emissions for 68.0%, to fertilizers for 9.2%, to transportation for 6.1%, to refining and packing for 4.7%, and to field operations for 3.6% [324]. So, removing rice straw will contribute to environmental mitigation of the cultivating process.

The number of rice straw barrels available for energy used is obtained both by considering the average decrease in moisture content from 50% to 20%, before bailing and and by excluding the 20% of the total amount of rice straw used for the pulp and paper industry. The result is the number of rice straw barrels that can be used in anaerobic digestion in order to obtain bio-methane.

In this PhD Thesis, the different ways of mass harvesting in different continents and countries must be taken into account, and it is done by introducing a new definition of rice straw barrel, based only on its weight. So, in the following, the *rice straw barrel* is consider *any packaging of rice straw, with a moisture content less of 20% and a mass of 430 kg*.

4.5.4 Anaerobic Digestion and Biomethanation

Anaerobic digestion of biomass has been shown to be the most favourable route to use the rice straw energy potential [256]. Indeed, anaerobic digestion represents a natural process, in which specific microorganisms degrade organic matter into intermediate products, that can be concerted into methane (CH_4). In relation to the concentration of total solids (TS), anaerobic digestion can be classified as [324]:

- Wet, when the total solid concentration results lower than 15%;
- Semi-dry, when the total solid concentration results in the range of 15-20%;
- Dry, when the total solid concentration results greater than 20%.

In [161], advantages and disadvantages of different biomass pretreatments and anaerobic straw digestion processes are summarised. Anaerobic digestion of rice straw results faster in wet conditions, even though the related methane yield is approximately the same in any condition [465]. Wet systems present advantages in relation to the less water use, the elimination of wastewater disposal, and the reuse of the solid residue as fertilizers [324]

Biomethanation is a complex biological process, that occurs following four different phases [62]:

- Hydrolysis phase: cellulose and other carbohydrates, proteins, and fats are broken down into monomers by hydrolyse enzymes of anaerobic bacteria. The time requires is from few hours for the hydrolysis of carbohydrates, to several days for the hydrolysis of proteins and lipids;
- Acidogenic phase: The results of hydrolysis are monomers, that can be degraded into short-chain organic acids, alcohols, hydrogen, and carbon dioxide by anaerobic bacteria;

- Acetogenic phase: The results of the acidogenic process become the substrates for bacteria in the acetogenic phase, which uses H_2 and CO_2 to form acetic acid. Methanogenic bacteria grow concurrently with acetogenic bacteria. Acetate production decreases if hydrogen partial pressure is great enough;
- Methanogenic phase: Methane is generated in anaerobic conditions; in relation to the substrate, methanogenesis can be divided into the following categories [62]:
  - Acetoclastic Methanogenesis: Acetate $\rightarrow CH_4 + CO_2$
  - Hydogenotrophic Methanogenesis: $H_2 + CO_2 \rightarrow CH_4$
  - Methyltrophic Methanogenesis: Methanol $\rightarrow CH_4 + H_2O$

Anaerobic digestion produces biogas of composition of 50–65% biomethane (CH_4) and 35–40% carbon dioxide (CO_2), with the balance consisting of nitrogen (N_2) and trace amounts of hydrogen sulphide (H_2S) and water vapour (H_2O).

Anaerobic digestion systems are designed in two possible configurations [324]:

- Batch reactors: all the substrate/inocula mixture is added at the beginning. They are much simpler and 40% less expensive, but with larger volume requirements and a related larger footprint for the reactors;
- Continuously-fed reactors: the substrate/inocula mixture is added incrementally over time.

Now, the first step is to evaluate the available biomethane production from rice straw. Following Meraj et al. [308], the rice straw substrates must be air-dried and mechanically pretreated, with the result of reducing the rice straw size up to 0.1 mm. The next step is to put the mechanically treated straw into an anaerobic bioreactors, at (35 ± 1) °C of temperature and a pH in the range of 7.0–7.5 [308]. In Table 4.21 the cellulose content related to the particle size is summarised.

Meraj et al. [308] showed experimentally that the kinetics of the biogas production processes can be modelled by using the Logistic Function Model [511]:

$$m(t) = \frac{m_0}{1 + \exp\left(2 + \dfrac{4\,\dot{m}_{max}\,(\ell - t)}{m_0}\right)} \tag{4.4}$$

Table 4.21 Cellulose content in relation to particle size [308].

Size [mm]	**Cellulose Content** [%]
<0.15	84
0.15–0.18	83
0.18–0.21	76
0.21–0.25	68
0.25–0.30	61
0.30–0.42	56
>0.42	50

where $m(t)$ represents the methane mass production (mL g_{VS}^{-1}), with VS volatile solids, m_0 is the methane yield potential (mL g_{VS}^{-1}), ℓ represents the lag phase (d), i.e., the minimum time required for methane production, t represents the time (d), and $\dot{m}_{max}$ represents the maximum methane production rate (mL $g_{VS}^{-1}d^{-1}$) [308]. The amount of methane yield in terms of total solids (TS) has been evaluated to fit the range 193-240 L kg_{TS}^{-1}. In Table 4.22 the methane yield is reported in relation to the volatile solids (VS) with respect to different pretreatments [324], see Tables 4.12, 4.13 and 4.14 for a deeper analysis of biomethane yields in relation to the pretreatment.

Table 4.22 Methane yield in term of volatile solids for different pretreatments [324, 92].

Type of Pretreatment	**Methane Yield** [10^{-3}**m**^{3} **kg**$_{VS}^{-1}$]	**Digestion Temperature** **[°C]**	**Time Period** **[d]**
Cut (3–5 mm)	280	22	120
Pulverized	215	35	120
Extrusion (<50 mm)	227	35	45
2% NH_3	190	35	24

On the base of these results, here, the average amount of total solids (TS) and volatile solids (VS) is calculated with respect to the RSB, obtaining information to assess the annual biomethane potential. Thus, the Ref. [256] is considered in relation to the average values of the proximate analysis of rice straw, while the Ref. [324] is considered in relation to the biomethane yields, $\dot{V}_{CH_4}$. These average values depend on different inocula, pretreatments, and working temperatures. The values here used are reported in Table 4.23.

Table 4.23 Values needed to perform the evaluations: empirical coefficient k (Eq.(4.2)), amount of volatile solids (VS) with respect to total solids ($\%TS$), biomethane yield ($\dot{V}_{CH_4}$).

Quantity	Minimum	Average	Maximum	References
k	0.70	1.35	1.50	[324, 121, 230, 282, 334, 393]
VS (% TS)	73.80	84.08	95.26	[256]
$\dot{V}_{CH_4}$ [$\times 10^{-3}$ m^3 kg$_{VS}^{-1}$]	92	186	280	[324]

4.5.5 Results of the *THDI* analysis

Now, the *THDI* indicator, Eq. (3.53), is used in the analysis of sustainability of the energy use of rice straw from anaerobic digestion. To do so, in relation to rice straw, the *THDI* index is evaluated in two different conditions:

- *THDI*: the Thermodynamic Human Development Index at present-condition, without the use of rice straw for energy use;
- $THDI_{rsad}$: the Thermodynamic Human Development Index when the rice straw is used for biomethane production.

