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Evaluation of alternatives for microalgae oil extraction based on exergy analysis

Y. Peralta-Ruiz, A.-D. González-Delgado, V. Kafarov *

Research Center for Sustainable Development in Industry and Energy, Department of Chemical Engineering, Industrial University of Santander, Colombia

HIGHLIGHTS

- ▶ Exergy analysis was used as decision-making tool for evaluation of microalgae oil extraction.
- ▶ A robust composition of *Chlorella* sp. biomass was modeled and used for simulation.
- ▶ Three solvent-based microalgae oil extraction methods at large scale were compared.
- ▶ Hexane based extraction presented the highest exergetic efficiency.

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ABSTRACT

Several technologies for microalgae oil extraction are being evaluated in order to find the most adequate for large scale microalgae processing. In this work, exergy analysis was used as an instrument for screening three design alternatives for microalgae oil extraction in a large-scale process and as a decision-making tool for evaluation and selection of novel technologies from the energy point of view. Routes were simulated using dedicated industrial process simulation software, taking as feedstock a representative and robust modeled composition of *Chlorella* sp. microalgae biomass. Mass, energy and exergy balances were performed for each alternative, and physical and chemical exergies of streams and all specific microalgae constituents modeled were calculated with the help of the thermodynamic properties of biomass components and operating conditions of streams.

Exergetic efficiencies, total process irreversibilities, energy consumption and exergy destruction were calculated for all solvent-based microalgae oil extraction pathways evaluated. It was shown that exergy analysis led to identify the hexane-based oil extraction (HBE) as the most adequate alternative of the routes assessed for scaling up from the energy point of view, presenting a maximum exergy efficiency of 51% and exergetic losses of 982,000 MJ considering a production of 104,000 t of microalgae oil per year.

1. Introduction

Nowadays, the continued use of fossil-derived fuels is recognized as unsustainable due to the exhaustion of supplies and their contribution to environmental pollution. This kind of fuels has to be replaced with clean and renewable energy. In response to this issue, environmental policies worldwide have favored the increase in research, development and the use of biofuels, mainly those that can replace fossil fuels used in transportation. Biofuels offer many benefits associated with energy security, economic stability and reduction of the environmental impact of greenhouse gases [1].

Third-generation biofuels are derived from microorganisms, such as yeast, fungi and microalgae, some of these microbes can biosynthesize and accumulate large amounts of lipids and/or sugars [2], fungi like *Trichosporon fermentans* have been studied for microbial oil production and biodiesel preparation [3,4], however, the most attractive source for third generation biofuels production are microalgae. They have recently been rediscovered as promising candidates for biotechnological applications and efficient energy production systems [5]. Depending on the strain, microalgae can grow in a wide range of temperatures, pH and nutrients availability. They have a growth rate between 20 and 30 times higher than other sources for biofuels, some microalgae species have the ability to produce up to 20 times more oil per unit area than palm [6], oil content of certain strains in some cases exceeds 80% in dry weight biomass under appropriate conditions [7]. Microalgae can grow in warm, tropical, and subtropical climates, for biomass production it only requires water, some nutrients, a carbon source and a high and constant sun irradiance. Microalgae can be cultivated in photobioreactors which offer high biomass productivities and an adaptable illumination, open ponds which can be natural systems

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* Corresponding author. Address: Research Center for Sustainable Development in Industry and Energy, Department of Chemical Engineering, Industrial University of Santander, K 27 Cll 9 Bucaramanga, Colombia. Tel.: +57 7 6344000x2603.

E-mail address: Kafarov@uis.edu.co (V. Kafarov).

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(e.g. lagoons and lakes) or artificial systems (e.g. stirred tanks and raceway ponds) which require low energy consumption and are easy to maintain. This condition makes feasible the use of non-arable lands for photobioreactor assembly or open pond building. Microalgae can also be cultivated using as culture media waste water or sea water. Due to its high growth rate, microalgae biomass can be harvested 365 days per year. Taking into account the issues mentioned above, microalgae presents a theoretical potential to become a viable alternative to replace petroleum-based liquid fuels in the future without the disadvantages associated with food vs. fuel discussion and use of land, showing a prospective of a continuous biofuel production chain as occurs in traditional oil refineries. However, to make this possible, it is important to improve technical, environmental and economic aspects such as water requirements, production costs, environmental impacts and process efficiency, among others [1].

However, biodiesel-from-microalgae production chain is still away from sustainability by several factors, in energy terms, Khoo et al. [8], presented a comparison of energy and environmental performance of biodiesel from microalgae case studies previously developed by several authors referenced in the paper, with two additional cases proposed by the authors mentioned, using the methodology of Life Cycle Assessment (LCA) including energy and CO_2 balance, in which, for all systems analyzed, the comparison of life cycle energy demands in MJ per MJ of biodiesel are positive, even if energy requirements of lipid extraction and biodiesel production are not included as occurs in two of compared cases. Total energy inputs for the system proposed by authors were calculated in 85% for lipid extraction, 13% for biomass production and 2% for transesterification, concluding that main bottleneck lie in high energy requirements for lipid extraction and pointing out this issue as a main challenge to overcome in order to make biodiesel from microalgae production chain feasible and practical. These results show the necessity of future studies related to microalgae lipid extraction in order to improve this process in terms of efficiency, purity of product, energy requirements, costs and environmental impacts.

