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1 7096 words

Greenhouse gas emissions and energy balance of biodiesel production from
microalgae cultivated in photobioreactors in Denmark: a life-cycle modeling
Chiara Monari ¹ , Serena Righi ^{1, 2*} , Stig Irving Olsen ³
¹ Centro Interdipartimentale di Ricerca per le Scienze Ambientali (CIRSA),
Alma Mater Studiorum - University of Bologna, via S. Alberto 163, 48123 Ravenna, Italy
² CIRI Energia e Ambiente, U.O. Biomasse,
Alma Mater Studiorum - University of Bologna, via S. Alberto 163, 48123 Ravenna, Italy
³ Department of Management Engineering (DTU-MAN), Quantitative Sustainability Section (QSA)
Technical University of Denmark, 2800 Lyngby, Denmark
*Corresponding author
Tel.: +39-0544-937306; fax : +39-0544-937411
E-mail address: serena.righi2@unibo.it

21 Abstract

22 The current use of fossil fuels is problematic for both environmental and economic 23 reasons and biofuels are regarded as a potential solution to current energy issues. This 24 study analyzes the energy balances and greenhouse gas emissions of 24 different 25 technology scenarios for the production of algal biodiesel from Nannochloropsis 26 cultivated at industrial scale in photobioreactors in Denmark. Both consolidated and pioneering technologies are analyzed focusing on strengths and weaknesses which 27 28 influence the performance. Based on literature data, energy balance and greenhouse 29 gas emissions are determined in a comparative 'well-to-tank' Life Cycle Assessment 30 against fossil diesel. Use of by-products from biodiesel production such as glycerol obtained from transesterification and anaerobic digestion of residual biomass are 31 included. Different technologies and methods are considered in cultivation stage 32 (freshwater vs. wastewater; synthetic CO₂ vs. waste CO₂), harvesting stage 33 (flocculation vs. centrifugation) and oil extraction stage (hexane extraction vs. 34 35 supercritical CO_2 extraction). The choices affecting environmental performance of the 36 scenarios are evaluated. Results show that algal biodiesel produced through current 37 conventional technologies has higher energy demand and greenhouse gas emissions 38 than fossil diesel. However, greenhouse gas emissions of algal biodiesel can be significantly reduced through the use of 'waste' flows (nutrients and CO_2) but there are 39 40 still technical difficulties with both microalgae cultivation in wastewater as well as 41 transportation and injection of waste CO₂. In any way, a positive energy balance is still far from being achieved. Considerable improvements must be made to develop an 42 43 environmentally beneficial microalgae biodiesel production on an industrial scale. In 44 particular, different aspects of cultivation need to be enhanced, such as the use of 45 wastewater and CO_2 -rich flue gas from industrial power plants.

47 HIGHLIGHTS

48 • The best existing technologies for algal biodiesel production via PBRs have

49 been compared.

- 50 Fossil diesel has been taken as reference product.
- 51 Energy balance and greenhouse gas emissions have been evaluated.
- 52 Algal biodiesel has higher impacts compared to fossil diesel.
- Great improvements must be achieved to develop algal biodiesel on industrial
 scale

55 **Keywords**

56 Biofuel; Renewable fuels; Biorefinery; Bioenergy; Biogas; Nannochloropsis

58 **1** Introduction

59 The use of fossil fuels is increasingly problematic from both an economic and an 60 environmental point of view. It has been necessary to identify compatible mitigation strategies to avoid the exhaustion of fossil fuels and minimize the excess of CO2 61 62 emissions related to energy production (Ribeiro et al., 2007). In recent times, the European Commission has presented the EU Directive 2009/28/CE aiming to establish 63 a target of 20% share of renewable energy sources in energy consumption by 2020. In 64 this context at least 10% of the energy for transportation must be based on renewable 65 energy sources (European Commission, 2009). As a renewable energy source, 66 67 biofuels are an attractive alternative to current petroleum based fuels (Festel et al., 2014). Biofuels refer to liquid, gas and solid fuels derived from biomass, including a.o. 68 dedicated energy crops, residues from agriculture, and algae. Biofuels are classified as 69 70 first (from crop based feedstock), second (from non-food feedstock), third (from algae) 71 and fourth (from genetically engineered crops) generation fuels on the basis of the biomass origin and production technology (Demirbas, 2011; Lü et al., 2011; Liew et al., 72 73 2014).