Consequently, it is possible to compare these two different conditions by evaluating their ratio:

$$\frac{THDI_{rs,ad}}{THDI} = \sqrt[3]{\frac{m_{CO_2}}{m_{CO_2} - m_{CO_2 rs}} \cdot 750^{-(II_{rs} - II)}} \tag{4.5}$$

where $m_{CO_2 rs}$ is the amount of CO_2 saved by production of biomethane from rice straw.

So, by using the *THDI* Equation (4.5), and taking into account the results of [445, 256], the positive effect can be evaluated in relation to substituting the current practice of burning rice straw on open fields with the here proposed anaerobic digestion and biomethanation.

To do so, some data must be considered in relation to the emissions for open field burning and for anaerobic digestion and biomethanation Refs. [445, 256], that can be summarised as [256]:

- Open field burning:
    - 1460.00 kg CO_2 (carbon dioxide);
    - 34.70 kg CO (carbon monoxide);
    - 13.00 kg PM (particulate matter);
    - 3.10 kg NO_x (oxides of nitrogen);
    - 2.00 kg SO_2 (sulphur dioxide);
    - 1.20 kg CH_4 (methane).
- Anaerobic digestion:
    - 2.05 kg CO_2 (carbon dioxide);
    - 0.67 kg CO (carbon monoxide);
    - 0.01 kg H_2S (hydrogen sulphide);
    - 0.04 kg NO_x (oxides of nitrogen);
    - 1.07 kg CH_4 (methane).

The $THDI$ analysis is first focused on the Novara district, and then extended to Italy. Then, the Italian values are compared to the results evaluated for the other worldwide major rice producing countries (Bangladesh, Brazil, China, India, Pakistan, Spain, Thailand, United States of America, and Vietnam). The rice production for those countries is summarised in the previous Table 4.17.

The case of Novara district

In 2020, $220 \cdot 10^3$ t of rice has been harvested in the Novara district; this quantity represents around the 15% of total Italian rice production.

Using the rice quantity, the mass of rice straw available for energy ($m_{rs,AD}$) can be evaluated, and, consequently, also the number of rice straw barrels available (RSB), the total amount of volatile solids (total solids minus ash content) in the biomass (m_{VS}), and the annual biomethane yield ($\dot{V}_{\mathrm{CH_4}}$). These quantities have been calculated by using the previous relations and are reported in Table 4.24.

In the worst case (the amount of rice straw around 70% of the mass of the rice grain collected, $k = 0.70$), 200558 rice straw barrels (*RSB*) can theoretically be obtained for energy use, corresponding to an annual biomethane yield ranging from $(1.09 - 3.32) \times 10^7$ m^3.

Now, considering $k = 1.50$, *RSB* results 429767, with a related potential annual biomethane yield of $(2.93 - 8.90) \times 10^7$ m^3.

Table 4.24 Results for the Novara area in the year 2020. The minimum, average, and maximum values are based on data from Table 4.23. Subscripts *A*, *B*, and *C* in $\dot{V}_{\mathrm{CH_4}}$ refer to biomethane yields of 92, 186, and 280 L kg$_{VS}^{-1}$, respectively.

Quantity		**Min.**	**Avg.**	**Max.**
$m_{rs,AD}$	[t]	86,240	166,320	184,800
RSB	$(\times 10^5)$	2.01	3.87	4.30
m_{VS}	[t]	118,410	260,171	317,959
$\dot{V}_{\mathrm{CH_4},A}$	$[\times 10^7$ m^3 yr$^{-1}]$	1.09	2.39	2.93
$\dot{V}_{\mathrm{CH_4},B}$	$[\times 10^7$ m^3 yr$^{-1}]$	2.20	4.84	5.91
$\dot{V}_{\mathrm{CH_4},C}$	$[\times 10^7$ m^3 yr$^{-1}]$	3.32	7.28	8.90

The case of Italy

Starting from the previous results for the Novara district, in relation to Italy, the total amount of *RSB* and the related potential amount of biomethane from rice straw can be obtained. The time period considered is from the years 2000 to 2020, as reported in Table 4.17.

Table 4.25 reports the minimum, average, and maximum values for Italy based on data from Table 4.23.

The average annual biomethane yield results in the range of $(0.71 - 2.15) \times 10^8$ m^3, with a rice straw yield of 1.35 based on milled rice in the year 2020. This result can be considered in comparison with the data available for the year 2019, when in Italy, the total amount of biomethane produced from other agricultural and zootechnical effluents result 2.2×10^9 m^3, with a gross production of 987 MW electrical power across 1629 different power plants [111]. The other agricultural and zootechnical sectors represents around 82% of electrical production from biogas.

So, biogas from rice straw could represent an improvement of the production of biogas, useful for green energy production. This can be realised by increasing the number of anaerobic digestion plants within 200 km of rice crops.

The result could be an improvement of the required circular economic framework by using field waste, which has not a second use, nut also a useful way to prevent its burning on fields. Nevertheless, the digestate obtained from anaerobic digestion can be employed as a fertilizer [324].

The case of the Major Rice-Producing Countries

Table 4.26 reports the results obtained also for some of the major rice-producing countries in the time range 2000–2020. The annual total number of *RSB* and the related potential biomethane yield are also shown in Table 4.26. The minimum, average, and maximum biomethane yields are based on the results obtained in literature for the different variety of rice and result 92, 186, and 280 L kg_{VS}^{-1} [324].

Several studies have reported higher biomethane yields (e.g., 325.76 L kg_{VS}^{-1} [232]), but, in order to develop a comparison among the different countries, here, only mechanical pretreatments are considered.

Table 4.25 Rice straw barrels (*RSB*) and potential annual biomethane production ($\dot{V}_{CH_4}$) in Italy. Subscripts *A*, *B*, and *C* refer to biomethane yields of 92, 186, and 280 L kg_{VS}^{-1}, respectively.

