



# 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 CO<sub>2</sub> and CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2</sub>-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 CO<sub>2</sub> (scCO<sub>2</sub>) 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

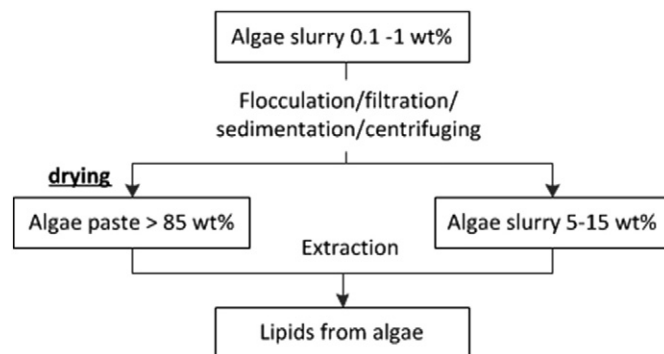


Fig. 1. Strategies of lipid extraction from dry and wet algae.

high flammability and toxic properties, and another important issue is the energy intensive solvent recovery [17]. Using scCO<sub>2</sub> 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. CO<sub>2</sub> switchable solvents, first reported by Philip G. Jessop and co-workers [19], show great potential in this field. CO<sub>2</sub> switchable solvents are liquids that can be converted from a non-ionic form to an ionic form by contacting with CO<sub>2</sub>. This process can be reversed by stripping the solution with N<sub>2</sub>. 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 CO<sub>2</sub>, and CO<sub>2</sub> switchable solvents on an energy consumption basis. Based on a literature review, a comparison between traditional extraction methods and CO<sub>2</sub> 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 CO<sub>2</sub>,

Table 1  
Comparison of microalgae with other biodiesel feedstocks.

Plant/source	Oil content (wt.% oil)	Oil yield (t/ha year)	Land use (m <sup>2</sup> 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	

**Table 2**

The methods and results of lipids extraction from wet algae using traditional organic solvent.

Solvent	Algae species	Conditions			Maximum final total lipid yield (wt.% of dry algae biomass)	Reference
		State of algae biomass at start of extraction	Enhanced method	Extraction temperature (°C)		
Hexane	<i>Scenedesmus dimorphus</i>	Concentrated	Bead-beater	Not specified	29.7	[23]
	<i>Chlorella protothecoides</i>	Concentrated	Bead-beater	Not specified	23.5	[23]
	<i>Chlorococcum</i> sp.	Water content = 70%	–	Not specified	1	[24]
	<i>Nannochloropsis gaditana</i>	Water content = 86%	high-pressure homogenization	20–22	10.9	[25]
Hexane:2-propanol ratio = 2:3 (v/v)	<i>Chaetoceros muelleri</i>	Water content = 85%	–	Near boiling point	87% of yield from five-step water/methanol/chloroform extraction	[26]
Hexane:methanol ratio = 7:3 (v/v)	<i>Chlamydomonas reinhardtii</i>	Concentrated	Osmotic shock (50–100 g/L of NaCl)	Not specified	20	[27]
Ethanol	<i>Chaetoceros muelleri</i>	Water content = 85%	–	Near atmospheric boiling point	82% of yield from five-step water/methanol/chloroform extraction	[26]
Ethanol:hexane ratio = 1:1 (v/v)	<i>Scenedesmus dimorphus</i>	Concentrated	Wet milling	Not specified	25.3	[23]
	<i>Chlorella protothecoides</i>	Concentrated	Bead-beater	Not specified	18.8	[23]
Chloroform:methanol ratio = 2:1 (v/v)	<i>Botryococcus braunii</i>	Concentrated	–	Not specified	28.6	[28]
Ethyl acetate:methanol:water ratio = 15:5:9 (v/v/v)	<i>Ankistrodesmus falcatus</i>	1.2–2.0 g/L	–	Not specified	0.22 ± 0.07	[29]
	<i>Ankistrodesmus falcatus</i>	1.2–2.0 g/L	Pulsed electric field	Not specified	0.51 ± 0.13	[29]
Dichloroethane: ethanol ratio = 1:1 (v/v)	<i>Cladophora</i> sp.	Concentrated	–	Not specified	~37	[30]
Dichloroethane:methanol ratio = 1:1 (v/v)	<i>Cladophora</i> sp.	Concentrated	–	Not specified	~40	[30]
Dimethyl ether	<i>Microcystis</i>	Water content = 91%	–	20	40.1	[31]
1,2-dimethoxyethane:water ratio = 6.5:1 (v/v)	<i>Botryococcus braunii</i>	Wet algae biomass	–	Not specified	96% of maximum yield from control extractions	[32]
1-butanol	<i>Chaetoceros muelleri</i>	Water content = 85%	–	Near boiling point	94% of maximum yield from control extractions	[26]
	<i>Monoraphidium minutum</i>	Water content = 85%	–	Near boiling point	81% of maximum yield from control extractions	[26]
p-Cymene α-Pinene	<i>Nannochloropsis oculata</i>	20% dry weight paste	–	Heating	21.45 ± 2.64	[33]
	<i>Dunaliella salina</i>	20% dry weight paste	–	Heating	3.29 ± 0.05	[33]

methanol and ethanol [34–36]. Although supercritical methanol and supercritical ethanol can convert lipid compounds in algae biomass directly into biodiesel, the operation temperature (about 260 °C) is much higher than that for supercritical CO<sub>2</sub> (scCO<sub>2</sub>) (31.2 °C), which will significantly increase the energy consumption. Due to the low critical temperature of CO<sub>2</sub>, thermal degradation of products is not observed, which is another advantage of CO<sub>2</sub> for extraction of high valuable, thermo-sensitive compounds [37]. ScCO<sub>2</sub> is considered as an important alternative for lipid extraction with organic solvents since CO<sub>2</sub> is non-toxic, non-flammable, relatively chemically inert and it produces a solvent-free crude lipid fraction.

Several studies on lipid extraction from algae for biodiesel using scCO<sub>2</sub> have been conducted in recent years. For example, in one study, lipid from freeze dried *Chlorella vulgaris* biomass was extracted using scCO<sub>2</sub> at temperatures of 40 and 55 °C and pressures up to 35 MPa [38]. It was found that by increasing the pressure from 20 MPa to 35 MPa, the lipid yield was increased from 4% to 5% with whole algae and from 5% to 13.3% with crushed algae. Cell disruption led to a significant higher lipid yield (8%) at the same conditions. However, the maximum extraction yield using scCO<sub>2</sub> is still significantly lower than when using the B & D method result (24.5 wt.% of dry biomass) [38]. In the study by Andrich, the effect of operating conditions on the kinetics of the supercritical fluid extraction (SFE) on process yields and on the fatty acid composition of lipid extracts was examined [39]. They found in their research that the yields for scCO<sub>2</sub> and n-hexane are comparable, but extraction using scCO<sub>2</sub> proved to be much faster. Couto et al. found that scCO<sub>2</sub> extraction is suitable for the production of value added products from *Cryptocodinium cohnii* that are directed towards pharmaceutical purposes because of the high DHA percentage of the obtained total fatty acids [40]. However, compared with the total lipids yield obtained using the B & D method, the scCO<sub>2</sub> extraction yield was less than one

third. In general it is found that scCO<sub>2</sub> extraction is more selective towards neutral lipids. In the study of Cheng et al., the efficiency of *Pavlova* sp. lipid extraction using organic solvents and supercritical CO<sub>2</sub> was compared [41]. The highest Fatty Acid Methyl Ester (FAME) extraction yield was obtained by the scCO<sub>2</sub> extraction.

