Exergy and exergy cost analysis of biochemical networks in living systems far from equilibrium

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ABSTRACT

Whilst humanity has reached a high level of technological development, finding efficient substitutes to petroleum energy is a challenging task. In this context, metabolically engineered microorganisms are used in biomass production. Considering the availability of data in genomic and metabolic fronts, Escherichia.Coli is one of the primary options for biofuel production, which could be later exploited as a 'solo' energy source, or coupled with nowadays available fuels. To survive, an organism must provide an amount of exergy greater than the exergy required to process equilibrium operations. Therefore, extra exergy amounts are needed for a living system to accomplish production, growth and evolution in time, as the above mentioned process is highly irreversible. This paper reviews the available studies on exergy analysis and exergy-cost theory-ECT application, along with the use of flux balance analysis-FBA and flux variability analysis-FVA, as a tool for gaining biological insights. The paper is structured as the following; first, a brief description of exergy analysis and the exergy-cost theory is presented. Second, the exergy analysis application on living cells is discussed through introducing exergy analysis of metabolic networks. Thirdly, the application on E.Coli is explained, highlighting its potential role in biofuel production. Finally, an approach, applied within a current PhD research project regarding the application of the exergy analysis to a generic metabolic network is introduced. In this approach, the exergy costs associated with all the flows present in the targeted network are calculated, according to the ECT. The perspective is to use the exergy cost information for defining additional constraints in the FBA of the metabolic network. Which could provide better insight about organisms and identify directions for the optimization of biomass production, and the enhancement of biofuel use.

CCS CONCEPTS

• **Css concept: Applied computing** → Life and medical sciences; Bioinformatics..

KEYWORDS

biofuel, exergy analysis, exergy cost theory, Escherichia.Coli, metabolic engineering, Research and application on bioinformatics

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1 INTRODUCTION

Since the industrial revolution, the world has been witnessing a constant, tremendous increase in the energy demand, in all sectoral levels. With this need for energy production, our understanding and awareness of fossil fuel use and the environmental challenges and threats to the accomplishment of the global reduction objectives for 2050 has been raised.

Using exergy analysis and exergy-cost theory [1] as a way to investigate the processes inefficiencies, along with combining different scientific fields such as energy engineering, marine biology and bioinformatics is likely to be an efficient way to create a suitable approach in order to study the network of a living cell from an "exergetic" point of view. Moreover, it is quite necessary to highlight that the mentioned approach aims to develop a source of understanding of certain microorganism's biological systems and their metabolism resulting in the availability of a wider picture of the targeted microorganism. Using exergy and exergy-analysis, in addition to flux variability analysis-FVA and Flux Balance Analysis-FBA, as an approach, to assess the metabolic network of the targeted living microorganism, or of a bacterial community, and a way to analyze it as a potential biofuel product.

In fact, exergy analysis applications are becoming more and more familiar among the industrial sector. One of the most common uses of the above mentioned one is the detection of the existing efficiency in an industrial process. In this sense, coupling exergy analysis along with environmental theories is spreading among the scientific research communities around worldwide. It is in this context that a theoretical approach is proposed through gathering the following concepts; exergy analysis and bioinformatics, along with renewable energy. The above mentioned method could be a promising tool to contribute to the sustainability scenarios related to renewable energy technologies, fulfilling the 40% renewables target set by the European Union for 2030.

One of the renewable technologies that is being explored and enhanced is biofuel production, which plays a major role in reducing the dependency on fossil fuels and in moving forward with the climate change mitigation scenario.

Global biofuels demand is still expected to increase by 5%, with a further expectation to rise by 3% more, by 2023. Transport fuel demand growth, although at a slower pace, and government policies continue to drive demand higher for global biofuels [2].

Metabolic engineering is a key factor in enhancing this technology by providing a biomanufacturing platform for biofuel industry, which consists in aiding the scientific communities to go further in this research field, and to contribute to fulfilling the sustainable use of renewables, in order to assure an environmentally friendly development of mankind.

The remainder of the paper is structured as follows. In the first Section, exergy analysis and exergy-cost theory are introduced, the second section is regarding the exergy analysis of living organisms, and its application on living cells. The following part of this paper discusses the potential use of E.Coli as a biofuel product, taking into consideration the advantages and the challenges of the mentioned process. Through the next sections, an approach regarding the application of exergy analysis to the metabolic network of living cells is presented and discussed, the discussion takes into consideration the chemical presentation of the biological reactions of the living system as a tool in the analysis of its metabolic pathways.

2 EXERGY ANALYSIS AND EXERGY-COST THEORY

Exergy analysis is a concept that is not yet widely applied in the industrial sector, which focuses on the quality of the different sort of energy in a system.