Quantity	**Year**														
	2000			**2005**			**2010**			**2015**			**2020**		
	Min.	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**
	Italy														
RSB ($\times 10^6$)	1.12	2.16	2.40	1.29	2.48	2.76	1.38	2.67	2.96	1.38	2.67	2.97	1.37	2.65	2.94
$\dot{V}_{CH_4,A}$ ($\times 10^7$ m^3yr^{-1})	2.62	5.75	7.03	3.01	6.61	8.08	3.23	7.09	8.67	3.23	7.10	8.68	3.21	7.05	8.62
$\dot{V}_{CH_4,B}$ ($\times 10^8$ m^3 yr^{-1})	0.53	1.16	1.42	0.61	1.34	1.63	0.65	1.43	1.75	0.65	1.44	1.75	0.65	1.43	1.74
$\dot{V}_{CH_4,C}$ ($\times 10^8$ m^3 yr^{-1})	0.80	1.75	2.14	0.92	2.01	2.46	0.98	2.16	2.64	0.98	2.16	2.64	0.98	2.15	2.62

Table 4.26 Rice straw barrels (*RSB*) and potential annual biomethane production ($\dot{V}_{\mathrm{CH_4}}$) for major rice-producing countries. Subscripts A, B, and C refer to biomethane yields of 92, 186, and 280 L kg_{VS}^{-1}, respectively.

Quantity	**Year**														
	2000			**2005**			**2010**			**2015**			**2020**		
	Min.	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**
	Bangladesh														
RSB ($\times 10^7$)	3.43	6.62	7.35	3.63	7.00	7.77	4.56	8.80	9.78	4.72	9.11	10.12	5.01	9.65	10.75
$\dot{V}_{\mathrm{CH_4},A}$ ($\times 10^9$ m^3 yr^{-1})	0.80	1.76	2.15	0.85	1.86	2.28	1.07	2.34	2.86	1.10	2.42	2.96	1.17	2.57	3.14
$\dot{V}_{\mathrm{CH_4},B}$ ($\times 10^9$ m^{3}yr^{-1})	1.62	3.56	4.35	1.71	3.76	4.60	2.15	4.73	5.79	2.23	4.90	5.99	2.36	5.19	6.35
$\dot{V}_{\mathrm{CH_4},C}$ ($\times 10^9$ m^3 yr^{-1})	2.44	5.36	6.55	2.58	5.67	6.92	3.24	7.13	8.71	3.36	7.38	9.01	3.56	7.82	9.55
	Brazil														
RSB ($\times 10^7$)	1.02	1.96	2.18	1.20	2.32	2.58	1.02	1.98	2.19	1.12	2.16	2.40	1.01	1.95	2.17
$\dot{V}_{\mathrm{CH_4},A}$ ($\times 10^8$ m^3 yr^{-1})	2.37	5.21	6.37	2.81	6.17	7.54	2.39	5.26	6.42	2.62	5.75	7.03	2.36	5.19	6.34
$\dot{V}_{\mathrm{CH_4},B}$ ($\times 10^9$ m^3 yr^{-1})	0.48	1.05	1.29	0.57	1.25	1.52	0.48	1.06	1.30	0.53	1.16	1.42	0.48	1.05	1.28
$\dot{V}_{\mathrm{CH_4},C}$ ($\times 10^9$ m^3 yr^{-1})	0.72	1.59	1.94	0.86	1.88	2.30	0.73	1.60	1.96	0.80	1.75	2.14	0.72	1.58	1.93
	China														
RSB ($\times 10^8$)	1.73	3.34	3.71	1.66	3.20	3.56	1.80	3.47	3.85	1.95	3.76	4.18	1.95	3.76	4.17
$\dot{V}_{\mathrm{CH_4},A}$ ($\times 10^{10}$ m^3 yr^{-1})	0.40	0.89	1.09	0.39	0.85	1.04	0.42	0.92	1.13	0.46	1.00	1.22	0.46	1.00	1.22
$\dot{V}_{\mathrm{CH_4},B}$ ($\times 10^{10}$ m^3 yr^{-1})	0.82	1.80	2.19	0.78	1.72	2.10	0.85	1.87	2.28	0.92	2.02	2.47	0.92	2.02	2.47
$\dot{V}_{\mathrm{CH_4},C}$ ($\times 10^{10}$ m^3 yr^{-1})	1.23	2.70	3.30	1.18	2.59	3.17	1.28	2.81	3.43	1.38	3.04	3.72	1.38	3.04	3.72
	India														
RSB ($\times 10^8$)	1.16	2.24	2.49	1.26	2.42	2.69	1.31	2.53	2.81	1.43	2.75	3.06	1.63	3.13	3.48
$\dot{V}_{\mathrm{CH_4},A}$ ($\times 10^9$ m^{3}yr^{-1})	2.71	5.96	7.29	2.93	6.44	7.87	3.07	6.74	8.23	3.33	7.32	8.95	3.80	8.34	10.20
$\dot{V}_{\mathrm{CH_4},B}$ ($\times 10^{10}$ m^3 yr^{-1})	0.56	1.21	1.47	0.59	1.30	1.59	0.62	1.36	1.66	0.67	1.48	1.81	0.77	1.69	2.06
$\dot{V}_{\mathrm{CH_4},C}$ ($\times 10^{10}$ m^3 yr^{-1})	0.83	1.81	2.22	0.89	1.96	2.40	0.93	2.05	2.51	1.01	2.23	2.72	1.16	2.54	3.10

[...] Table 4.26 - Continuation.