74 Due to several features, algae are regarded as a promising source of biofuels and are 75 considered an interesting alternative to current biofuel crops (Singh et al., 2011; Aitken 76 et al., 2014). The production of fuel from algae provides many advantages: algae do 77 not compete with land use and crop production since they are aquatic organisms; their 78 growth rate is higher than that of terrestrial plants from which the first-generation 79 biofuels derive (Scott et al., 2010); they do not need chemicals, herbicides, pesticides for growth (Kumar et al., 2010; Yang and Chen, 2012); they can remove nitrogen and 80 81 phosphorus from wastewater (Clarens et al., 2010); and, under certain conditions, such 82 as nitrogen stress, algae are characterized by high lipid accumulation, a feature that 83 increases biofuel production (Rodolfi et al., 2009).

On the other hand, there are several difficulties associated with the production of the 84 85 third-generation biofuels and, until now, their commercial production has not been 86 achieved on industrial scale in a cost-efficient manner (Biofuel.org.uk, 2010). Currently, only a few pilot plant projects have been developed (e.g. BFS Bio Fuel Systems, 2015; 87 All-gas, 2012). At present, microalgae have been commercially cultivated only to obtain 88 89 valuable products like carotenoids (β-carotene and astaxanthin) and long-chain poly-90 unsatured fatty acids (Hannon et al., 2010). The main challenge that the algae biofuels 91 sector is facing is to reduce capital and operating costs and so far only few studies 92 have suggested the development of biodiesel production from microalgae on a 93 commercial scale (Brentner et al., 2011; Sevigné Itoiz et al., 2012).

Cultivation of microalgae can be done in open systems (lakes, ponds) or in controlled 94 95 closed systems called photobioreactors (PBRs). Open ponds and lagoons have lower costs but also suffer from low productivity and contamination problems. PBRs enhance 96 97 productivity, avoid cultivation contamination and are more reliable but they have high 98 capital construction and operating costs (Demirbas, 2010; Benson et al., 2014). In both 99 open and closed systems, there is a high energy requirement for mixing water with nutrients and CO₂ during the cultivation stage (Rodolfi et al., 2009). Moreover, 100 101 harvesting and dewatering of biomass lead to high costs for production facilities as well 102 as a high energy use (Brennan and Owende, 2013).

As part of the increasing research activities on algal biofuels, several Life Cycle Assessment (LCA) studies on biodiesel production from algae have been performed in order to assess their environmental performances. The results of these LCAs are conflicting, showing that only under specific conditions and assumptions the thirdgeneration biofuels could be energetically and environmentally sustainable (Lardon et al., 2009; Khoo et al., 2011; Holma et al., 2013).

This study takes origin in the encouraging results obtained by Brentner et al., 2011 on
flat panel PBRs hypothetically located in Phoenix, AZ. The location of PBRs has been

111 moved to Denmark, and a variety of technologies and implementation strategies to 112 produce biodiesel from microalgae has been analyzed. Some of these technologies have already been developed on an industrial scale to produce valuable algal 113 114 compounds while others are still on an experimental laboratory scale. Combing through 115 different technologies in the different production stages, a total of 24 scenarios have 116 been created. The energy demand and GHG emissions of the 24 scenarios and of the 117 fossil diesel have been benchmarked and compared using a 'well-to-tank' life cycle approach. The sensitivity of some parameters that could affect biodiesel production 118 119 have been evaluated.