The scCO<sub>2</sub> extraction studies mentioned above used lyophilized algae or dry algae powder as starting material. Besides those studies, a few studies reported on scCO<sub>2</sub> extractions using wet algae. Soh and Zimmerman tested the impact of algae water content to extraction efficiency. They used *Scenedesmus dimorphus* which was frozen, and compared with centrifuged algae or lyophilized algae to which water was added incrementally [42]. Their results suggest that scCO<sub>2</sub> extraction can possibly be used for wet algae and the quantity and profile of FAME produced did not change with the water content [42]. In the study of Halim et al., the performance of scCO<sub>2</sub> extraction of lipids from dewatered *Chlorococcum* sp. paste (30 wt.% DM) was examined [24]. The maximum lipid yield (7.1 wt.% relative to dry biomass) was obtained at temperatures of 60 °C and pressures of 30 MPa. One important observation here is that the total lipid yield of wet extraction was higher than for the extraction of dry algae powder (5.8 wt.% to dry biomass) [24]. In their experiments, the wet algae were used directly after centrifugation, without further treatment, and the dry algae were dried in an oven and then grinded into powder by a ring mill [24]. This suggests that by using scCO<sub>2</sub> extraction, the energy used for the drying and milling step could be avoided. The positive role of water was said to contribute to the extraction because of its swelling of the cellular matrix and its acting as a polar co-solvent.

### 2.3. CO<sub>2</sub> switchable solvents for extraction and separation

Switchable solvents [19] were first reported by Philip G. Jessop and co-workers of Queen's University, in Kingston, Ontario. Switchable

solvents are liquids that can be converted from one form to another, where the two forms differ in their physical properties such as conductivity, polarity, solubilizing capability or viscosity [43]. As media for reactions, extractions or separations, switchable solvents are advantageous compared to conventional solvents. In a multi-step chemical process, each step may require a particular solvent for optimal activity. Solvents used must then be completely removed before the next step is carried out. This solvent–solute separation is often energy intensive and increases production costs and environmental waste over the entire process [21].

Switchable solvents have proven to be useful for certain applications where the processes of reaction and separation were simplified; e.g., in the polymerization of styrene [21]. In the case of lipid 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<sub>2</sub>) 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 removing the CO<sub>2</sub> by N<sub>2</sub> stripping, with- or without heating. The concept is shown in Fig. 2.

### 2.3.1. Two-component switchable solvent systems

The first switchable solvent system was reported by Jessop et al. [19] and consisted of an equimolar mixture of an alcohol and an amidine such as DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene).

Exposure of a 1:1 mixture of the binary liquids—namely DBU and 1-hexanol—to gaseous CO<sub>2</sub> at one atmosphere and at room temperature converts the DBU and 1-hexanol into the ions DBUH<sup>+</sup> and RCO<sub>3</sub><sup>-</sup>, and with that, the liquid mixture obtains the character of an ionic liquid (see Scheme 1A) [19]. Key properties, such as polarity, viscosity, miscibility and conductivity, change significantly. This conversion is reversed by removing the CO<sub>2</sub> via the use of an inert stripping gas, such as N<sub>2</sub> or argon [19]. For a more rapid reaction, elevated temperature (50 °C) may be applied for shifting the equilibrium reaction with CO<sub>2</sub> [19]. The polarity changes are demonstrated by testing the solubility of decane—a non-polar compound—in each of the liquids. Decane is found to be miscible with the liquid under a N<sub>2</sub> atmosphere but not with the one under a CO<sub>2</sub> atmosphere (see Scheme 1B) [19].

The reaction with CO<sub>2</sub> causes a marked increase in the viscosity of the liquid, which does depend on the choice of the alcohol [19]. The choice of the alcohol is therefore critical, as for proper liquid–liquid operation a limited viscosity is desired. DBU alkyl carbonate salts, prepared by contacting CO<sub>2</sub> with the equimolar mixtures of DBU and ethanol, methanol, or water are solids at room temperature. However, DBU salts with longer alkyl chains are liquids at room temperature, and are therefore more suitable for the extraction process. Also the polarity switch of the switchable solvent system is influenced by the length of

the alkyl chain. Using shorter alcohols gives a greater difference between the polarities of the ionic and neutral forms of the solvent [21].

In the research by Samorì et al., the DBU/octanol system exhibited a better extraction yield than n-hexane, both with dried and wet algae samples (7.8% and 5.6% hydrocarbons yield respectively) [44]. The best results were obtained when the equimolar mixture DBU/octanol was used to extract freeze-dried algae at 60 °C for 4 h (16 ± 2% total hydrocarbons yield). The extraction of lipids from algae cultures (0.8 g algal dry weight/L) with the equimolar mixture DBU/octanol at room temperature for 24 h gave 8.2 ± 1% hydrocarbon yield. While these solvents were shown to be able to extract oil from microalgae and be separable from the oil without distillation, both the switchable solvents and the algae had to be rigorously dried to prevent the unwanted formation of the (solid) bicarbonate salt of DBU. For large scale application, the feasibility of these DBU based systems is therefore questionable.

Amine/amidine (guanidine) mixtures form another type of switchable solvent that can be triggered by CO<sub>2</sub> and N<sub>2</sub>. Compared with alcohol/amidine (guanidine) mixtures, they are less water sensitive [45]. In the study by Yamata et al. primary amines were chosen because they react more readily with CO<sub>2</sub> than secondary (or tertiary) amines [46]. After CO<sub>2</sub> exposure, the polarity of the solvents exhibits a marked change. This polarity is measured using the absorption spectrum of the solvatochromatic dye Nile Red as measured by a UV spectrophotometer. After mixing the solvent with Nile Red, the wavelength for maximum absorbance, which is indicative of the solvent polarity, can be determined.

For example, at room temperature, the equimolar mixture of compound **3** (Scheme 2) and N-hexyl amine is a molecular liquid. Through spectroscopic measurements it is found that its 423 nm absorption maximum indicates an environment slightly less polar than toluene ( $\lambda_{\max} = 425$  nm) [46]. After CO<sub>2</sub> exposure, it converts to the ionic liquid **4**, and the absorption maximum is shifted to 438 nm, indicating an environment more polar than acetone ( $\lambda_{\max} = 433$  nm) and less polar than N, N-dimethylformamide (DMF,  $\lambda_{\max} = 446$  nm) [46]. After stripping with N<sub>2</sub>, the ionic liquid **4** switches back to the molecular form **3** and the polarity changes accordingly [46].

### 2.3.2. Single component switchable solvent systems

2.3.2.1. *Amidines.* Switchable hydrophilicity solvents (SHS) form a special class of single component switchable solvents. Upon switching they not only change their polarity, but also can switch from having poor miscibility with water to having excellent miscibility with water. CO<sub>2</sub> at atmospheric pressure is used to switch the solvent to its hydrophilic form, and air and/or heat can be used to switch it back again [47]. N,N,N'-tributylpentanamidine was reported as a SHS (Scheme 3).

In conventional extraction processes, the solvent/product separation is an energy intensive process. Besides the large necessary energy input,