Quantity	Year														
	2000			**2005**			**2010**			**2015**			**2020**		
	Min.	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**
	Pakistan														
$RSB\ (\times 10^7)$	0.66	1.27	1.41	0.76	1.46	1.63	0.66	1.27	1.41	0.93	1.79	1.99	0.77	1.48	1.64
$\dot{V}_{\mathrm{CH_4},A}\ (\times 10^8\ \mathrm{m^3\ yr^{-1}})$	1.53	3.37	4.12	1.77	3.89	4.76	1.54	3.38	4.14	2.17	4.77	5.83	1.79	3.94	4.81
$\dot{V}_{\mathrm{CH_4},B}\ (\times 10^8\ \mathrm{m^3\ yr^{-1}})$	3.10	6.81	8.33	3.58	7.87	9.62	3.11	6.84	8.36	4.39	9.65	11.84	3.62	7.96	9.73
$\dot{V}_{\mathrm{CH_4},C}\ (\times 10^9\ \mathrm{m^3\ yr^{-1}})$	0.47	1.03	1.25	0.54	1.18	1.45	0.47	1.03	1.26	0.66	1.45	1.78	0.55	1.20	1.47
	Spain														
$RSB\ (\times 10^6)$	0.75	1.45	1.62	0.75	1.45	1.61	0.86	1.63	1.81	0.77	1.49	1.65	0.67	1.30	1.44
$\dot{V}_{\mathrm{CH_4},A}\ (\times 10^7\ \mathrm{m^3\ yr^{-1}})$	1.76	3.87	4.73	1.75	3.86	4.71	1.98	4.34	5.30	1.80	3.96	4.84	1.57	3.46	4.23
$\dot{V}_{\mathrm{CH_4},B}\ (\times 10^7\ \mathrm{m^3\ yr^{-1}})$	3.56	7.82	9.56	3.55	7.79	9.53	3.99	8.78	10.70	3.65	8.01	9.79	3.18	6.99	8.54
$\dot{V}_{\mathrm{CH_4},C}\ (\times 10^8\ \mathrm{m^3\ yr^{-1}})$	0.54	1.18	1.44	0.53	1.17	1.43	0.60	1.32	1.61	0.55	1.21	1.47	0.48	1.05	1.29
	Thailand														
$RSB\ (\times 10^7)$	2.36	4.54	5.05	2.79	5.39	5.99	3.25	6.28	6.97	2.53	4.87	5.41	2.76	5.32	5.91
$\dot{V}_{\mathrm{CH_4},A}\ (\times 10^9\ \mathrm{m^3\ yr^{-1}})$	0.55	1.21	1.48	0.65	1.43	1.75	0.76	1.67	2.04	0.59	1.30	1.58	0.64	1.41	1.73
$\dot{V}_{\mathrm{CH_4},B}\ (\times 10^9\ \mathrm{m^3\ yr^{-1}})$	1.11	2.44	2.99	1.32	2.90	3.54	1.54	3.38	4.13	1.19	2.62	3.20	1.30	2.86	3.49
$\dot{V}_{\mathrm{CH_4},C}\ (\times 10^9\ \mathrm{m^3\ yr^{-1}})$	1.67	3.68	4.50	1.99	4.36	5.33	2.31	5.08	6.21	1.80	3.94	4.82	1.96	4.30	5.26
	U.S.A.														
$RSB\ (\times 10^7)$	0.79	1.52	1.69	0.92	1.78	1.97	1.01	1.94	2.15	0.80	1.53	1.70	0.94	1.81	2.02
$\dot{V}_{\mathrm{CH_4},A}\ (\times 10^8\ \mathrm{m^3\ yr^{-1}})$	1.84	4.05	4.95	2.15	4.73	5.78	2.35	5.16	6.30	1.86	4.08	4.99	2.20	4.83	5.90
$\dot{V}_{\mathrm{CH_4},B}\ (\times 10^9\ \mathrm{m^3\ yr^{-1}})$	0.37	0.82	1.00	0.44	0.96	1.17	0.48	1.04	1.27	0.48	0.83	1.01	0.44	0.98	1.19
$\dot{V}_{\mathrm{CH_4},C}\ (\times 10^9\ \mathrm{m^3\ yr^{-1}})$	0.561	1.23	1.51	0.66	1.44	1.76	0.72	1.57	1.92	0.57	1.24	1.52	0.67	1.47	1.80

[...] Table 4.26 - Continuation.

Quantity	**Year**														
	2000			**2005**			**2010**			**2015**			**2020**		
	Min.	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**	**Min.**	**Avg.**	**Max.**
	Vietnam														
RSB $(\times 10^7)$	2.97	5.72	6.35	3.27	6.30	7.00	3.65	7.03	7.82	4.11	7.93	8.81	3.90	7.52	8.35
$\dot{V}_{\mathrm{CH_4},A}$ $(\times 10^9\ \mathrm{m^3\ yr^{-1}})$	0.69	1.52	1.86	0.76	1.68	2.05	0.85	1.87	2.29	0.96	2.11	2.58	0.91	2.00	2.44
$\dot{V}_{\mathrm{CH_4},B}$ $(\times 10^9\ \mathrm{m^3\ yr^{-1}})$	1.40	3.08	3.76	1.54	3.39	4.14	1.72	3.78	4.62	1.94	4.26	5.21	1.84	4.04	4.94
$\dot{V}_{\mathrm{CH_4},C}$ $(\times 10^9\ \mathrm{m^3\ yr^{-1}})$	2.11	4.63	5.66	2.32	5.10	6.24	2.59	5.70	6.96	2.92	6.42	7.85	2.77	6.09	7.44

4.6 Considerations and Conclusions

Biofuels from renewable organic biomass could represent an interesting resource to decrease the use of fossil fuels and greenhouse gas emissions (particularly related to transportation) and to improve local economies [360]; the production of sustainable fuels has been estimated to eliminate the 68% of the global warming potential [324]. Recently, great effort has been put into research to establish biofuel production from not only second-generation biomass, but also third-generation biomass. In this context, straw or wood residues represent field residue [173].

Rice is the most important staple food, providing nutrition and calories for over half of the world's human population [23]. Consequently, rice straw could represent an ideal resource for biofuel production because it is a waste product of food production; consequently, it does not compete with food availability [477]. Indeed, in 2009, 915 Mt of rice straw were produced [324]; this amount represents great potential for bio-methane, biofuel, and bioplastic production. In some areas of the world, the surplus of rice straw is frequently removed from fields by open-field burning, which consequently increases environmental pollution, even if it is economically convenient for the farmer.

Thus, biofuel production from rice straw is a way to assign economic value to this residue, allowing farmers to use it in a more sustainable way. In this context, the rice straw barrel [65] could represent a metric for the financial market, analogous to a barrel of oil for fossil fuels.

Waste rice straw can be converted into biofuels by biological processes that use bacteria to convert the biomass into biofuel in anaerobic digestion conditions for methane production or fermentation of sugars for ethanol generation [324]. In particular, anaerobic digestion is a useful technology to treat animal and agro–industrial wastes and municipal sludge containing high organic content [319]. During anaerobic degradation of organic substrates, CO_2 and CH_4 are obtained as end products, with biomethane productivity depending on the reduced amount of organic carbon [378]. Among the variety of field residues available, rice straw presents an interesting capability for conversion into biomethane [369]. However, anaerobic digestion is conditioned by some constraints, as outlined in [290]:

- The high C/N ratio of rice straw: This is a favourable nutrient balance both for anaerobic bacteria and for maintaining a steady environment. The C/N ratio can be in the range of 20–30 for anaerobic digestion and methanogenesis, 16–45 for hydrolysis, and 20–30 for methanogenesis [24];

- The lignin, hemicellulose, and cellulose percentages of rice straw affect the microorganisms effects on the substrate;
- The volatile fatty acids, temperature, and the pH. Volatile fatty acids (acetic acid, propionic acid, butyric acid, valeric acid, lactic acid, and formic acid) represent the most crucial intermediaries produced in anaerobic digestion and affect its stability [290]. They are generated when acids produced from hydrolysis and acidification cannot be consumed by methanogenic bacteria (for example *Clostridium thermosuccinogenes* and *Clostridium cellulovorans* [324]), resulting in a pH decrease and process destabilisation [319]. Indeed, the pH range for anaerobic digestion is from 6.8–7.2, with 6.5–7.3 providing the best results, 7.0 required for methanogenesis [324], and hydrolysis and acidogenesis occurring in the range of 5.5–6.5 [434]. Temperature affects the reaction velocity, the transport phenomena (diffusion), and chemical dissociation. Acceptable temperature ranges for digestion by anaerobic microorganism are 10–20 °C for psychrophilic, 30–40 °C for mesophilic, and 50–60 °C for thermophilic microorganisms, with thermophilic conditions preferred to inactivate pathogenic populations [319];
- The quality of inoculum, the feedstock-to-inoculum ratio, and the organic loading rate;
- The pretreatment involved, mainly classified as: physical pretreatments (e.g., particle size reduction [324]), chemical pretreatments (e.g., alkaline pretreatment [90]), and biological pretreatments (e.g., fungal pretreatment [547]).