120

121 **2** Material and methods

This study applies Life Cycle Assessment (LCA) to evaluate the environmental performance of the different scenarios. LCA quantifies the environmental impacts of a product system considering its entire life cycle and is standardized by ISO 14040/14044 (ISO, 2006a and 2006b). The method has four phases: goal and scope definition, life cycle inventory (LCI), life cycle impact assessment (LCIA), and interpretation of results. Below, data used and approaches applied in each of these phases are described.

129 2.1 Goal and scope definition

The goal of this LCA study was to assess algal biodiesel production on a hypothetical commercial scale by analyzing and comparing both consolidated (from algae-based industry) and pioneering technologies, focusing on strengths and weaknesses which influence the performance.

Assuming 39.35 MJ/kg as high heating value (HHV) (Brentner et al., 2011), the functional unit was 1 MJ of biodiesel and the system boundaries were 'well-to-tank' (i.e. from cultivation to biodiesel storage). The stages included were (Fig. 1): cultivation,

137 harvesting, drying, oil extraction, transesterification, anaerobic digestion of residual 138 biomass with subsequent biogas combustion to generate energy (Zhang et al., 2013), 139 and use of the by-product glycerol for the synthesis of propylene glycol. Substitution by 140 system expansion was considered for biogas production and glycerol use. Substitution 141 of glycerol in the production of propylene glycol has been chosen since this use is 142 claimed to be the most economically attractive within the chemical industry (Pagliaro 143 and Rossi, 2010). The algae selected was Nannochloropsis cultivated in flat panel 144 PBRs and the production was assumed to be located in Denmark. Manufacturing, 145 facilities maintenance, and use of infrastructures were not taken into account, except 146 for the materials used for PBRs. The PBRs manufacturing is included since Sevigné-147 Itoiz et al. (2012) state that construction of PBRs contributes significantly to energy use 148 and environmental impacts. On the other hand, Brentner et al. (2011), who included also construction materials in the assessment, find that those materials contribute less 149 150 than 1% to the cumulative energy demand (CED). The biodiesel combustion is not 151 included by system boundaries.

152 2.2 Life cycle inventory (LCI)

All main inventory data are shown in Table 1. As indicated most of the data were compiled from previous works and were adapted to a Danish scenario (Table 2). The databases used for obtaining the additional process data were Gabi Professional 2006 (PE International, 2007) and Ecoinvent 2.2 (Ecoinvent Centre, 2007).

157 2.2.1 Scenarios

A summary of the cultivation system and technologies assumed for each of the 24 scenarios are reported in Table 3. As shown, cultivation in either freshwater (scenarios from 1 to 6) or wastewater (scenarios from 7 to 12) were considered. The algae require an injection of CO_2 into the growth medium for optimal growth and each scenario alternatively assumed the use of either pure CO_2 (where the carbon dioxide is delivered

in tanks) or waste CO_2 (named w CO_2 , with flue gas pumped from a nearby cement production plant into the PBRs). In the harvesting stage, three techniques were assessed: flocculation with aluminum sulfate (scenarios 1, 4, 7, 10), flocculation with lime (scenarios 2, 5, 8, 11), and centrifugation (scenarios 3, 6, 9, 12). Finally, both hexane extraction (scenarios 1, 2, 3, 7, 8, 9) and s CO_2 (supercritical CO_2) extraction (scenarios 4, 5, 6, 10, 11, 12) were assessed in the oil extraction stage.

169 Consolidated technologies of the current market (i.e. flocculation, centrifugation, 170 extraction with hexane, algal cultivation in freshwater and with pure CO_2) have thus 171 been compared with advanced technologies not implemented on large scale (i.e. use of 172 wastewater and waste CO_2 , and extraction with sCO_2). The next sections, describe 173 each stage in details.

174 **2.3** Algal biomass cultivation and harvesting

Inventory data for cultivation and harvesting are showed in Table 1 and parameters
used for modeling the *Nannochloropsis* cultivation in PBRs are illustrated in Table 4.