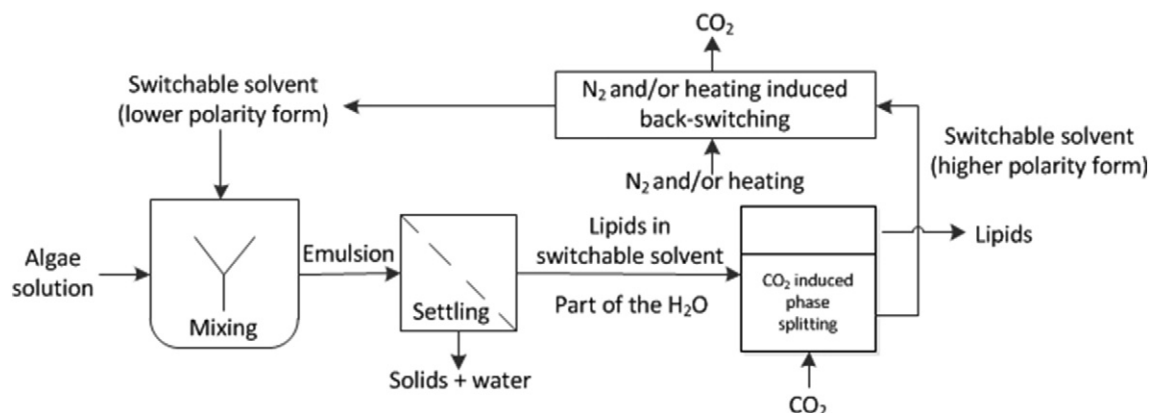
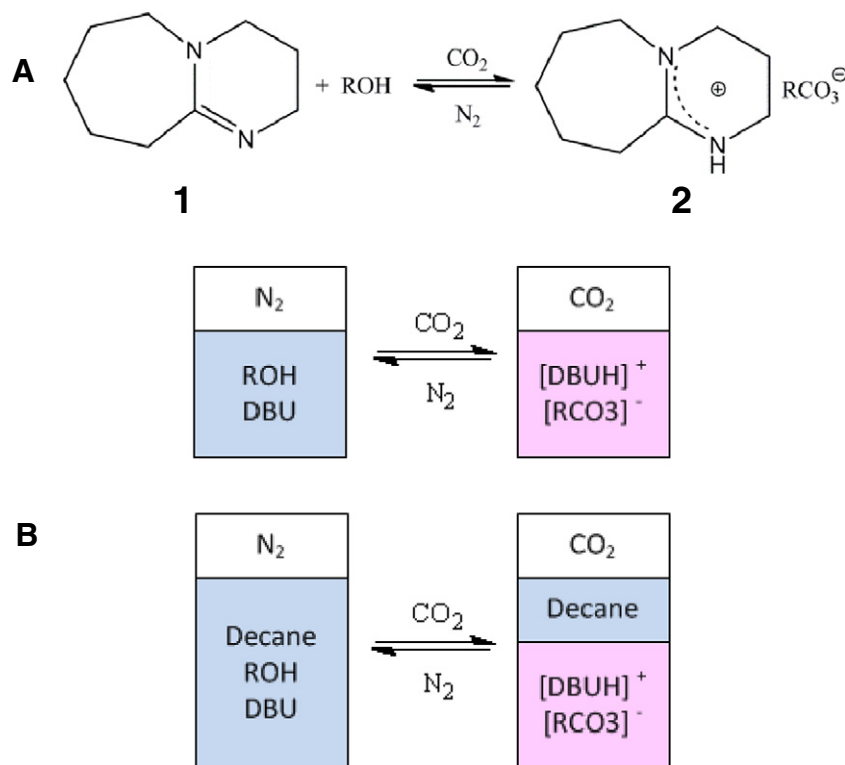


Fig. 2. Concept of lipid extraction from algae solution using switchable solvent.



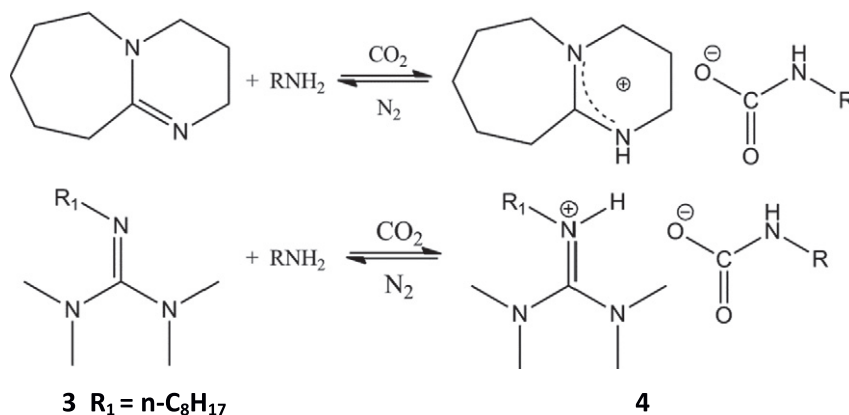
**Scheme 1.** Switchable mechanism of alcohol / amidine (guanidine) mixtures [19,21]. A, Protonation equilibrium of DBU in the presence of an alcohol and carbon dioxide. B, The different polarity of each liquid under the two conditions is illustrated by the miscibility of decane with the hexanol/DBU mixture under nitrogen; a decane phase separates out once the solvent mixture becomes polar in the presence of  $\text{CO}_2$ . This process is reversible.

distillation or evaporation requires the use of a volatile solvent, with the disadvantage of vapor losses and resulting emissions to the environment. The SHS can be used for the extraction of low-polarity organic products, followed by the removal of the solvent from the product by carbonated water, hence without distillation [47]. The SHS, separated from water by switching the solvent back to the hydrophobic state, can then be reused [47].

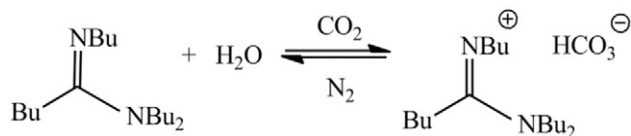
For comparison, the current industrial process for obtaining soybean oil involves extracting the oil using hexane and then removing the hexane by distillation. In the research of Sheenhan et al. [48], the soybean extraction has a solvent: bean mass ratio of 1.2 and the reported hexane losses are 2.4 kg per ton of flaked beans processed. SHS make it possible to extract soybean oil from soybeans, and then to separate the solvent from the extracted oil without distillation, by solvent switching using  $\text{CO}_2$  and water [49].

**2.3.2.2. Secondary amines.** Within the class of secondary amines, some compounds can function as switchable solvent using  $\text{CO}_2$  as a trigger. Secondary amines are cheaper than amidines and have a significantly lower polarity form. Moreover, secondary amine switchable solvents are less sensitive than DBU/Alcohol systems to small amounts of water. They react with  $\text{CO}_2$  to form carbamate salts via carbamic acids (see Scheme 4).

For a solvent system to be classified as a switchable solvent, the carbamate salt and the amine must be liquids and exhibit a significant change in polarity. Most liquid amines (including primary alkylamines, allylamine, piperidine, pyrrolidine, and benzylamine) are converted into solid carbamates [50], whereas some secondary amines yield room temperature liquid salts. Light secondary amines—such as ethyl methyl amine, di-ethyl amine, and methyl-propyl amine—are less preferred, because these amines are very volatile and highly flammable.



**Scheme 2.** Switching mechanism of aliphatic primary amines/ amidine (guanidine) mixtures [46].

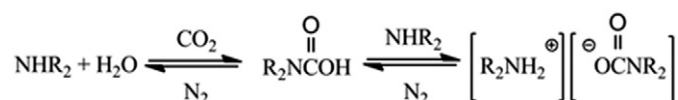


**Scheme 3.** Switching mechanism of switchable hydrophilicity solvent N,N,N'-tributylpentanamidine [47].

Four liquid amines that potentially could be used as switchable solvent have been reported: N-ethyl-N-butyl amine, N-ethyl-N-propyl amine, di-propyl amine, and benzyl methyl amine [50].

Du et al. proposed a process for lipid extraction from wet algae using secondary amines [51]. The proposed process configuration is illustrated in Scheme 6c. First, the oil is extracted from the algae using the switchable solvent in its lower polarity (lipophilic) form. The solvent phase with the extracted lipid oil is then phase-separated from the aqueous stream containing the algae residue. Then, by contacting the separated solvent phase with CO<sub>2</sub>, the solvent is switched into its more polar, ionic form, indicated in the figure as 'Switching forward' and phase-separates from the apolar lipid oil. The solvent is then converted back to its original state ('switching backward') by N<sub>2</sub> stripping at elevated temperature. Key enabling steps in this process are (1) uptake rate of CO<sub>2</sub> and the extent of the reaction of CO<sub>2</sub> with the solvent in the liquid mixture to change the solvent from lipophilic to lipophobic state and (2) the rate and extent of the back-switching reaction. To increase the rates and shifting equilibria, water could be added (or not totally removed from the previous stage), and the solvent might be heated up. Additional points of attention are the solubility of the solvent in water (which might affect algae cultivation when recycling the untreated water) and the solubility of the solvent in the lipid oil phase. For practical purposes, if a portion of the switchable solvent ends up in the aqueous phase after extraction, this may introduce a significant problem if the aqueous phase would be re-used for growing again algae since many alkyl amines are toxic even at low concentrations [52]. It would also be a problem for the environment if the water is discarded without any further treatment. Thus solvent recovery is mandatory before recycling the aqueous phase. On the other hand, if a significant fraction of the solvent leaves the process being dissolved in the product oil, this also requires an additional recovery operation (e.g., washing with water) to limit the loss of solvent and the contamination of the oil product. Therefore, a set of selected solvents was tested for the desired phase behavior: immiscibility with water under extraction conditions and immiscibility with oil in the presence of CO<sub>2</sub> at atmospheric pressure, next to their extraction performance to harvest lipid oil from microalgae slurries. The results showed that N-ethyl-N-butyl amine and di-propyl amine have good switching behavior [51].