Thus, due to the complex organic structure of rice straw, it requires different catalytic activities by several enzymes to be broken down. The efficiency of cellulose degradation can be improved by symbiotic cooperation between cellulolytic and noncellulolytic bacteria [467]. In this context, it has been experimentally proven that microbial communities cultivated in mixtures of rice straw, chicken feces, pig feces, cattle feces, and sugar cane dregs are able to degrade more than 60% of the rice straw within four days [196]. The bacterium able to initiate degradation have been identified by polymerase chain reaction *Clostridium thermosuccinogenes*. It is a strict anaerobe that lives in manure, beet pulp, soil, and mud [324]. A synergist effect has been shown during the degradation of rice straw by *Clostridium cellulovorans* involving both cellulosome and non-cellulosome enzymes working under mesophilic conditions [467]. The result of this symbiotic cooperation is the degradation of the rice straw in around 10 days without any type of pretreatement [324].

In order to improve anaerobic digestion, novel two-stage digesters have been developed [90], such as a novel, continuous anaerobic digester that uses hyacinth water as feedstock [33]. Moreover, some analytical models have been developed to optimise and control the anaerobic digestion process [143].

Rice straw conversion into biofuels has a long history, dating back to the 1930s when Richards and Norman [390] analysed the factors influencing anaerobic decomposition of rice straw, and Acharya [2] improved the study of anaerobic decomposition of rice straw. However, the current growing interest in anaerobic rice straw digestion is driven by the requirements of a more efficient use of renewable energy sources in order to reduce greenhouse gas emissions and to mitigate climate change. Indeed, rice straw can be utilized to produce biofuels (e.g., a potential of 205 GL yr^{-1} of ethanol to replace 147 GL yr^{-1} of gasoline [324]) and bioplastics, but it requires pretreatment in order to alter the interactions of cellulose, hemicellulose, and lignin and to increase the accessibility of cellulose, to remove the lignin–carbohydrates complexes, and to reduce the cellulose crystallinity.

Lastly, it must be highlighted that the sustainable use of rice straw must also consider the needs of some countries where approximately 20% of the rice straw produced is already used for other purposes, such as the pulp and paper industry: this biomass can not be used for energy applications because of the social and economic needs of people in these countries. For example, in some Regions of rural China, out of a total of 740 Mt of rice straw in 2006, an estimated 47% was used for household cooking and heating [324]. When rice straw is stolen from these people, access to sustainable and affordable energy systems should be ensured for them.

Methanization of rice straw is considered one of the most environmentally friendly processes to convert this biomass into biofuels, as it reduces greenhouse gas emissions, mitigating climate change. Indeed, less energy input is required compared to other conversion or feedstock processes [324].

In this Chapter, the $THDI$ index has been applied to a specific case: the biomethane production from an abundant agricultural waste (rice straw). First, the number of rice straw barrels available from defined areas (the ones which present the highest rice production) has been evaluated. Then, the calculated the total annual biomethane yield for these areas by considering the specific biomethane yield potential in the range of 92–280 L kg_{VS}^{-1} (depending on different inocula, pretreatments, and working temperature) [324] .

For each straw barrel, depending on the specific biomethane yield, we obtained the following quantities: 23.36 m^3 ($VS = 73.8\%\ TS$, 92 L kg_{VS}^{-1}), 26.61 m^3 ($VS = 84.08\%\ TS$, 186 L kg_{VS}^{-1}), and 29.27 m^3 ($VS = 95.26\%\ TS$, 280 L kg_{VS}^{-1}). Moreover, equivalent carbon dioxide emissions can be reduced by approximately 754 kg for each *RSB* by substituting the current practice of burning rice straw in open fields with methanation *via* anaerobic digestion. In this context, the $THDI$ index was introduced in order to evaluate the effect on sustainability of converting rice straw into biomethane instead of its open-field burning for the major rice producing countries.

In this Chapter, biomethanation by anaerobic digestion has been considered as a sustainable alternative to burning rice straw on field. Thus, the related possible $CO_{2,eq}$ reduction has been analysed by considering the data summarised in [445, 256] together with the AR5 Global Warming Potentials (GWP). Then, the sustainability of the biomethanation was analysed by introducing the $THDI$ indicator. This index has been evaluated using Equations (3.53) and (3.52).

It should be pointed out that the countries considered presented different trends in carbon dioxide equivalent emissions, $CO_{2,eq}$, during the period 2000–2018, as shown in Figure 4.9. Indeed, if we consider the overall ratio $(CO_{2,eq\ 2018} - CO_{2,eq\ 2000})/CO_{2,eq\ 2000}$, the values are positive (increased emissions) for most developing countries, such as: Bangladesh +64%, China +175%, India +123%, Pakistan +86%, Thailand +61%, and Vietnam +477%, while it is negative (decreased emissions) for the following countries: Brazil −21%, Italy −21%, Spain −4%, and U.S.A. −10%.

On the other hand, all the countries improved their Life Expectancy Index (*LEI*), Income Index (*II*), and Educational Index (*EI*) during the time period considered, as shown in Table 4.27.

Thus, we calculated the $THDI$ (Equation (4.5)) in order to quantify the effect on sustainability of biomethanation by rice straw anaerobic digestion. The amount of rice straw considered in this analysis was the half of the total that was

