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Secondary amines as switchable solvents for lipid extraction from non-broken microalgae

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HIGHLIGHTS

- Secondary amines can extract lipid oil from both dried and fresh, non-broken algae.
- Effective lipid–solvent phase splitting is achieved upon contacting with CO_2.
- Energy efficient lipid oil extraction from algae without drying or cell disruption.

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ABSTRACT

Lipids from algal biomass may provide renewable fuel and chemical feedstock in large quantities. The energy intensity of drying and milling of algae prior to extraction and of solvent recovery afterwards is a major obstacle. The objective is to use switchable solvents to extract oil directly from wet microalgae slurries without the need for drying and milling, and subsequently recover the extracted oil and solvent by simple phase splitting, using CO_2 as trigger. In this work secondary amine solvents were investigated for lipids extraction, polarity switching and phase splitting ability upon contacting with CO_2. For strain *Desmodesmus sp.* extraction yields from the wet algal slurries, with and without cell disruption, were comparable with Bligh & Dyer method yields. Oil and solvent recovery via phase separation was realized by CO_2 induced phase splitting, making secondary amines a candidate for further development of an energy efficient lipid extraction technology for non-broken microalgae.

1. Introduction

The demand for fossil fuels is outstripping the reserves. According to the British Petroleum statistics the reserves/production (R/P) ratio of the world's fossil oil is around 54 years (BP, 2012). Currently, a strong focus on gas as alternative fossil energy source is dominating energy research in the oil and gas sector (McFarland, 2012). However, next to the strong developments in the gas-to-liquids technology, abundant, affordable, and sustainable liquid fuel alternatives to fossil energy sources are needed to avert an impending energy crisis. Among other potential sustainable energy sources, algae are particularly interesting as biofuel feedstock. The advantages of algae over traditional terrestrial crops as a source of transportation biofuels include (1) algae grow rapidly and algae productivity can offer high biomass yields per acre of cultivation (Chisti, 2007), (2) 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 (Godos et al., 2009; Mulbry et al., 2008), (3) algae can recycle carbon much faster than other crops from CO_2-rich flue emissions from stationary sources, including power plants and other industrial emitters (Packer, 2009), (4) algae cultivation does not need herbicides or pesticides (Rodolfi et al., 2009), (5) the growth rate and lipid content of algae can be controlled by varying growth conditions (Rodolfi et al., 2009).

Several process steps are needed to produce liquid biofuels from algae, such as algal cultivation, harvesting and dewatering, extraction and fractionation, fuel conversion, distribution and utilization, etc. To efficiently and economically viable produce oils from algae, a considerable investment in technological development is still needed. Significant progress is made in recent years, especially in the areas of algae cultivation, harvesting and extraction. For the cultivation of algae, the effects of pH, nitrogen, CO_2 concentration, aeration and light intensity have been examined by various

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authors Breuer et al. (2013), Chiu et al. (2009), Illman et al. (2000) and Kaewpintong et al. (2007) and several cultivation systems have been tested. For the extraction of oil from microalgae, different process strategies may be utilized. For example, algae could be harvested, dried, milled and the oil can be extracted from the dried biomass. Another strategy involves concentration of the algae, followed by a wet extraction. The extraction from wet algae could be done *in situ* without disrupting the algal cells, or alternatively extraction could be improved by destroying the wet cell integrity prior or during extraction, e.g. through wet milling, ultrasonic treatment or using a solvent that destroys the cell walls (this may even be a supercritical solvent) (Mercer and Armenta, 2011). An overview is given in Table 1.

Liquid extraction is a very energy efficient separation technology in itself. However, solvent regeneration is needed as a second operation and often the efficiency of the extraction and the energy requirements of the recovery operation are trading off, i.e. the higher the affinity of the solvent for the solute, the more difficult it is to recover the solvent. Common recovery technologies that could yield the product in a pure form are distillation, evaporation and stripping, all thermal processes that are not necessarily energy efficient.