**2.3.2.3. Tertiary amines.** The use of tertiary amines has been proposed as another type of switchable hydrophilicity solvent (SHS), easier to prepare and (often) commercially available, in contrast to the amidine system reported previously [53]. Again, these tertiary amines are hydrophobic solvents that have very low miscibility with water under a nitrogen atmosphere, but become hydrophilic in the presence of CO<sub>2</sub> at atmospheric pressure. The change in miscibility is caused by a chemical reaction of the CO<sub>2</sub>, water and the SHS, giving a water-soluble bicarbonate salt of the protonated SHS. The switching mechanism of tertiary amines is illustrated in Scheme 5.



**Scheme 4.** Switching mechanism of secondary amines [50].

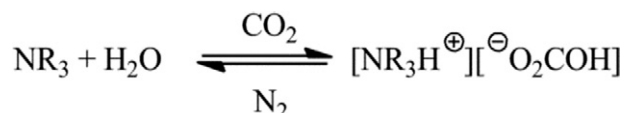
By stripping with e.g., N<sub>2</sub> or air through the [NR<sub>3</sub>H][O<sub>2</sub>COH]/water (single phase) mixture the reaction is reversed and CO<sub>2</sub> is removed via the gas phase. Consequently, the mixture splits again into two liquid phases. Operating at elevated temperature helps to shift the equilibrium to the side of CO<sub>2</sub> and the hydrophobic tertiary amine. Due to the reaction stoichiometry an equimolar amount of H<sub>2</sub>O is required, in contrast to e.g., primary and secondary amine systems. Tertiary amines are normally less reactive towards CO<sub>2</sub> than secondary amines, which may lead to longer reaction times needed to switch the solvent, but require less energy input to reverse the reaction.

The tertiary amine N,N-dimethylcyclohexylamine (DMCHA) was reported for extraction of lipids from microalgae. In the research published by Jessop et al., the algae *Botryococcus braunii* and DMCHA were used in the experiments [54]. The amount of crude lipids extracted with DMCHA and isolated from the solvent was up to 22% of the dry cell weight when the extraction was performed at 60 to 80 °C and the residual amine content in the extracts was 18–24 wt.% [54]. Extractions performed at room temperature yielded up to 19% crude lipids and the residual amine content in these extracts was about 4–8 wt.% [54]. However, 4–8 wt.% residual amine in extract is still a lot, which indicates that additional recovery operation is needed [54]. Samorì et al. used DMCHA for extracting and recovering lipids directly from wet algae samples (about 80% water content) and directly from cultures (biomass concentration around 2 g/L) of three microalgae strains: *Nannochloropsis gaditana*, *Tetraselmis suecica*, and *Desmodesmus communis* [52]. This work is remarkable, since this was the first time that extraction of lipids from dilute cultivation media without any treatment for cell disruption was reported. The total lipid content expressed on algal dry weight basis obtained through DMCHA extraction of wet samples (50 mg/mL, 24 h extraction) of *D. communis*, *N. gaditana* and *T. suecica* was 29.2 ± 0.9%, 57.9 ± 1.3% and 31.9 ± 1.5% respectively, which was comparable with extraction yields using the B & D lipid extraction method, commonly applied for analytical purpose [52].

From the few works reported on extracting lipids from algae by switchable solvents [51,52,54], promising results have been obtained with regard to the amount of lipid extracted when compared with traditional analytical extraction methods, such as the B & D method. However, these laboratory results do not elucidate on large scale processes and on potential benefits of using these solvents at large scale still not much is known. Moreover, for sustainable use of the switchable solvents in extraction from wet algae feed streams, the method and condition of solvent recovery from both aqueous raffinate and from the lipid fraction after or during back-switching need to be developed, since the solubility of these switchable solvents in their neutral form in the water phase is not negligible. In the following sections, an estimation and comparison of the potential benefits for the various solvent extraction systems is made on an energy consumption basis. These estimations were made using conceptual process designs including necessary solvent recovery operations, and based on the conclusions some directions for further research are given.

### 3. Conceptual process designs

In this section, the process schemes and the descriptions of the different extraction methods are provided. The design of these processes is mainly based on experimental data published by Halim et al. [24], Soh et al. [42] and Du et al. [51]. The process schemes of the extraction methods are illustrated in Scheme 6. Subsequently, the extraction



**Scheme 5.** Switching mechanism of tertiary amines [53].

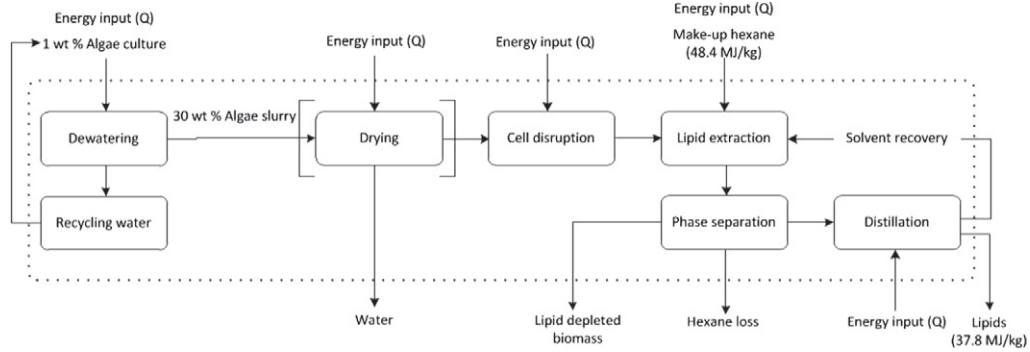
processes will be discussed and the specific energy consumption will be estimated.

3.1. Hexane extraction

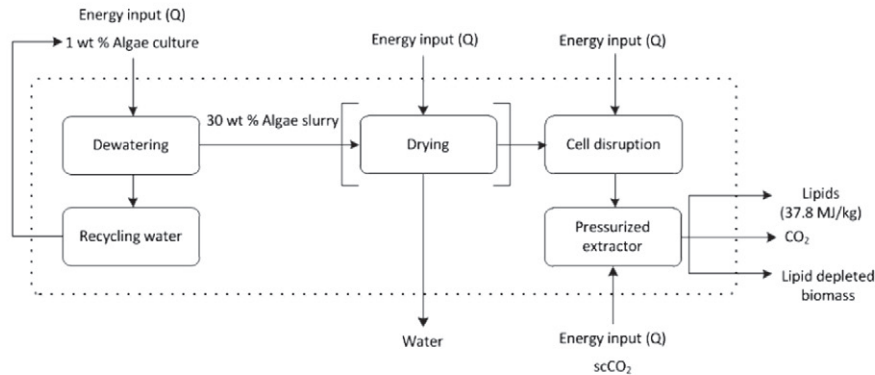
As is visible in Scheme 6a, in the extraction scheme using hexane as solvent, a slurry of 1 wt.% algae of the strain *Desmodesmus* sp. was selected as the starting material, and this condition was selected for all extraction methods to be able to make a fair comparison. After dewatering

to 30 wt.%, the algae slurry was subjected to bead milling for cell disruption and then used for wet extraction. For extraction from dry algae, the algae slurry after dewatering was dried in a thermal dryer and subsequently the dry algae biomass was broken by grinding before use in the extraction process.