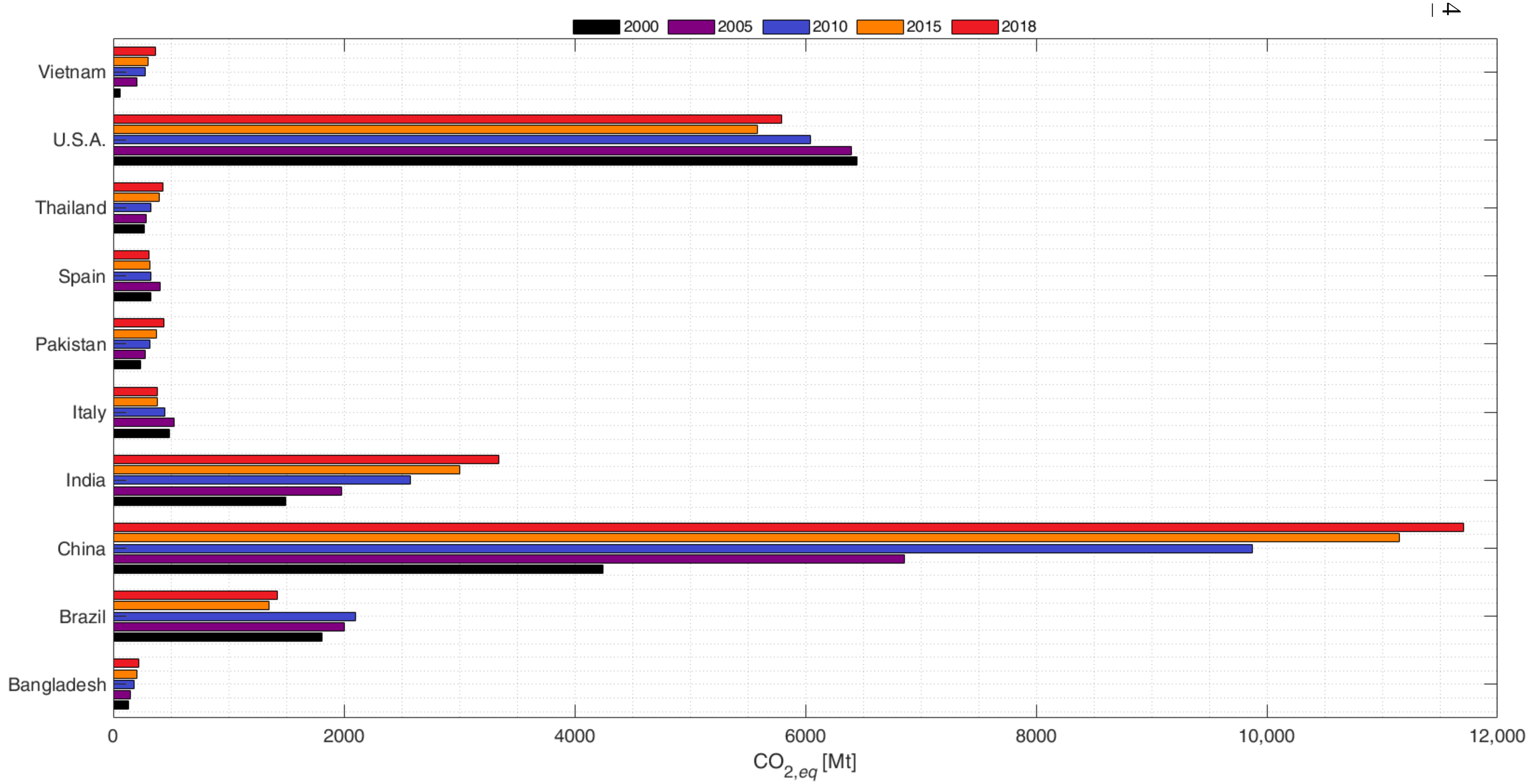

Figure 4.9 Carbon dioxide equivalent emissions $CO_{2,eq}$ [Mt] in Bangladesh, Brazil, China, India, Italy, Pakistan, Spain, Thailand, United States of America, and Vietnam from 2000 (bottom bar for each country) to 2018 (top bar for each country); data from [216].

Table 4.27 Variation of the indicators *LEI*, *II*, and *EI* during the period 2000–2018. The percentage variation was evaluated by $(I_{2018} - I_{2000})/I_{2000}$ [%].

Indicator	**Variation in the Period 2000–2018 [%]**									
I	**Bangladesh**	**Brazil**	**China**	**India**	**Italy**	**Pakistan**	**Spain**	**Thailand**	**USA**	**Vietnam**
LEI	38	21	16	31	12	18	11	14	7	10
II	43	7	89	46	3	15	7	22	7	56
EI	111	50	62	78	32	96	41	76	7	81

available in each country, which corresponds to the actually estimated amount of rice straw burned in open fields. In Figures 4.10–4.12, the ratio $(THDI_{rs} - THDI)/THDI$ is reported, considering, respectively, the previous k coefficient values (from Equation (4.2)) of 0.70, 1.35, and 1.50. $THDI$ was evaluated only in relation to the reduction in carbon dioxide equivalent emissions due to anaerobic digestion of rice straw; indeed, at first approximation, the socio–economic effect of biomethane production from anaerobic digestion of rice straw should result in income redistribution. Rice straw barrels represent a new source of income for farmers and a reduction in sales of fossil-fuel-derived methane. Consequently, in this introductory approach the income index is considered unchanged for all the continents.