By definition, it is the optimal work performed while bringing a system into equilibrium with an environment (which is the maximum work for power production and minimum work for bringing a low pressure system into equilibrium with an environment) [3]. It is regarded as a tool for an efficient analysis and assessment of the energy losses to the environmental and internal irreversibility in an industrial process. In fact, exergy-based indicators have proven to be more efficient than energy-based measures in resolving such issues. In this context, the exergy approach tends to be a rigorous engineering accounting technique in contrast to 'emergy' and to LCA applied methods.

Simply, exergy can be defined as the upper limit of a given kind of energy or material to produce useful work as it comes to complete equilibrium with the reference environment; this upper limit is achieved through reversible processes. Therefore, the amount of thermodynamic irreversibility of an engineering process is revealed by exergy analysis and is closely related to its resource depletion, revealing its degree of sustainability. Furthermore, various authors state that there is a direct association between economic value and exergy.

Although the biofuel industry targets, at least partially, the energetic and the environmental issues, its activities utilize matter, energy and also generates wastes, potentially affecting the environment and human health. Hence, careful and serious consideration of the environmental sustainability aspects of this industry is necessary.

3 EXERGY ANALYSIS OF LIVING ORGANISMS

Since the last decades, scientists have been witnessing a noticeable flow of Data in diverse scientific fields, which has led to a significant development in the research field on diverse levels. This Data flow has contributed to the advancement of a lot of scientific fields, including Biology, resulting in several discoveries and novelties of all levels. Although the up-named field is in continuous development, it has been facing critical challenges regarding its ability to obtain biological insights to provide a better understanding of the microorganism metabolic system.

Energy is a key factor occurring in the entire universe, providing life, and assuring the continuity of all processes. For all enhanced and adapted systems in biology, an exact amount of useful energy goes through the process of extraction, conversion and storage, to be used in different energy driving processes. The above described process is known as bioenergetics, which consists of the energy management within a living cell. On the other hand, the useful amount of energy is known as exergy, which according to thermodynamics, is destroyed in all irreversible processes due to the entropy production [4].

Exergy analysis is based on the two first laws of thermodynamics. It is a good indicator of energy degradation's location in a process. Furthermore, Exergy analysis methods can be applied to detect the processes inefficiencies [5]. In this context, aiming to develop the interconnection between the environmental and the exergetic theory, renewable technologies and exergy efficiency are suggested, in order to make concrete contribution to sustainability on many levels.

Exergy is not generally conserved but is destroyed. A limiting case is when exergy would be completely destroyed [6], as would occur if a system were to come into equilibrium with the environment spontaneously with no provision to obtain work. As a matter of fact, it is an applied tool utilized in metabolic engineering for the assessment of the energy conversion quality processes in living cells [7], as revealing thermodynamic loss is a major goal when using exergy analysis approach.

In order to provide the dissipated energy by heat exchange, the system must convert a certain amount of exergy. The exergy of a system is defined as the maximum work that could be accomplished by the composite of a system in addition to a specified reference environment (which is considered as infinite, in equilibrium, and ultimately to enclose all other systems, the environment is determined through temperature, pressure and chemical composition) [9]. Therefore, when introducing exergy, it is essential to mention that it is not simply a thermodynamic property, but rather it is linked to the reference environment.

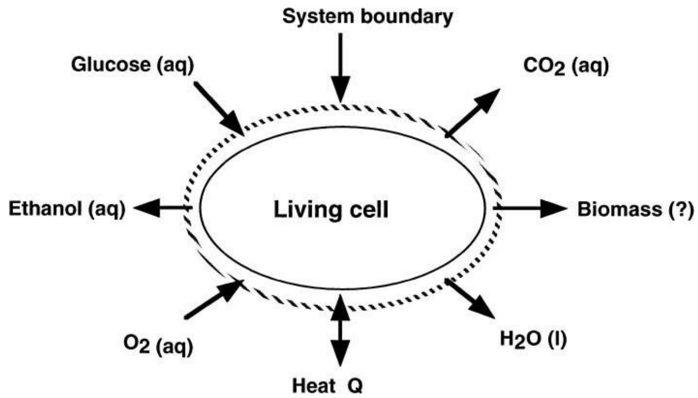

Figure 1: Living cell as an open system

Exergy in living cells is treated in a different way, chemical exergy and exergy of mixing have the big share of contribution to the whole intercellular compounds. As the chemical exergy refers to the chemical bonds of the compounds, and the mixing energy refers to the different interactions that may occur with other compounds. it is necessary to mention that the chemical exergy is more important than the physical exergy when performing the exergy analysis. The exergy of biochemical compounds, at biochemical standard conditions [8] [9], could be calculated as the following:

$$E^{0^F}_{x_{compound}} = \sum_i \nu_i E_{x_{Element,\ i}} + \Delta_f G^{0^F}_{compound} \tag{1}$$

Where$E^0_{x\ Element,\ i}$ is the exergy of element in standard chemical conditions, $\nu_i$is its stoichiometric number, $\Delta_f G^{0^F}_{\text{compound}}$ refers to the Gibbs energy of formation of the compound, in biochemical standard conditions.