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. In this work, the extraction of oil from algae by CO_2-switchable solvents is studied. CO_2-switchable solvents were first reported by Jessop et al. (2005) and are liquids that can be converted from a non-ionic form to an ionic form by bubbling CO_2 through the solvent and can be converted back by bubbling N_2. Switchable solvents can be reversibly converted from the initial state to the ionic carbamate form by changing the CO_2 pressure. The reverse reaction is enhanced by heating, both with respect to kinetics as to the thermodynamics of the amine–carbamate equilibrium, which shifts towards CO_2 and the amine at higher temperature.

Switchable solvents can be advantageous as media for reactions, extractions or separations (Jessop and Subramaniam, 2007) 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 (Phan et al., 2008). In the case of lipid oil extraction from microalgae in (concentrated) aqueous solutions, the high affinity of the switchable solvent system (SSS) towards non-polar compounds is exploited to extract oil from algae, while the polar form of the SSS (obtained after contacting with CO_2) is used to recover oil from the SSS after the induced solvent–lipid phase separation. The SSS cycle is completed by transforming the SSS to the non-polar form by bubbling N_2 and/or heating.

In particular with respect to extraction of lipids from algae, Samorì et al. (2010) found that switchable solvents of the amidine/alcohol class could extract lipids in higher extent than hexane from both dried and wet algal samples. Next to the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)/octanol mixture investigated by Samorì et al. (2010), also a switchable solvent of the class of tertiary amines has been applied for the extraction of lipids from algae (Boyd et al., 2012; Samorì et al., 2013). A list of published work on the use of switchable solvents for extraction of lipids from algae is provided in Table 2.

CO_2-switchable solvents are all amines and among them are primary, secondary and tertiary amines, including as well amidines and guanidines. Among the switching reactions, the primary and secondary amines, which can be switched into an ammonium carbamate salt upon the addition of CO_2, have not been investigated for extraction of lipids from algae, but could contain interesting molecules suitable for extraction applications. Molecular property constraints for the solvents include a limited volatility, low viscosity and low water solubility, at least in the more apolar form. Therefore, short chain primary amines were left out of consideration and this study was further limited to some secondary amines, such as N-ethylbutylamine and dipropylamine. For comparison, the DBU-based switchable solvents were included in this study.

With respect to algae types, only a few types of algae have been studied, including *Desmodesmus communis*. This is a rather robust algae species that grows fast and is easy to cultivate. However, since it has thick cell walls the extraction of lipids from fresh non-broken algae might be more difficult. The aim of this study is to investigate the possible use of secondary amines as switchable solvent for the extraction of lipids from wet *Desmodesmus* algae slurries, by evaluating extraction efficiency, with and without cell disruption, and lipid/solvent recovery via CO_2 induced phase separation.

Table 1
Extraction techniques to extract lipids from algae.

Extraction technique	Advantages	Disadvantages	Ref.
Solvent extraction	• Solvents are relatively cheap • High lipid recovery yields • Reproducible results	• Solvent recovery is expensive and energy intensive • Most organic solvents are flammable and/or toxic • Large volumes of solvent needed	Demirbaş, (2009); Fajardo et al. (2007), Galloway et al. (2004) and Herrero et al. (2004)
Supercritical CO_2 extraction	• Absence of solvent in residue and/or extracts • Non-flammable and simple in operation • Time efficient	• Often fails in quantitative extraction of polar analytes, insufficient interaction between $scCO_2$ and samples • Expensive due to high pressure equipment	Macías-Sánchez et al. (2005) and Pawliszyn, (1993)
Ultrasound assisted solvent extraction	• Extraction time is reduced • Reduced solvent use • High lipid recovery yields • Release of cell contents into the bulk medium	• High power consumption • Difficult to scale-up	Luque-García and Luque De Castro, (2003), Pernet and Tremblay, (2003) and Wiltshire et al. (2000)
Microwave assisted extraction	• Solvent use is reduced • Extraction time is reduced • Extraction yield is higher • Good reproducibility	• Heat force control is difficult	Kaufmann and Christen, (2002) and Proestos and Komaitis, (2008)
Pulsed electrical fields (PEF) assisted extraction	• Short processing times • Low temperatures	• High capital cost • Restricted to products with no air bubbles and with low electrical conductivity	Floury et al. (2006), Sale and Hamilton, (1968)