The wastewater scenarios did not involve synthetic nutrients since wastewater is supposed to contain an adequate amount of nutrients to serve as a suitable growth medium for microalgae (Pittman et al., 2011). The CO_2 taken up during algal growth was subtracted from the total amount of CO_2 emissions in both 'pure CO_2 ' and 'waste CO_2 ' scenarios, whereas the CO_2 emissions from the production process of pure CO_2 are accounted for.

183 The water content of wet algal biomass after harvesting is assumed to be about 70%184 (Singh et al., 2012).

185 2.4 Drying and algal oil extraction

Inventory data for drying and algal oil extraction are showed in Table 1. Drying stage
was only assumed to be a requirement for hexane oil extraction since sCO₂ extraction
is carried out directly from wet biomass (Xu et al., 2011; Mendes et al., 1995).

189 We assumed the use of thermal dryers with an energy consumption around 3.3 MJ per190 kilogram of evaporated water (Xu et al., 2011).

A dry biomass content in Nannochloropsis of 29% lipid, 10% carbohydrates and 30% 191 192 proteins is hypothesized (Rodolfi et al., 2009; Razon and Tan, 2011). According to Brentner et al. (2011), the extraction efficiency with hexane is assumed to be 0.91. 193 194 Supercritical CO₂ for algal lipids extraction has been applied in laboratory on a number 195 of algal species: Skeletonema costatum and Ochromonas danica (Polak et al., 1989), Chlorella vulgaris (Mendes et al., 1995), Botryococcus braunii, Dunaliella salina, 196 197 Arthrospira maxima (Mendes et al., 2003), Haematococcus pluvialis (Thana et al., 198 2008). Recently, experiments have also been started on Nannochloropsis sp. (Andrich 199 et al., 2005; Douglas, 2011; Crampon et al., 2013) but little information is reported on 200 extraction efficiency even if the authors analyze the effects of operating conditions on 201 the kinetics of the supercritical fluid extraction (Andrich et al., 2005; Crampon et al., 202 2013; Baskette, 2015). In scenarios assuming extraction with supercritical CO_2 , 27.5 203 MPa and 47.5 °C were chosen as operating conditions (Mendes et al., 1995) and the 204 extraction efficiency is assumed to be equal to the one with hexane (0.91). Neither 205 hexane nor CO_2 recycling were considered in the LCI analysis.

206 2.5 Transesterification and use of glycerol

The amount of electricity and heat used in transesterification stage are shown in Table 1. The conversion efficiency was hypothesized 98% (Brentner et al., 2011) and the catalyst used was methanol. The avoided production of propylene oxide has been calculated on the basis of the stoichiometric ratio and the process yields of the involved reactions. Data for propylene oxide to propylene glycol were from Ecoinvent 2.2 (Ecoinvent Centre, 2007), data for glycerol to propylene glycol were from Pagliaro et al. (2007); the yields were 95% and 73%, respectively.

214 2.6 Life cycle impact assessment (LCIA)

The LCIA method applied was IMPACT 2002+ which proposes a feasible implementation of a combined midpoint/damage approach (Humbert et al., 2012). The chosen impact categories have been: global warming potential (GWP) and nonrenewable energy consumption. For each scenario, the performances of algal biodiesel were compared with those of fossil diesel (from Ecoinvent 2.2; Ecoinvent Centre, 2007).

221 2.7 Sensitivity analysis

The sensitivity analysis estimates the influence of assumptions, i.e. changes in input parameters, on the model outcome (ISO, 2006a; ISO, 2006b). Among all the possible parameters to be considered for the sensitivity analysis, we have selected two. The first parameter is the extraction efficiency ranging from 0.91 in the Base case (extraction efficiency with hexane, Brentner et al., 2011) to 0.95 in the Case 1 (extraction efficiency with supercritical CO_2 , Brentner et al., 2011).

The second parameter considered is the lipid content in the algal biomass which can vary dramatically as a result of the nitrogen supply (Jorquera et al., 2010; Khoo et al., 2011; Razon and Tan, 2011). The considered range of lipid content varies from 29% (lipid content experimentally observed in standard conditions by Rodolfi et al., 2009) to 60% (lipid content experimentally observed under nitrogen deprivation conditions by Rodolfi et al., 2009).