As the exergy at biochemical standard conditions is approximately poor compared to the exergy in real intracellular condition [8], additional terms such as ionic dissociation, compound concentration in the environment, metallic formation, electrical potential, etc.. have to be added to the above mentioned equation for more consideration of the real state of the living system and its interaction with the environment.

4 EXERGY ANALYSIS APPLICATIONS ON LIVING CELLS

As exergy analysis is based on the two first laws of thermodynamics, it is a good indicator of energy degradation's locations in a process. It is proposed and lifted to study the industrial sector [5].

Biochemically speaking, exergy transfer is usually achieved through transferring chemical groups, thermodynamically activated, from one group to another. [Figure 1]

Analyzing biological reactions could be performed through a chemical representation, where electrical charges of each compound are taken into account, and a biochemical representation, where all biochemical compounds are considered neutral, when performing the calculation.[10]

5 ESCHERICHIA.COLI FOR POTENTIAL BIOETHANOL PRODUCTION

In order to accomplish the upcoming targets of the European Union for a zero emission net, it is necessary to enhance the renewable technologies present nowadays, and the ones to develop to be in the market for the coming years. One of the most important renewable technologies is the biofuel or biomass production. The latest mentioned one could be extracted from different bio resources, living bacteria is one of the above mentioned ones, and in this research paper, we will be targeting the Escherichia.Coli along with bacterial communities. Research has been conducted to describe the process of extracting biomass from E.Coli through a biological process called microbial fermentation, which consists of ethanol production [12].

Biofuels are essential to reduce dependency on fossil fuels and in mitigating impending climate crisis. [13] Rapidly evolving field of metabolic engineering is providing a biomanufacturing platform for the biomass industry and is a sort of forward to sustainable enhancement. Success milestones in creating innovative biofuel bugs have been achieved through metabolic engineering of microbes. Socioeconomic and environmental impacts of biofuels are recognized worldwide, resulting in formation and development towards circular economy. Bioprospecting novel pathways will contribute for the future advances in this domain [14].

In the last decades, the rapid development in both, the metabolic engineering and the synthetic biology fields for microorganisms such as bacteria, algae, etc.. provides a tremendous scope for the use of such techniques and approaches in engineering the microbes for higher production of various fuel molecules.

Ethanol has the dominant share in the biofuel industry [15]. Despite the limitations that the above mentioned presents such as corrosiveness and low energy, it is commercially presented as a biofuel source.

As a bacteria, E.Coli is capable of converting sugars into ethanol through hetero-fermentive process, it is one the primary options of biomass production. In fact, sugar is the alimentary source for bacteria, the process consists in converting it to adenosine triphosphate (ATP), and through a fermentation process, energy carriers are converted into biofuel products. More specifically, under anaerobic conditions, pyruvate is converted into acetyl-CoA and formate lyase [12]. Escherichia.Coli can endogenously produce ethanol through a process where "one mole of glucose is metabolized into two moles of formate, two moles of acetate, and one of ethanol".

Metabolic engineering provides important tools for engineering non-native organisms to produce a broad class of fuel grade molecules. Although further improvement of production is required, advanced biofuels offer significant advances over the traditional biofuel, ethanol. In order to make these applicable from an economic point of view, yield titer and productivity need to be further improved. In this context, continued enhancement of the experimental and computational methods for pathways and strain optimization is important to achieve high- efficiency production.

E.Coli cells have the ability of harboring more than four thousand genes, hundreds of metabolic pathways, and thousands of metabolites. It can ferment glucose into a wide range of short-chain alcohols. Despite the ability of ethanol to blend with gasoline, other alcohols have inherent advantages as transportation fuels. Escherichia.Coli has proven to be efficient in producing highly deoxygenated or even fully deoxygenated hydrocarbons via fatty acid or isoprenoid biosynthetic pathways.

6 EXERGY ANALYSIS OF LIVING ORGANISMS: THEORETICAL APPROACH

Through this research work, we aim to reveal and to discuss a suggested approach, explained theoretically, which consists in applying the constructal principles, introduced by A.Bejan in 1996, along with exergy-cost theory and the exergy analysis approach, in order to fulfill the analysis and assessment of the metabolic network of a targeted microorganism, or a living cell community such as bacteria, in our case of investigation work.