Studies about microalgae oil extraction for biodiesel production are taking significance because the efficiency of biodiesel production chain from microalgae depends in a great way on the oil extraction efficiency. There are several oil extraction methods which have been used on microalgae, these methods can be divided in:

- Methods assisted by mechanical disruption which uses cell homogenizers, ball mills, pressing systems, among others; these methods are not suitable for a lab-scale oil extraction because presents high biomass losses and low selectivity to lipids.
- Enzyme-assisted extraction methods, where microalgae cell wall is degraded by enzymes allowing lipids release, however, enzymatic activity is affected by several variables including concentration and ratio of system compounds, fatty acid profile, microalgae composition, temperature, among others. These issues make this route hard to maintain in this moment for a large scale biomass processing.

Other methods evaluated on microalgae are ultrasound-assisted extraction, microwave-assisted extraction, supercritical fluid extraction, autoclave and solvent based extractions [9].

A wide variety of organic solvents are often used to extract oil from microalgae, where hexane and ethanol are the most popular. However, ethanol is a polar solvent and its selectivity to lipids is relatively low compared to other solvents, so in extractions with ethanol, other microalgae components may also appear, such as sugars, pigments or aminoacids. Using a mixture hexane-ethanol, around of 80% of fatty acids presents into biomass can be extracted [10]. Solvent based lipid extraction methods as Folch, and Bligh and Dyer's method which uses a methanol–chloroform mixture have been tested successfully in oil extraction from microalgae [11], although this method is not very environmentally friendly due to the toxicity of the solvents used. Ethers present the disadvantage of high volatility, this increase solvent losses at long extraction times. Hexane is frequently used for soxhlet extraction using microalgae biomass as raw material [12], hexane is cheaper than other non-polar solvents like cyclohexane, which is easy to recover after extraction and it is selective to neutral lipids. In addition, it can be used in mixture with isopropanol [13], which is considered safe in an industrial scale and is used for lipid extraction from soybean.

2. Exergy analysis

Thermodynamic techniques like energy analysis, exergy analysis, emergy analysis, among others have been widely used for evaluation of industrial systems and thermal energy storage processes [14–17]. Energy analysis includes balances based on the first law of thermodynamics, and calculation of energy efficiencies for the steps studied. However, an energy balance neither offers information related with the energy degradation nor quantifies the usefulness or quality of the mass and energy streams of the system evaluated. Exergy analysis is presented as an alternative which overcomes the limitations of the first law of thermodynamics. Exergy analysis shows the sites of energy degradation in a process and can help to improve a unitary operation, a technology or a process [18]. In addition, exergy analysis allows to evaluate and select different alternatives to improve the design of a process, which makes it an appropriate tool for evaluation of novel technologies for advanced biofuels production.

The term exergy can be defined as the maximum theoretical useful work that could be obtained from a system that interacts only with the environment if this has not reached the thermodynamic equilibrium [19], taking into account that, the exergy of a system depends on the reference state selected, for this reason, a good choice of reference state must be made in order to avoid erroneous results.

For a general steady state, steady-flow process, four balance equations must be applied in order to find the work and heat interactions. These equations are the principle of mass/matter conservation given by Eq. (1), the first law of thermodynamics given by Eq. (2), the second law of thermodynamics given by Eq. (3), and the global exergy balance given by Eq. (4).

$$\Sigma_i(\dot{m}_\imath)_{in} = \Sigma_i(\dot{m}_\imath)_{out} \tag{1}$$

$$\Sigma_i(\dot{m}_\imath * h_i)_{in} = \Sigma_i(\dot{m}_\imath * h_i)_{out} + \dot{Q} - \dot{W} = 0 \tag{2}$$

$$\Sigma_i(\dot{m}_\imath * s_i)_{in} = \Sigma_i(\dot{m}_\imath * s_i)_{out} + \Sigma_i \frac{\dot{Q}_\imath}{T_i} = \dot{S}_{gen_i} \tag{3}$$

$$\dot{E}x_{mass,in} - \dot{E}x_{mass,out} + \dot{E}x_{heat} - \dot{E}x_{work} = \dot{E}x_{loss} \tag{4}$$

Mass exergy component expressed as is shown in Eq. (5), is divided into four specific components: the physical exergy ($\dot{E}x_{phy}$) related to temperature, enthalpy and entropy given by Eq. (6); chemical exergy ($\dot{E}x_{chem}$) related to the chemical exergy of each compound per mol (Ex^o_{ch}); potential exergy, $\dot{E}x_{pot}$ and kinetic exergy, $\dot{E}x_{kin}$. The calculation of the chemical exergy of each compound per mol (Ex^o_{ch}) is given by Eq. (7), and is a function of the chemical exergy of each elemental compound ($Ex^o_{ch,elem}$), the number of atoms of each element contained into the stream (n_{elem}) and the Gibbs free energy of formation for the compound (ΔG^o_f) [20]. The