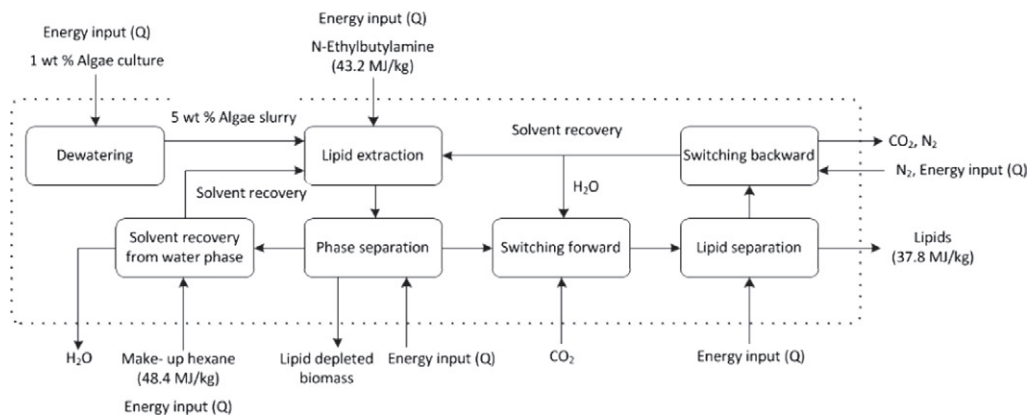
In the subsequent stages, hexane was added to either microalgae powder or wet algae paste (having the same algae biomass input, on dry matter basis, as the algae powder). All extraction mixtures were agitated at ambient conditions. After that, cell residue was removed by



a. Process scheme of hexane extraction of lipids from dry/wet microalgae.



b. Process scheme of scCO<sub>2</sub> extraction of lipids from dry/wet microalgae.



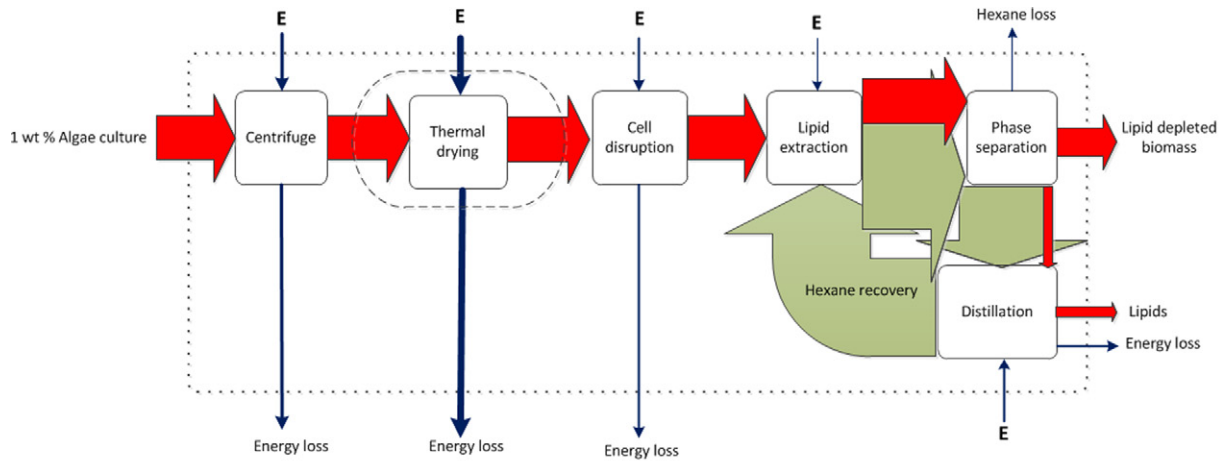
c. Process scheme of switchable solvent extraction of lipids from wet microalgae.

**Scheme 6.** Process schemes of different lipid extraction methods using hexane (Scheme 6a); supercritical CO<sub>2</sub> (Scheme 6b) and switchable solvents (Scheme 6c). a. Process scheme of hexane extraction of lipids from dry/wet microalgae. b. Process scheme of scCO<sub>2</sub> extraction of lipids from dry/wet microalgae. c. Process scheme of switchable solvent extraction of lipids from wet microalgae.

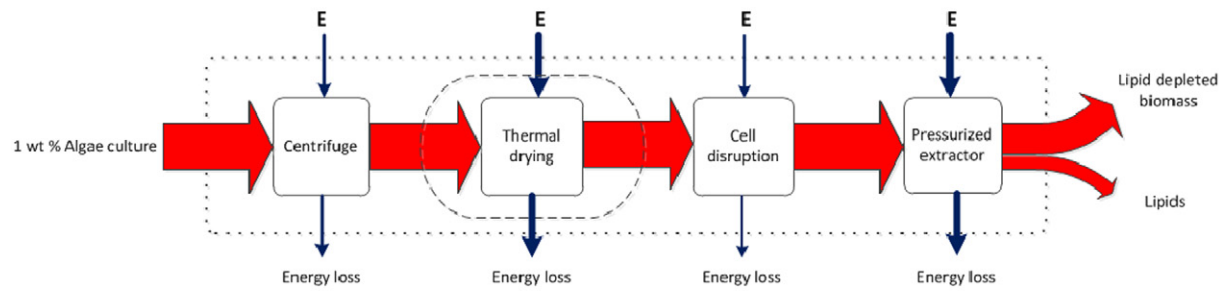
filtering and the filtrate was transferred into a settler to partition the hexane layer from the water layer. The lipid was collected after removing hexane via distillation. The hexane is recovered by vapor condensation and can be reused for a next extraction.

3.2.  $scCO_2$  extraction

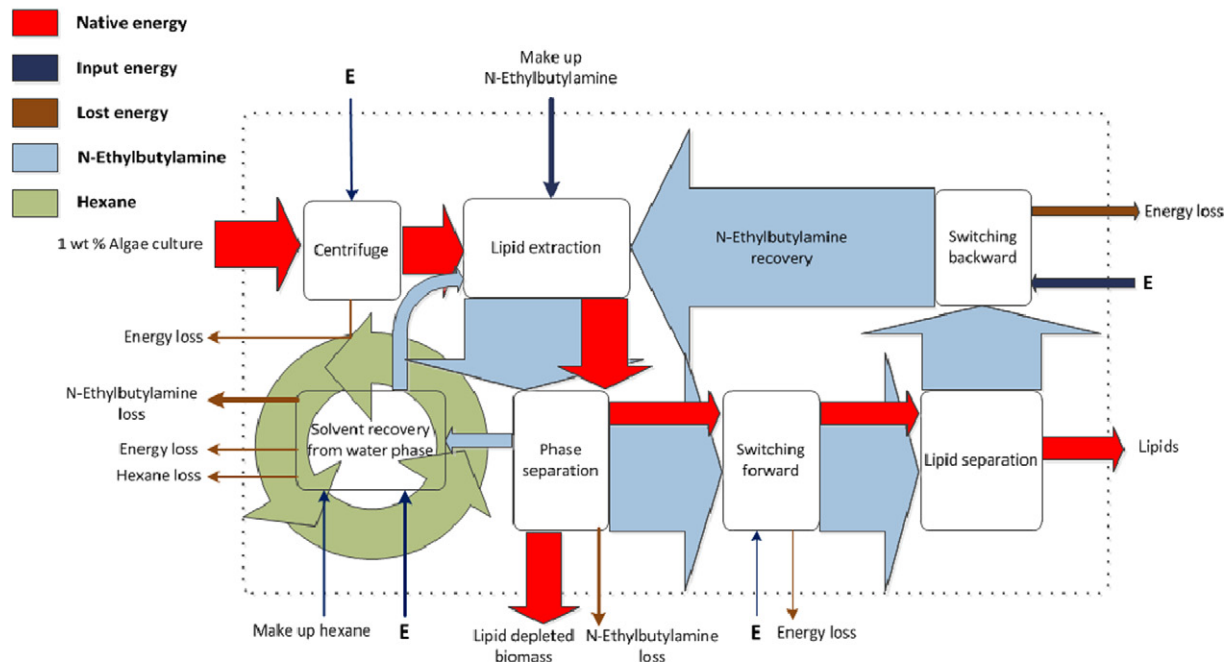
In the case of  $scCO_2$  extraction (shown in Scheme 6b), first, the algae feed materials were prepared in the same way as for hexane (dry or



a) Sankey diagrams for hexane extraction of lipids from dry/wet microalgae



b) Sankey diagrams for  $scCO_2$  extraction of lipids from dry/wet microalgae



c) Sankey diagrams for switchable solvent extraction of lipids from wet microalgae

Fig. 3. Sankey diagrams of different lipids extraction methods. a. Sankey diagrams for hexane extraction of lipids from dry/wet microalgae. b. Sankey diagrams for  $scCO_2$  extraction of lipids from dry/wet microalgae. c. Sankey diagrams for switchable solvent extraction of lipids from wet microalgae.



