



Opportunities for switchable solvents for lipid extraction from wet algal biomass: An energy evaluation



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ABSTRACT

Algae are considered an important sustainable feedstock for lipid extraction to produce food ingredients, cosmetics, pharmaceutical products and biofuels. Next to the costs for cultivation, this route is especially hindered by the energy intensity of drying algae prior to extraction and solvent recovery afterwards. Most commonly used lipid extraction methods that can be applied on wet algae biomass were reviewed in this paper. In this work the methods for wet extraction of algae lipids using traditional organic solvents, supercritical CO₂ and CO₂ switchable solvents are compared with dry extraction on an energy consumption basis. Conceptual process designs have been made to calculate and compare the energy flows. Results show that a significant positive energy balance for lipid extraction is only achieved using a switchable solvent extraction method, making this a very promising method for extracting lipids from algae for use in energy applications.

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1. Introduction

Fossil fuels form an integral part of human daily life, and due to the increasing world-wide consumption the prices are expected to rise significantly in the next decades. In addition, the CO₂-emissions due to burning of fossil fuels are a serious concern [1]. Hence, the mission of finding abundant, affordable and sustainable liquid fuel alternatives to fossil energy sources has become very important. In the past few decades, the search of sustainable energy supply has evolved rapidly all over the world. In many countries, renewable energy sources such as wind power, solar photovoltaic, tides, geothermal and energy from biomass are now increasingly being used as part of the nations' energy demand. In the research of Lam and Lee [2], it was predicted that in the near future, as an alternative renewable energy, biofuel will play a more important role in energy structure of the world. Among other liquid fuels such as bioethanol [3] and biobutanol [4], that are bio-based alternatives for petroleum, biodiesel is currently recognized as a promising bio-based alternative to fossil based diesel fuel. The main advantages of biodiesel over fossil diesel are that it can provide a significant reduction of greenhouse gas emissions and its use can be adapted to current transportation systems with almost no additional modification [5,6].

Among other potential sources, algae are particularly interesting as biofuel feedstock. There is a comparison of microalgae with other biodiesel feedstocks in Table 1. The oil content of algae (10–70 wt.%) is comparable to other biodiesel feedstocks and it can be influenced by varying growth conditions [7]. However, as algae grow rapidly they can offer high oil yields and high biodiesel productivity per hectare of cultivation [8]. The land use for growing algae is much less than the other crops. Besides above advantages, algae can be cultivated in waste water, produced water or saline water on non-arable land, thereby reducing competition with arable land, limited freshwater and nutrients used for conventional agriculture [9,10]. Algae can recycle carbon much faster than other crops from CO₂-rich flue emissions from stationary sources, including power plants and other industrial emitters [11] and algae cultivation does not need herbicides nor pesticides [7].

However, there are also limitations in using algae. Since they grow in water it is difficult to obtain a good business case due to the high energy costs for obtaining the oil from the very dilute aqueous algae slurries/solutions. Algae dewatering is the most energy intensive step in the process of extracting oil from algae. Although it is not infeasible to use solar drying [13], this method relies on the sunlight which is limited in some countries at certain time of a year. Furthermore, this process is time consuming and requires a large area. An alternative way of drying algae was studied by Sander and Murthy [14]. In their research, 69% of the entire energy input was provided by burning natural gas as fuel for drying algae. Another strategy involves concentration of the algae, followed by a wet extraction, see Fig. 1.

Organic solvent extraction and supercritical fluid extraction are the most common methods being used for algae lipid extraction. Organic solvent extraction is widely used since the chemical solvents are relatively inexpensive and high lipid recovery yields can be achieved [15]. Supercritical CO₂ (scCO₂) extraction, is seen as an efficient, 'green' and mild extraction method for complete extraction of lipid compounds [16]. Both the methods have their own advantages but also some drawbacks. The drawbacks of using organic solvents such as hexane are the

Table 1
Comparison of microalgae with other biodiesel feedstocks.

Plant/source	Oil content (wt.% oil)	Oil yield (t/ha year)	Land use (m ² year/kg biodiesel)	Source
Corn/maize	44	0.17	66	[12]
Soybean	18	0.64	18	[12]
Jatropha	28	0.74	15	[12]
Sunflower	40	1.07	11	[12]
Palm oil	36	5.37	2	[12]
Microalgae	25	>10	<1	

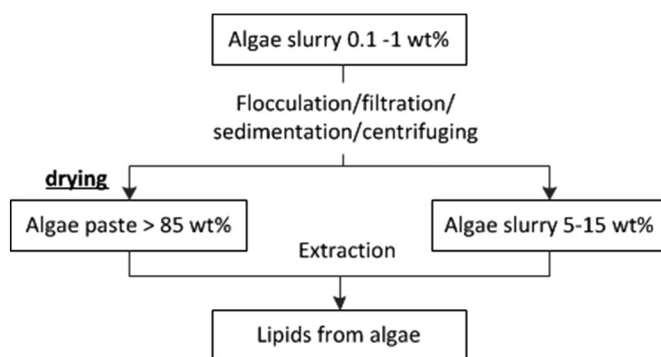


Fig. 1. Strategies of lipid extraction from dry and wet algae.

high flammability and toxic properties, and another important issue is the energy intensive solvent recovery [17]. Using scCO₂ is expensive due to the high pressure equipment and operating cost and is more difficult to scale up because of the combination of high pressure equipment with dry solids handling [18].

Although liquid solvent extraction is an energy efficient technology in itself, the common solvent regeneration technologies such as distillation, evaporation and stripping are energy intensive. A recovery method based on phase splitting might offer an energy efficient alternative. This phase splitting could be induced by changing the nature of the solvent or process conditions. CO₂ switchable solvents, first reported by Philip G. Jessop and co-workers [19], show great potential in this field. CO₂ switchable solvents are liquids that can be converted from a non-ionic form to an ionic form by contacting with CO₂. This process can be reversed by stripping the solution with N₂. Switchable solvents can be advantageous as media for reactions, extractions or separations [20] especially when in a multi-step chemical process solvents are used for a specific reaction step and must be completely removed before the next step is carried out [21].

In this paper, the objective is to compare wet extraction of algae lipids using traditional organic solvents, supercritical CO₂, and CO₂ switchable solvents on an energy consumption basis. Based on a literature review, a comparison between traditional extraction methods and CO₂ switchable solvents is made including conceptual process designs and Sankey diagrams to present the energy flows.

2. Overview of wet extraction methods

2.1. Organic solvent extraction with traditional solvents

Organic solvent extraction is generally based on the concept of "like dissolves like". Several solvents have been proposed for the extraction of algae lipids, such as methanol/chloroform, hexane/isopropanol, hexane/ethanol, dichloromethane/ethanol etc. In those co-solvent systems, the polar alcohols disrupt the hydrogen bonding and electrostatic forces between the membrane-associated polar lipids and protein and make it porous. This enables the non-polar solvent (e.g., chloroform, hexane) to enter the cell and interact with the hydrophobic neutral lipids [22]. In other cases, pure solvents as 1-butanol, ethanol, hexane, etc. have also been tried. However, the extraction performances of pure alcohols are never more than 90% of the yield obtained by the Bligh & Dyer (B & D) method [22]. The methods and typical results of lipids extraction from wet algae using traditional organic solvent are summarized in Table 2.

2.2. Supercritical fluid extraction

An extraction method popular for extracting valuables from biomass material is the use of supercritical fluid extraction. Several supercritical fluids have been investigated for biodiesel production, such as CO₂,

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