In fact, the goal of thermoeconomic analysis to reduce the unit exergy cost of the products, can be inferred from the Constructal Law if the energy system is described in thermoeconomic terms and the current that flow through it is identified with the flow of its useful product [16]. This support the option of regarding exergy cost- based constraints more effective than other ones, based on arbitrary “thermodynamic cost” definition [17].

Escherichia.Coli has been selected as a targeted organism, to study its potential ability of producing biomass. Thus, enhancing the knowledge about such bacteria, could help in optimizing biomass production procedure through the intervention in the glycolysis pathway, for instance, the development of the ATP production.

In fact, Escherichia.Coli is being explored extensively thanks to their high ability of biofuel production due to the presence of good established tools for genetic modification [18], well investigated growth metabolism, not to mention their high rate presence in various industrial applications. It has been subjected as the model sources. To enhance the knowledge regarding their metabolic network, taking into account one of the major goals of these investigation, which is the enhancement of biofuel production for a more reliable share of commercial biofuel. E.Coli represents a suitable candidate when it comes to biomass production, thanks to the availability of data about this bacteria.

Organism in terms of gene regulation and expression, and also as an organism with the largest molecular tools available for genetic engineering.

A brief description of the approach is presented through the following diagram, which consists of the application of Flux balance analysis and flux variability analysis, along with the exergy analysis, aiming to determine the exergy values of the involved biochemical compounds of the targeted metabolism, later on, and by the application of the exergy-cost theory, the exergetic cost of the product, which is in this case the biomass, is determined. [Figure 2]

In order to optimize the biomass production process, it is crucial to reformulate the constraints, adding other constraints related to the exergy cost of the product ECP (biomass), when performing the flux balance analysis of the metabolic network. The minimum exergy cost of the product is expected to be more realistic than the maximum biomass production or the minimum resource consumption.

7 CONCLUSION

Since the last decade, renewable energy technologies has been moving towards an urgent need. Biofuels is one of the most relevant renewable technologies. The share of bio-ethanol, biodiesel, along with other sorts of biomass products is getting higher as substitutes to fossil fuels thanks to their long-term availability as an energy source.

Through the use of the proposed approach, the expectation is to improve its metabolic network, and yet, to optimize the biomass production process. In addition, performing these analysis will help in obtaining wider insights about the target living organism. The use of exergy-cost analysis could be a key factor in this case, as it could help to develop these applications though giving a clear idea about the chosen biological system.

During times where the threat of irreversible environmental damage looms, cleaner energy may simply not be enough, and so the future of biofuels remains uncertain.

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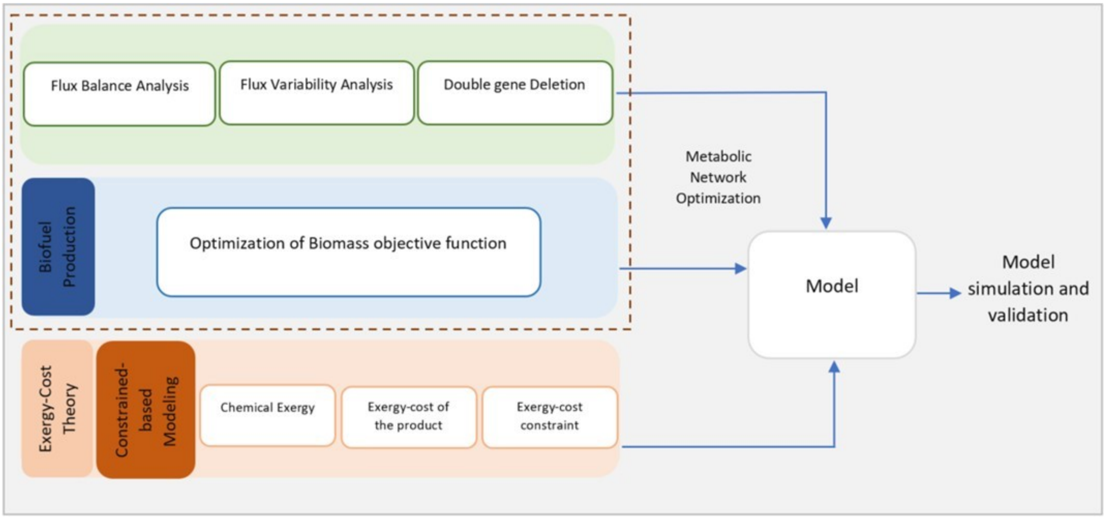

Figure 2: Application of exergy analysis and exergy cost theory to a living organism: Theoretical approach

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