**Table 3**Input/output data of the various methods for producing 1 kg of lipids from 1 wt.% *Desmodesmus* sp. in the base case scenario.

Unit (MJ/kg lipids) (ref)	Hexane		ScCO <sub>2</sub>		Switchable solvent
	Dry	Wet	Dry	Wet	
<i>Harvesting and dewatering</i>					
Centrifuge (1 ~ 5 wt.%) ([57])					1.0
Centrifuge (1 ~ 30 wt.%) ([55])	2.5	2.5	2.5	2.5	
Thermal dryer (30~ > 85 wt.%) ([56])	28.8		28.8		
<i>Lipid extraction</i>					
Cell disruption ([57])	1.9	11.1	1.9	11.1	
Assumed lipid yield (wt%)	15	15	15	15	15
Extraction process			30.9 [51,59–61]	30.9 [24,51,59–61]	0.1
Solvent recovery ([57])	3.2	8.9			[51]: 12.8
Solvent lost ([48])	0.9	2.6			[51]: 5.9
<i>Total energy</i>					
Consumption	37.2	25.1	64.1	44.6	19.8
Production	37.8	37.8	37.8	37.8	37.8
Net energy yield	0.6	12.7	–26.3	–6.8	18.0
Estimated lipid yield (wt%)	[57]: 12.2	[24]: 8.2	[39]: 12.8	[24]: 15.7	[51]: 16.8
Net energy yield (at estimated lipid yield)	–8.1	–8.5	–37.3	–4.9	20.1

wet) extraction. ScCO<sub>2</sub> extraction was performed using a supercritical fluid extractor. After passing through the extractor, the scCO<sub>2</sub> rich solvent stream containing the lipids is lowered in pressure and the extracted lipid oil is recovered. Expanded CO<sub>2</sub> is recompressed and reused.

### 3.3. Switchable solvent extraction

For the switchable solvent extraction system described in Scheme 6c, the design was based on experimental work using the algae *Desmodesmus* sp. In Scheme 6c the algae feed is concentrated to around 5 wt.% and used directly without further treatment. First, the algae slurry was mixed with a selected switchable solvent. In this study, experimental data for N-ethyl butylamine were used. After extraction, cell residue and aqueous phase were removed. A small amount of water was added into the organic solvent/lipid phase to participate in the switching step. Next, CO<sub>2</sub> was contacted with the organic phase, in the presence of water, to switch the solvent into its hydrophilic form. As the extracted lipids remain hydrophobic, the solvent and the lipids will phase separate and the lipids form a separate layer in the settler, which can be collected. Then the bottom phase, containing water and switched solvent in its hydrophilic form, was separated and heated (or combined with N<sub>2</sub> flushing) in order to switch back the solvent by removing CO<sub>2</sub> from the reaction equilibrium. The solvent thus recovered can be collected as separate, hydrophobic phase and reused for extraction, while the water phase can be reused in

the forward switching step. Because of the large aqueous stream and the nonzero solubility of the solvents in water, a recovery step is needed to recover the solvent that is leached into the aqueous raffinate. For this process step, a recovery solvent like hexane can be applied, which afterwards can be separated from the switchable solvent by distillation or a second phase switching procedure (not shown).

## 4. Energy evaluations

### 4.1. Energy calculation methods and approaches

The unit operations in the conceptual process schemes displayed in Scheme 6 were applied to make an estimation of the energy consumption in the various types of lipid extraction and also to study the sensitivity of several key process parameters, such as the lipid content in the algae and the concentration in the algae slurry. As there are many algae species in nature, the variety in lipid content and composition is large. In this study, *Desmodesmus* sp. was selected as typical example, since it is a robust, widely studied (freshwater) algae species with a reasonable strong cell wall, but modest lipid content. Depending on the type of growth reactor and optional pre-concentration method, the concentration of algae will typically range from 0.1–1 wt.%. For sake of consistency in the calculations, all of the here described calculations started with a 1 wt.% *Desmodesmus* sp. algae slurry. Depending on the

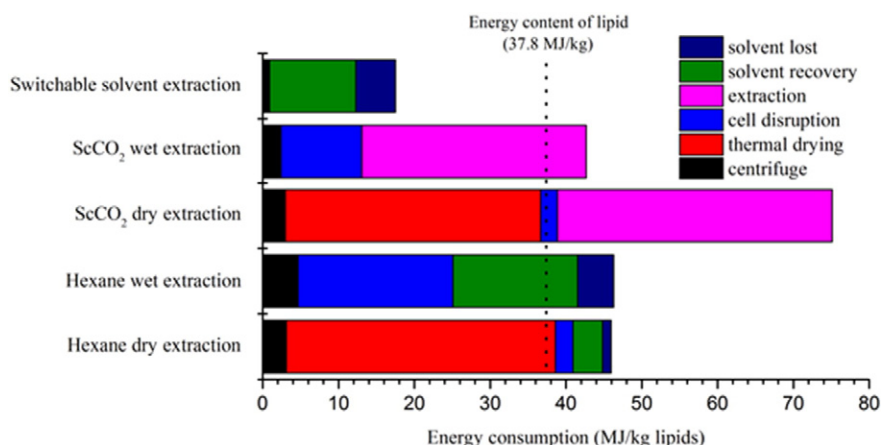


Fig. 4. Energy requirements in MJ/kg lipids produced for the different extraction methods.

extraction method, the following data from the literature was applied. Sankey diagrams for hexane (dry and wet) extraction,  $\text{scCO}_2$  (dry and wet) extraction and switchable solvent extraction are shown in Fig. 3. The width of the arrows shown is proportional to the energy of the stream involved. Detailed results can be found in Supplementary material.

#### 4.1.1. Extractions from dried algae

In cases of dry extraction, the algae slurry was first concentrated up to 30% dry weight (DW) by mechanical means and then followed by drying using a thermal dryer. An Evodos dryer ( $1.05 \text{ kWh/m}^3$ ) was selected for concentrating up to 30 wt.% [55]. Based on the Delta-Dryer concept, to dry the algae from 30% DW up to >85% DW, 2 MJ per kilogram of evaporated water is required [56]. The power used for cell disruption was 0.24 MJ per kilogram of dry algae [57].

For hexane extraction, it is reported that typically 2.4 g of hexane is lost for each kilogram of dry biomass [48], which is about 0.2% of the

total hexane amount. Considering the Higher Heating Value (HHV) of hexane ( $48.4 \text{ MJ/kg}$ ), the energy cost due to the solvent lost is  $0.097 \text{ MJ}$  per kilogram of hexane. For the HHV of the extracted lipids, the value of biodiesel ( $37.8 \text{ MJ/kg}$ ) was assumed [58]. The hexane phase from each extraction was distilled to recover the lipids and to recycle the hexane. It is assumed that 70% of that heat could be recovered at the hexane condenser and be used for heating hexane (or hexane-*N*-ethyl butylamine solutions) to  $69^\circ\text{C}$ , the atmospheric boiling point of hexane. As the sensible heat requirement is much less than energy required for hexane evaporation, overall the energy used for recovering hexane is taken to be just the enthalpy of vaporization, which is  $0.33 \text{ MJ}$  per kg of hexane.