234

235 3 Results and discussion

The results generally show that 'pure' CO_2 (grey columns, Fig.2 and Fig.3) causes GHG emissions and energy consumption at least 25%-30% higher than waste CO_2 (white columns, Fig.2 and Fig.3). This agrees well with the results obtained by Borkowski et al. (2012) which demonstrated that the use of waste CO_2 for algae cultivation in PBR from a nearby power plant decreased GHG emissions by about 50%
compared to the use of 'pure' CO₂.

In general, GWP of biodiesel scenarios is one order of magnitude higher than GWP of 242 fossil diesels (black column, Fig.2). Only the last three scenarios (Sc10-wCO₂, Sc11-243 wCO₂ and Sc12-wCO₂) show GHG emissions similar to or lower than those of fossil 244 245 diesel. The last three scenarios achieve the best performances also considering non-246 renewable energy consumption (Fig. 3), even if this is considerably higher compared to fossil diesel. This indicates that the coupling of the 'waste flows' for algal cultivation 247 with the use of sCO₂ for algal oil extraction – that avoids the drying stage – could be an 248 249 interesting production system. The best scenario is Sc10-wCO₂ (flocculation with 250 aluminum sulphate) which shows a negative GWP indicating a GHG sequestration and 251 the lowest energy consumption. The result is in accordance with the studies by Lardon 252 et al. (2009) which observed that only wet extraction can save GHG emissions in algal 253 biodiesel production and by Vasudevan et al. (2012) which calculated very low GHG 254 emissions (0.053 kg of CO₂ eq/MJ) when wet extraction was applied. Also Xu et al. 255 (2011) observed that wet extraction dramatically decreases energy consumption.

Interesting information is provided by the 'non-renewable energy investment in energy 256 257 delivered' (NEIED) (Yang and Chen, 2012). NEIED is expressed as the ratio between the non-renewable energy used directly and indirectly in the production process and 258 the energy content in the biofuel. In this study the NEIED is >1 in all 24 scenarios. In 259 260 particular, in our simulations algal biodiesel production requires from 20 MJ (Sc10-261 wCO₂) to 90 MJ (Sc3-CO₂) for producing 1 MJ of biodiesel. These values are very high 262 but comparable with results obtained by other authors. Jorquera et al. (2010) find a 263 consumption of about 14 MJ/MJ for tubular PBRs including only cultivation stage and Sevigné Itoiz et al. (2012) report a consumption of 901 MJ/kg of DW biomass for indoor 264 PBRs. In fact, cultivation in PBRs has a large energy demand due to the CO_2 pumping 265 266 and nutrients mixing (Weinberg et al., 2012; Borkowski et al., 2012; Khoo et al., 2011).

Below we evaluate the relative contributions to GWP and non-renewable energy consumption of each stage in the worst (Sc3-CO₂) and the best scenarios (Sc10wCO₂). The stages analyzed are: 1) algae cultivation; 2) harvesting; 3) (drying and) oil extraction; 4) transesterification; 5) anaerobic digestion (of residual biomass) and 6) use of glycerol.

272 Figure 4 illustrates the relative contributions in the worst scenario. As shown, the 273 cultivation stage has the highest contribution to GWP and non-renewable energy 274 consumption (62% and 66%, respectively), followed by drying and oil extraction (23% 275 and 24%, respectively) and harvesting through centrifugation (15% and 13%, 276 respectively). Anaerobic digestion contributes by avoiding GHG emissions and non-277 renewable energy consumption (both about -2%) while transesterification and use of 278 glycerol in the propylene oxide industry do not give a relevant contribution. These 279 results completely agree with previous studies. Many authors observed that cultivation 280 (Batan et al., 2010; Borkowski et al., 2012; Weinberg et al., 2012), drying (Razon and 281 Tan, 2011; Xu et al., 2011) and lipid extraction (Khoo et al., 2011) were the most 282 impacting stages for biodiesel production both in terms of GHG emissions and energy 283 requirements.