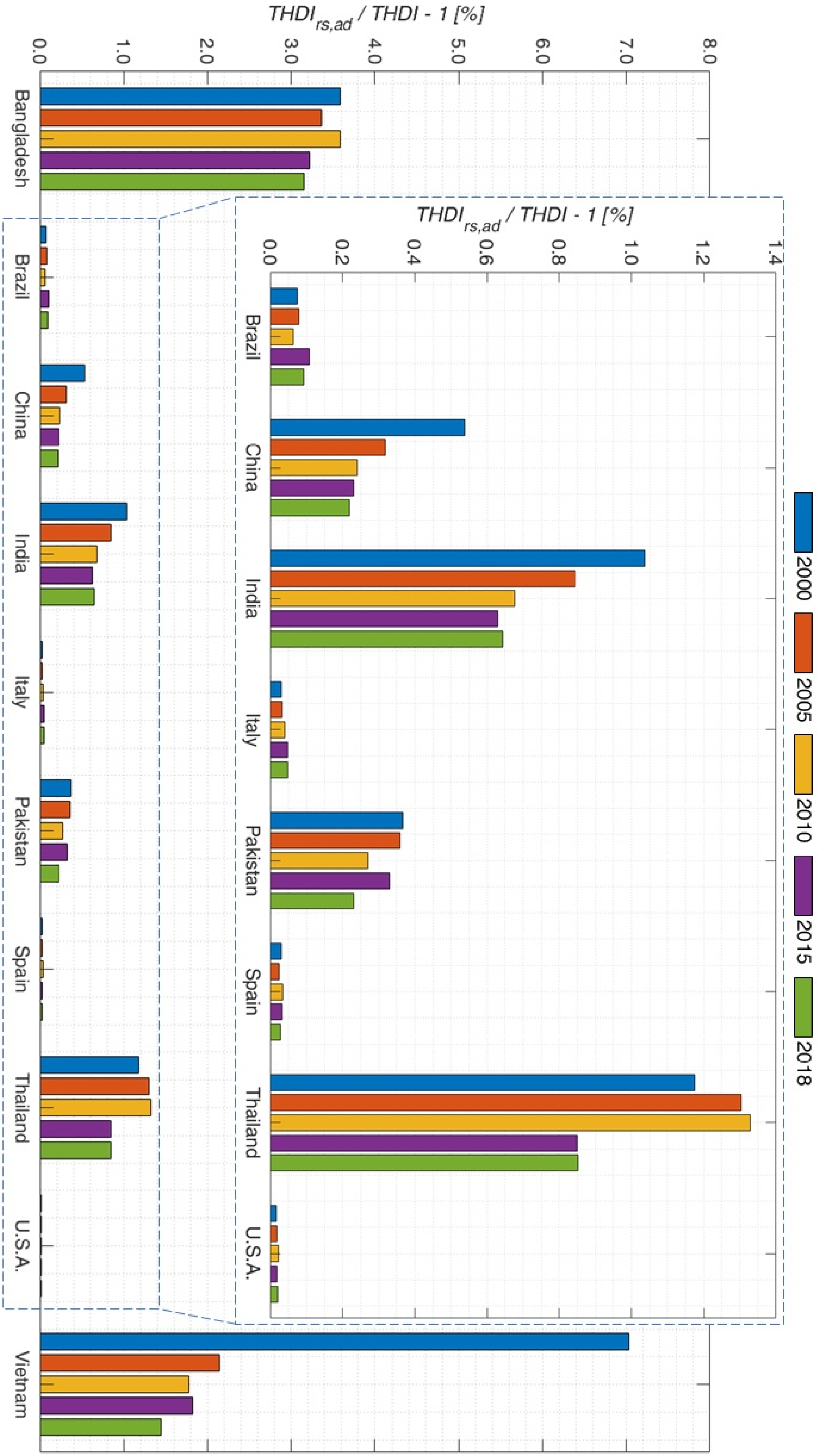

Figure 4.10 Yearly annual variation of the sustainability indicator *THDI* using Equation (4.5) to compare the current situation (50% of total rice straw burned on field) with anaerobic digestion of the same amount of rice straw to obtain biomethane using $k = 0.70$ in Equation (4.2).

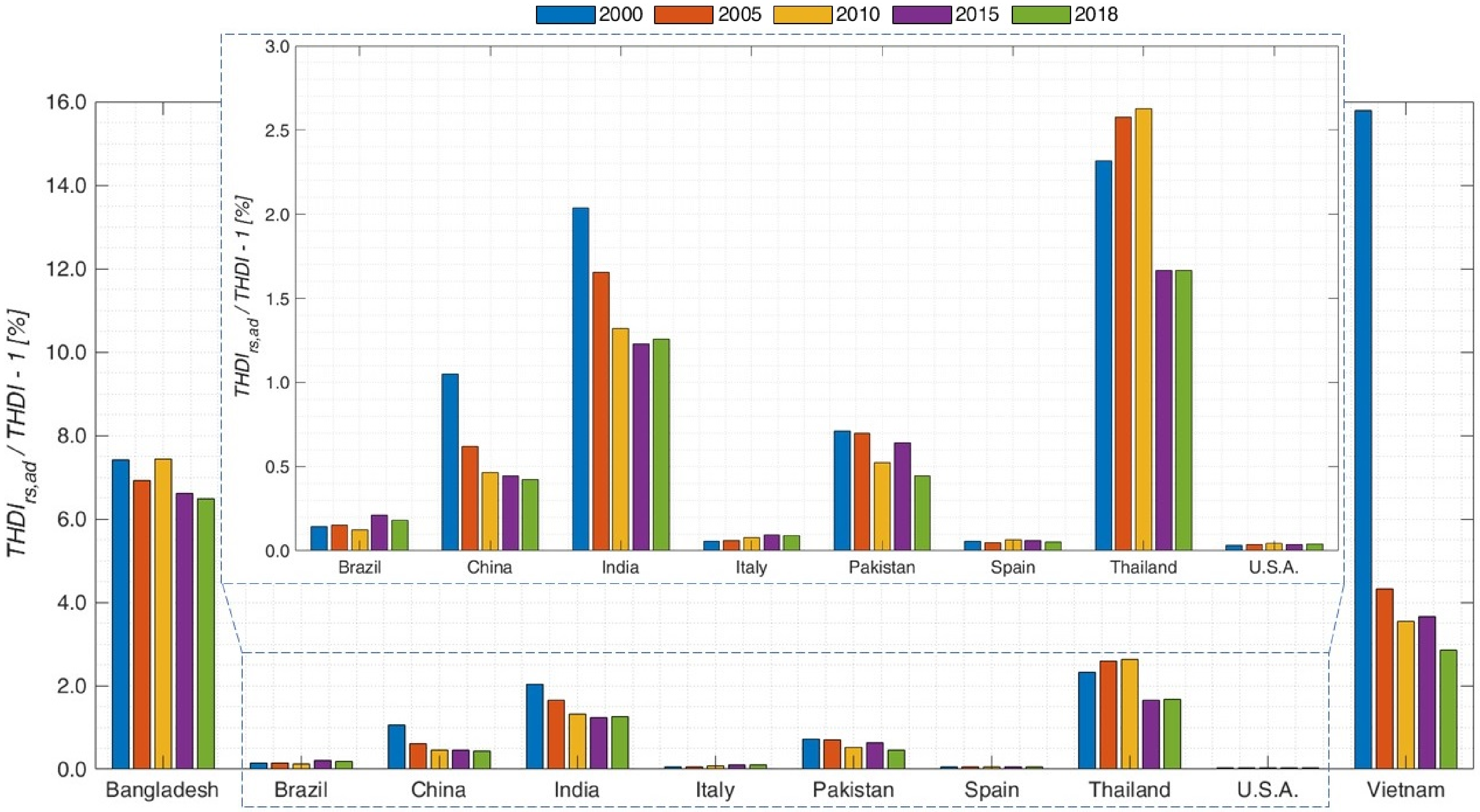

Figure 4.11 Yearly annual variation of the sustainability indicator *THDI* by using Equation (4.5) to compare the current situation (50% of total rice straw burned on field) with anaerobic digestion of the same amount of rice straw to obtain biomethane, using $k = 1.35$ in Equation (4.2).