The energy cost of  $\text{scCO}_2$  extraction was calculated based on results presented in literature. In the research of Brentner et al.,  $1830 \text{ kWh}$  ( $508 \text{ MJ}$ ) is required solely for extraction to produce  $10^4 \text{ MJ}$  of algae biodiesel [59]. The lipid content, extraction efficiency and HHV of biodiesel were assumed to be 25%, 95% and  $34 \text{ MJ/L}$  respectively [59]. The density

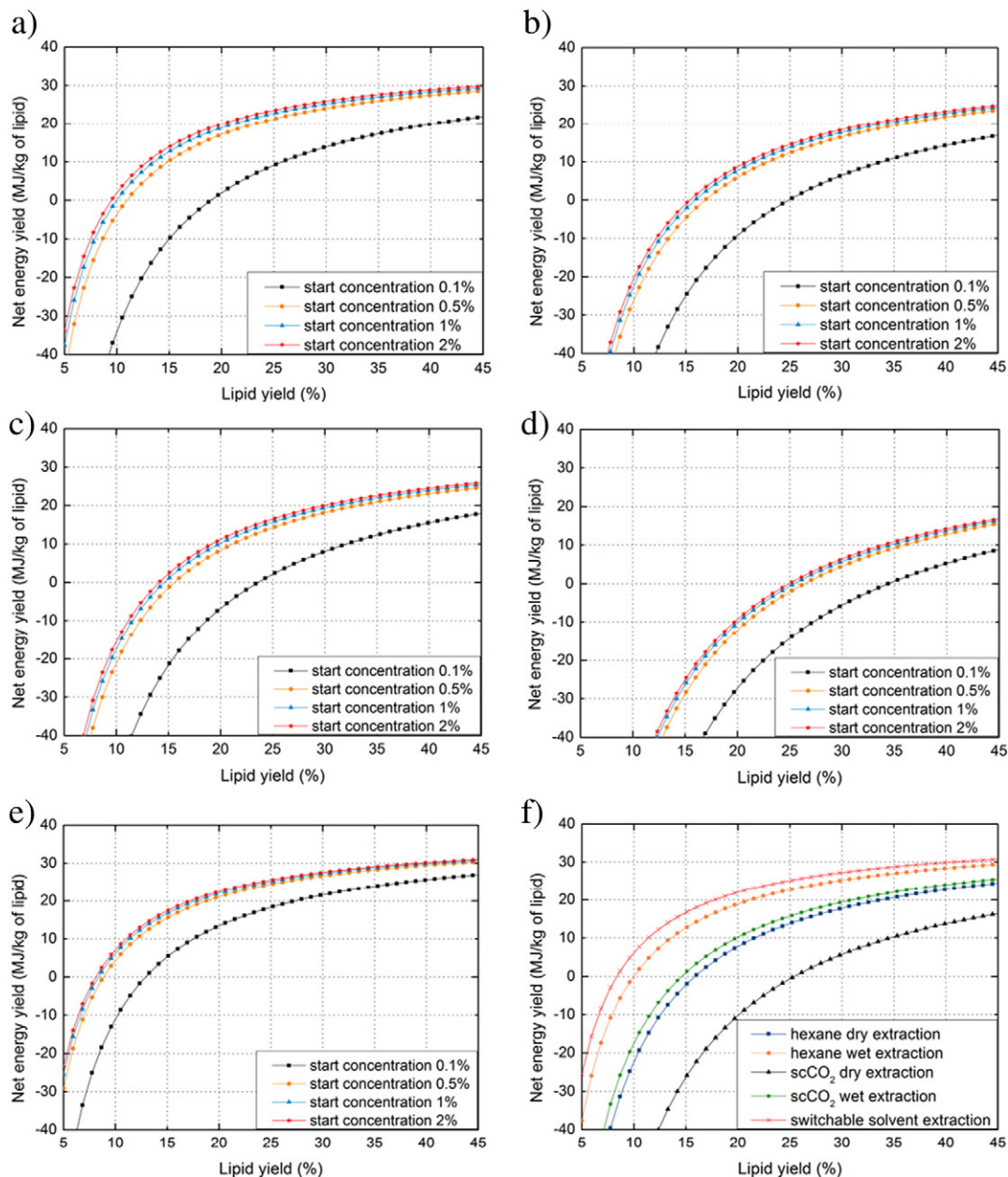


Fig. 5. Effect of different start algae concentration in the slurry and lipid extraction yield. (A) Hexane wet extraction. (B) Hexane dry extraction. (C)  $\text{ScCO}_2$  wet extraction. (D)  $\text{ScCO}_2$  dry extraction. (E) Switchable solvent extraction. (F) Net energy yields of different extraction methods when the start algae concentration is 1 wt.%.

of biodiesel is 0.88 kg/L [60]. It was calculated that per kilogram of dry algae biomass 1.68 kWh or 6.05 MJ energy for scCO<sub>2</sub> is required. Alternatively, in the study by Garcia Alba an algae biorefinery process concept was evaluated which incorporated the scCO<sub>2</sub> extraction of lipids [61]. In that research, the scCO<sub>2</sub> extraction required 3.23 MJ energy per kilogram dry algae. In this study, an average energy demand of 4.64 MJ/kg dry algae was taken for further calculation.

#### 4.1.2. Extractions from wet algae slurry

For extraction from wet slurries it is assumed that the algae slurry is first concentrated, e.g., by an Evodos dryer (1.05 kWh/m<sup>3</sup>), up to 30% DW prior to hexane or scCO<sub>2</sub> wet extraction. After dewatering and prior to the extraction step itself, the algal cells were broken by ball milling, requiring a power input of 0.5 MJ per kilogram of 30 wt.% algae slurry [57]. The hexane added for extraction was assumed to be 1.2 times the processed material which was 4 kg. The energy penalty due to solvent loss in hexane wet extraction was calculated as the heating value of the assumed loss of 2.4 g of hexane per kilogram of dry algal biomass, resulting in 0.39 MJ per kilogram of dry biomass.

For the switchable solvent extraction, an algae slurry concentration of only 5 wt.% DW is needed and is used directly without further treatment. Here, the Alfa Laval PX-110 centrifuge (85 m<sup>3</sup>/h, 45 kW (0.53 kWh/m<sup>3</sup>)), which can dewater the algae to 16 wt.% DW was selected [57]. N-ethyl butylamine was added to algae slurry in a mass ratio of 1:5. The switchable solvent loss due to its solubility in water (4.19 wt.%, 30 °C) [62] can now be calculated. After collecting the lipids, the bottom liquid phase which contained water and switched solvent in its hydrophilic form was reconverted by heating at 90 °C and N<sub>2</sub> stripping in order to remove CO<sub>2</sub>. The heat capacity of N-ethyl butylamine is assumed to be the same as dipropylamine which is 2.5 kJ/(kg·K) [63]. Because they are both secondary amine and have the same number of carbon atoms, this seems a reasonable assumption for the heat capacity. Besides the energy required for heating up, the heat used for breaking the bond between CO<sub>2</sub> and amine group was also considered. The binding energy of primary amine e.g., monoethanolamine (MEA) is around 80 kJ/mol CO<sub>2</sub>, which is higher than for secondary and tertiary amines [64]. For secondary amines the binding energy is assumed to be 70 kJ/mol CO<sub>2</sub>. It is in the same range as reported by Kim et al. [65].

Another important element in the switchable solvent extraction process is to recover the N-ethyl butylamine that leaches into the aqueous raffinate. In a laboratory experiment, a hexane extraction was applied with hexane added to this waste water in a volume ratio of 1:10 to recover the solvent. In a single (equilibrium) extraction step, already more than 98% of the switchable solvent was recovered. The hexane loss was assumed to be the same as in hexane extraction which was about 0.2%.

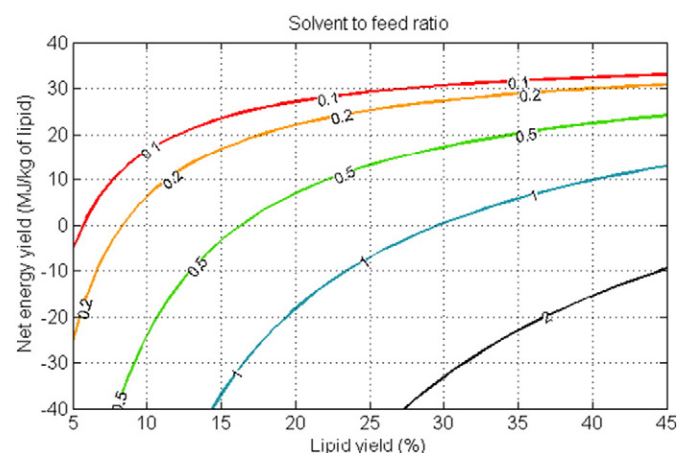


Fig. 6. Effect of solvent to feed ratio in switchable solvent system.