284 Figure 5 illustrates the best scenario. As far as GWP concerns, cultivation (-40%) and anaerobic digestion (-25%) contribute by avoiding GHG emissions while the most 285 impacting stages are harvesting (15%) and sCO₂ extraction (15%). Transesterification 286 287 and the glycerol use are negligible. Regarding non-renewable energy consumption, the 288 most significant process is algae cultivation (92%) while the other stages have a very 289 low contribution. The negative contribution of cultivation on GHG emissions is due to 290 the sequestration of CO_2 in the algal cells and to the use of wastewater which eliminate 291 the need of fertilizer production. However, these improvements do not eliminate the 292 need of electric power during the cultivation stage. As a final result, in the best-case scenario we have an increment of the cultivation stage contribution to the energy 293

consumption. This is due to the fact that the energy demand of the algal harvesting and
lipid extraction stages decreases in comparison to the worst case.

296

The percentage contribution analysis has identified three stages as the bottlenecks of algal biodiesel production: cultivation, drying and oil extraction, and harvesting.

299 Regarding the cultivation stage, the contribution of the different processes to the 300 environmental impact are detailed in the Supplementary Data, figures 2.1, 2.2, 2.3 and 301 2.4. Electricity is always a significant contributor and when 'pure' CO₂ and/or nutrients 302 are required these contribute significantly as well. The contributions of nutrients, CO_2 , 303 and electricity vary for the different scenarios. Contributions from construction 304 materials, low density polyethylene (LDPE) sheets and reinforcing steel, are always negligible. Considering the performances of Sc10-wCO₂, Sc11-wCO₂ and Sc12-wCO₂ 305 306 scenarios, it is evident that the capability to cultivate algae using waste flows (aqueous 307 and gaseous) plays a fundamental role for an environmental beneficial development of 308 large scale biodiesel production from microalgae. Anyway, these technologies need to be improved further to become efficient, affordable and accessible. Currently, the 309 cultivation of algae in wastewater has not been developed on commercial scale yet but 310 311 only on pilot plants. Several challenges exists, e.g. the high turbidity of wastewater 312 restricting the light penetration and making the algal cultivation inefficient (Pedroni et al., 2001). Therefore, a water clarification pre-treatment could be necessary in order to 313 314 reduce the presence of suspended matter and organic load (Pedroni et al., 2001). Also 315 the use of waste CO_2 is still experimental on a pilot scale. The main issues to be solved 316 are the transfer of waste flue gas from an industrial plant to PBRs and the CO₂ losses 317 during this transfer. In fact, the energy demand for pumping the flue gas and the 318 distance from the plant to PBRs limit this transfer (Pedroni et al., 2001). Moreover, it is 319 challenging to control the O₂-concentration and the temperature which has to be 320 reduced from above 100℃ to app. 25℃ (Dorminey, 20 13). Additionally, flue gases

321 contain pollutants such as NOx and SO_2 which may have adverse effects on the algal 322 species. However, first findings from studies reveal that the presence of pollutants in 323 the flue gas in today's industrial emissions seems to be less of a problem in relation to 324 the growth of the algae (Mortensen and Gislerød, 2014).

325

326 The drying and oil extraction stage is the second relevant bottleneck. Oil extraction with 327 the sCO₂-process decreases the impact contribution because it does not require drying of the algal biomass. Also in this case, the 'key' technology is very innovative and must 328 329 be further enhanced. Mendes et al. (1995) observed that higher pressures and 330 temperatures led to higher efficiencies in the extraction of lipids but Santana et al. 331 (2012) found a correlation between the pressure and the presence of unsaturated compounds, i.e. high pressure leads to high amounts of unsaturated compounds in the 332 algal oil thus reducing the biodiesel quality. 333