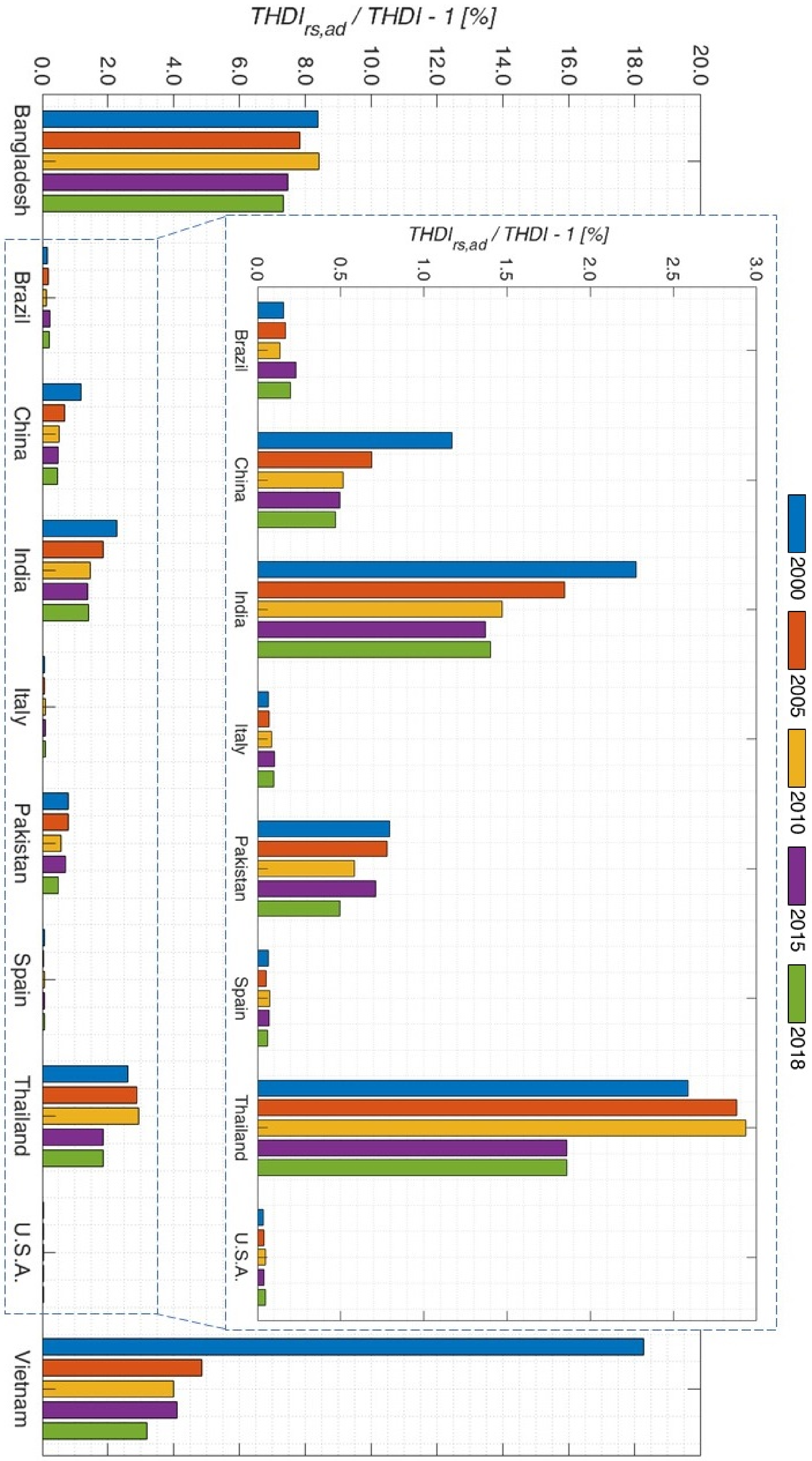

Figure 4.12 Yearly annual variation of the sustainability indicator *THDI* by using Equation (4.5) to compare the current situation (50% of total rice straw burned on field) with anaerobic digestion of the same amount of rice straw to obtain biomethane, using $k = 1.50$ in Equation (4.2).

A more detailed analysis requires designing the biomethane production chain, which can be developed by a local techno-economic analysis because agricultural processes are different across continents and are locally dependent. For instance, in Italy, biomethane production from agricultural and zootechnic wastes has been estimated to have generated approximately 12,000 new jobs through the year 2019 [111].

The results highlight how the use of rice straw could be very interesting from a sustainable viewpoint, specially from the environmental viewpoint, but also from the socio-economic one. However, at the moment we are unable to estimate the economic value of rice straw barrels, due to the cost fluctuations in the energy market. This could be the next step, but it must be based on local energy market constraints and legislation.

Conclusions and Future Perspectives

The aim of this PhD Thesis has been to introduce an irreversible thermodynamic approach to improve the biomass formation for biofuels production from micro-organisms, in the context of sustainable development and on the measure of sustainability itself.

In order to develop the analysis, some items have been identified as fundamental topics. The first is the introduction of a thermodynamic approach for the comprehension of the thermo-physical mechanisms of the micro-organisms interaction with their environment, considering the micro-organisms themselves as the fundamental unit of a biorefinery. Then, the need to improve the measure of sustainable development emerges in relation to link its socio-economic to environmental pillars. So, the conditions for the improvement of the biomass formation must be pointed out in the context of the biofuels production. Last, in order to highlight the energy use of the previous results, the valorisation of a field residue must be studied in relation to biofuel production.

To achieve all these aims, the thermodynamics of non-equilibrium has been introduced, obtaining the following results:

- A thermodynamic model of analysis of heat and mass transport through membrane in micro-organisms, with related application to their metabolic and biochemical activities;
- A new index, the Thermodynamic Human Development Index, for the analysis of sustainable development, with the result of linking the socio-economic to the technical and environmental pillars;
- The improvements of the UN's index related to Education, by introducing the $OECD-PISA$ results;

- Mutualism as a mean of improvement of the biomass formation by microorganisms for the biofuels production;
- Some results on the valorisation of the rice straw from field residue to energy resource, in the context of bio-methane production from anaerobic digestion.

All the aim of the PhD Thesis have been achieved, with related some applications and validation of the models obtained, both in the thermodynamic analyses of microorganisms behaviour and in the introduction of a new indicator of sustainability. These two aspects have been merged together by considering the valorisation of the rice straw by means of anaerobic digestion, giving a second life to a waste in energy terms.

Furthermore, some aspects could further be improved in future developments. First, in the thermodynamic model of mutualism, some experimental activities could be carried out in bioreactors in order to obtain information in relation to the chemical physical conditions (temperature constrain, pH effect, molecules positive and negative effects, pressure constrain, etc.). Moreover, in relation to $THDI$, some pillars could be improved, with particular regards to the well-being conditions in different countries in relation to the Life Expectancy link to health care systems, quality of air and access to water. Last, as concerns the rice straw use in energy sector, a pilot plant could be built in order to verify the results theoretically obtained.

In summary, in this PhD Thesis, the fundamental role of thermodynamics emerges in relation to the systems analyses, both in biophysics, and in bioeconomics, but also in the engineering approach to the valorisation of wastes. In particular, thermodynamics appears as a powerful tool to improve the present approaches to sustainable development. In this context, irreversibility emerges as a natural constrain, as just shown in the Second Law, which must always taken into account in any approach towards the improvement of the systems. Irreversibility represents the limit and the constrain of the optimisation approach, but the possibility of their evaluation in thermodynamics represents also the support to point out the effective approach to achieve environmental aims. In this context, the field residues are shown to represent a possible future development as an energy resources, but also in the socio-economic context to improve the well-being of different societies in different countries.

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