The calculation is based on the current available technologies and the process schemes showed in Scheme 6. The energy flow for producing 1 kg of lipids is summarized in Table 3. More information for energy calculation can be found in Supplementary material.

#### 4.2. Results for the base case

As explained in the previous subsection, the base case involves a starting slurry of 1 wt.% *Desmodesmus* sp. and a comparison has been made for the various extraction technologies, assuming a 15 wt.% lipid yield for all methods.

Table 3 summarizes the most impacting energy consumption contributions for producing 1 kg of lipids via each of the methods described above. The net energy yield was calculated when the lipid yield for each method was assumed to be 15%. The distribution of energy consumption and production shows that all methods have a high energy requirement compared to the energy produced by lipids. ScCO<sub>2</sub> extraction even cost more energy than the calorific value of the lipids produced. It should be noticed that different extraction technologies applied to the same algal biomass will lead to different yields; assuming all methods to result in 15% lipid yield is not realistic. Therefore, also an estimation for the energy yields using the different lipid yields for the different extraction methods has been made, based on B & D extraction yield (12.8 wt.% to dry biomass) of *Desmodesmus* sp. published by Du et al. [51]. Hexane dry extraction efficiency was assumed to be 95% [57] of that for the B & D method, which corresponds with 12.2 wt.% lipids from DW. In the research of Halim et al., hexane extraction yield from wet paste was 33% less than the dry extraction yield [24]. In this case, the extraction efficiency was assumed to be 8.2 wt.%. The lipid yield for scCO<sub>2</sub> dry extraction is slightly higher than hexane dry extraction [39], so it was assumed that scCO<sub>2</sub> extraction from dry algae biomass could get the same lipid yield (12.8 wt.% to dry biomass) as B & D method. The lipid yield for scCO<sub>2</sub> wet extraction was in one study found to be 22.4% higher than the extraction of dry algae powder [24], which would correspond here with 15.7 wt.% lipids. In the research of Du et al. [51], the extraction yield of switchable solvent (N-ethyl butylamine) was 131% of the one for the B & D method, which corresponds with 16.8 wt.% lipids on DW basis. The calculated results were also shown in Table 3. The results indicate that in the base case scenario, there is no advantage of hexane and scCO<sub>2</sub> extraction from the energy point of view. In the work by Xu et al., the lipid depleted biomass could be further used for producing pyrolysis oil and biogas which also can produce large amounts of energy [57]. If the energy contained in solid waste algae biomass (residual mass) is taken into account, the energy balance of hexane and scCO<sub>2</sub> wet extraction becomes positive again. It is obvious, however, that these methods are not suitable for industrial production of lipids from microalgae for energy production alone. CO<sub>2</sub> switchable solvents have proven to be able to extract lipid from both dry and wet algae by several researchers now [44,51,52,54]. From the calculation results, it turns out that switchable solvent extraction requires much less energy than the other methods, making it a better candidate when energy applications are considered. A sensitivity study was performed to analyze the impact of different process aspects requiring energy.

The energy requirements for base case are evaluated in Fig. 4. Different types of energy e.g., thermal energy, electricity energy and chemical energy are plotted in one single bar. It is realized that the efficiency of the different forms of energy is not the same, but since switchable solvent extraction uses the least amount of electrical energy comparing with other methods, this kind of combination will not influence the final result negatively and make the switchable solvents, by comparison, even more favorable. It can be noticed that for hexane and scCO<sub>2</sub> dry extraction, algae dewatering and drying is the most energy consuming step, accounting for about half of the overall energy requirement. Since this drying part cannot be avoided; it makes dry extraction less interesting, unless abundant, cheap low grade heat for drying is available.

In case of scCO<sub>2</sub> wet extraction, the high energy cost for the extraction operation makes it less competitive than other methods. In hexane wet extraction, cell disruption and solvent recovery consume a significant amount of energy. If hexane can extract a comparable amount of lipids from wet non-broken algae as from broken ones, it will be a promising method for lipid extraction. The results above indicate that the drying process and cell disruption are the major energy consumers. At this point, the use of switchable solvents which do not need drying and cell disruption was found to be the most energy efficient extraction method. In the switchable solvent extraction, the most energy consuming step was the solvent recovery and the solvent loss which accounted for about 65% and 30% of the total energy requirement of 17.7 MJ/kg lipids. Since the solvent recovery temperature was not too high (between 50 °C to 90 °C with N<sub>2</sub> stripping) and no substantial amount of electrical energy is required, besides that for the centrifuge, potentially waste heat can be used. It is expected that the use of a counter-current, multiple step solvent recovery system can further minimize the amount of solvent lost and hence further reduce the total cost for lipid extraction.

#### 4.3. Process parameter sensitivity

The energy balances for the different extraction methods described in Section 3 were modeled using MATLAB software to be able to perform sensitivity analyses towards key solvent properties and to show the effect of different operating conditions. Changes in start algae concentration and lipid yield are inputs and the energy consumption (in MJ per kg of lipid produced) is the main output for comparison of the extraction methods. The results of simulation are shown in Fig. 5.

It is clear that the net energy yield increased significantly by increasing the initial algae concentration when it is below 1 wt.%. So it is suggested to start the extraction process from an algae concentration of 1 wt.% which often can be easily reached by flocculation. When the start algae concentration is 1 wt.%, the net energy yields of different extraction methods were illustrated in Fig. 5(F). In case of hexane and scCO<sub>2</sub> extraction, in order to get positive results of energy balances, the lipid yields have to be at least 15.9 wt.% (hexane dry extraction), 10.1 wt.% (hexane wet extraction), 25.4 wt.% (scCO<sub>2</sub> dry extraction) and 14.6 wt.% (scCO<sub>2</sub> wet extraction). Comparing with the other extraction methods, the switchable solvent extraction system has obvious advantages. The effect of solvent to feed ratio in the switchable solvent extraction system is illustrated in Fig. 6.

Setting the initial algae concentration at 1 wt.%, the effect of solvent to feed ratio (kg solvent per kg algae slurry (5%)) was analyzed in Fig. 6. From the results it is visible that the more solvent used, the higher the energy consumption is. If the solvent to feed ratio is 1, at least 29.8 wt.% lipids must be extracted in order to get a positive net energy yield. With increasing lipid yield, the solvent to feed ratio has less effect on the energy balance.

In the case above, we haven't considered the effect of the solvent to feed ratio on extraction efficiency. The solvent to feed ratio can however have a significant influence on lipid extraction efficiency, as shown e.g., in the research of Yang et al. where ethanol was used as extraction solvent [66]. At this stage, it is however not known how this solvent to feed ratio will influence the extraction efficiency of N-ethyl butylamine. Nevertheless, based on the scarce information available, the energy balance is favorable. In the future, more work is needed to study the interaction between solvent to feed ratio, extraction time, temperature and extraction efficiency to find out optimum extraction conditions to reach the highest net energy yield.

## 5. Conclusions

Hexane-, scCO<sub>2</sub>- and CO<sub>2</sub> switchable solvent extraction methods were compared on their specific energy consumption and efficiency. From calculations it was found that a significant positive energy balance

for lipid extraction is only achieved using a switchable solvent extraction method.

For the dry extraction methods, involving hexane and/or scCO<sub>2</sub>, the drying process is the major energy consumer, whereas in the wet extraction methods the cell disruption and solvent recovery consume a significant amount of energy. In the switchable solvent extraction method, the most energy consuming step is related to solvent recovery and losses. The simulation results further show the effect of algae harvesting concentration and lipid content. For wet extraction methods, the energy balance can be further improved via the solvent recovery procedure, preferably based on low cost waste heat. All the results reveal that the CO<sub>2</sub> switchable solvent extraction is a very promising method for extracting lipids from algae for use in energy applications.

## Acknowledgments

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.algal.2015.07.004>.

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