334

In terms of energy consumption and GHG emissions, the harvesting stage also played 335 336 a significant role. In general, flocculation requires less energy than centrifugation; in 337 particular, Nannochloropsis centrifugation has a large energy demand due to the small 338 size of the cells (Rodolfi et al., 2009). This in line with Sander and Murthy (2010) who also identified a high energy demand of centrifugation (50% higher than flocculation) in 339 340 comparison to other algal harvesting technologies such as separation or filtration. 341 Flocculation with aluminum sulphate (scenarios 1, 4, 7, 10) and with lime (scenarios 2, 342 5, 8, 11) show similar GHG emissions and energy performances, see Fig. 2 and Fig. 3. 343 However, although flocculation requires less energy than centrifugation, both 344 flocculants present some disadvantages. The main product of flocculation with aluminum sulphate is aluminum hydroxide which forms aggregates with algal biomass 345 rendering it toxic for methanogens during anaerobic digestion (Demirbas, 2010). Even 346

if lime is less toxic than aluminum sulphate, it is less used for flocculation due to the precipitate formation, i.e. $CaCO_3$, in the water (Pedroni et al., 2001).

A possible improvement with respect to both flocculation and centrifugation could be the development of bio-flocculation (Pedroni et al., 2001). Bio-flocculation is biologically induced by bacteria (Lee et al., 2009). Recently, a naturally flocculating diatom *Skeletonema* was used to form flocs of *Nannochloropsis* (Schenk et al., 2008). Bioflocculation is not toxic for microalgae, it requires low operating costs, and has a low energy demand. However, bio-flocculation is affected by environmental conditions which are the most relevant aspects to improve (Schenk et al., 2008).

356 **4 Sensitivity analysis**

Tables 5A and 5B present the results of the sensitivity analysis. Increasing extraction efficiency from 0.91 to 0.95, results in lower values for GWP and non-renewable energy consumption (about 5% less than Basic Case).

Likewise, increasing the lipid content from 29% to 60% reduces both GHG emissions 360 and energy consumption by app. 50%. Therefore, lipid content was confirmed as an 361 important parameter for biodiesel production. Nonetheless, even with high lipid content 362 the energy and GHG emissions performances of algal biodiesel are still inferior to 363 those of diesel from fossil sources. These results are in agreement with the observation 364 of Khoo et al. (2011) and Razon and Tan (2011). In particular, Khoo et al. (2011) 365 demonstrated that increasing the lipid content by about 10% and 20% decreased the 366 367 energy consumption by about 4% and 6%, respectively.

368 **5** Conclusion

Algal biodiesel produced through current conventional technologies shows higher energy demand and GHG emissions than those of fossil diesel. 'Wastewater scenarios' coupled with waste CO_2 have the lowest impact in GHG-emissions and non-renewable energy consumption, in some cases even better than fossil diesel in terms of GHG-

373 emissions. However, a positive energy balance is still far from being achieved by algal 374 biodiesel. Thus, further improvements are required in order to achieve a beneficial development of biodiesel production on an industrial scale. In particular, different 375 376 aspects of cultivation need to be enhanced, such as the use of wastewater as source of nutrient and CO₂-rich flue gas from industrial power plants as source of carbon. The 377 378 research has been addressed towards algae cultivation with 'waste flows', that seems 379 to be the key to reduce both the demand of energy and the GHG-emissions of biodiesel from microalgae. Additionally, the energy demand for mixing, pumping, etc. of 380 381 the cultivation stage should be dramatically decreased. Considering the extraction, 382 supercritical CO₂ extraction appears to be an interesting technology. However, further studies are needed to address the main limitations; how to achieve high temperatures 383 and high pressures and still avoiding the formation of unsaturated compounds. 384

385

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393 **References**

Aitken, D., Bulboa, C., Godoy-Faundez, A., Turrion-Gomez, J.L., Antizar-Ladislao, B.,
2014. Life cycle assessment of macroalgae cultivation and processing for biofuel
production. J. Clean. Prod. 75, 45–56.

- 397 Andrich, G., Nesti, U., Venturi, F., Zinnai, A., Fiorentini, R., 2005. Supercritical fluid
- 398 extraction of bioactive lipids from the microalga *Nannochloropsis sp.* Eur. J. Lipid Sci.
- 399 Technol. 107, 381–386.
- 400 Batan, L., Quinn, J., Willson, B., Bradley, T., 2010. Net energy and greenhouse gas
- 401 emission evaluation of biodiesel derived from microalgae. Environ. Sci. Technol. 44,
- 402 **7975–7980**.
- 403 Benson, D., Kerry, K., Malin, G., 2014. Algal biofuels: impact significance and 404 implications for EU multi-level governance. J. Clean. Prod. 72, 4–13.
- Borkowski, M.G., Zaimes, G.G., Khanna, V., 2012. Integrating LCA and thermodynamic
 analysis for sustainability assessment of algal biodiesel. Sustainable Systems and
- 407 Technology (ISSST). Proceedings of IEEE International Symposium. Boston, 16th-18th
 408 May 2012.
- Brentner, L.B., Eckelman, M.J., Zimmerman, J.B., 2011. Combinatorial Life Cycle
 Assessment to inform process design of industrial production of algal biodiesel.
 Environ. Sci. Technol. 45, 7060–7067.
- 412 Brennan, L., Owende, P., 2013. Biofuels from microalgae: towards meeting advanced
- fuel standards, in: Lee, W.J. (Ed.), Advanced Biofuels and Bioproducts. Springer, New
 York, pp. 553–599.
- Clarens, A.F., Resurreccion, E.P., White, M.A., Colosi, L.M., 2010. Environmental life
 cycle comparison of algae to other bioenergy feedstocks. Environ. Sci. Technol. 44,
 1813–1819.
- Crampon, C., Mouahid, A., Toudji, S.A., Lépine, O., Badens, E., 2013. Influence of
 pretreatment on supercritical CO2 extraction from *Nannochloropsis oculata*. J.
 Supercrit. Fluid. 79, 337–344.
- 421 Demirbas, A., 2010. Use of algae as a biofuel sources. Energ. Convers. Manage. 51,
 422 2738–2749.

- 423 Demirbas, A., 2011. Biofuels from algae for sustainable development. Appl. Energ. 88,
 424 3473–3480.
- Douglas, N., 2011. Extract characteristics of supercritical carbon dioxide extraction of
 Nannochloropsis oculata. Thesis, Colorado State University, pp. 89.
- 427 Ecoinvent centre, 2007. Ecoinvent Data and Reports v2.0 Final Reports Ecoinvent
- 428 2000. Swiss Centre for Life Cycle Inventories, Dübendorf, Switerland.
- 429 European Commission, 2009. Directive 2009/28/EC of the European Parliament and of
- 430 the Council of 23 April 2009 on the promotion of the use of energy from renewable
- 431 sources and amending and subsequently repealing Directives 2001/77/EC and
- 432 2003/30/EC. Official Journal of the European Union, Volume 52, 5 June 2009.
- 433 Festel, G., Würmseher, M., Rammer, C., Boles, E., Bellof., 2014. Modelling production
- 434 cost scenarios for biofuels and fossil fuels in Europe. J. Clean. Prod. 66, 242–253.
- Foley, P.M., Beach, E.S., Zimmerman, J.B., 2011. Algae as a source of renewable
 chemicals: opportunities and challenges. Green Chem. 13, 1399–1405.
- 437 Grima, E.M., Belarbi, E.H., Acien Fernandez, F.G., Robles Medina, A., Chisti, Y., 2003.
- 438 Recovery of microalgal biomass and metabolites: process options and economics.
- 439 Biotechnol. Adv. 20, 491–515.
- 440 Grobbelaar, J.U., 2004. Algal nutrition, in: Richmond, A. (Ed.), Handbook of microalgal
- 441 culture: biotechnology and applied phycology. Blackwell Publishing Ltd., Oxford, pp.442 97–115.
- Hannon, M., Gimpel, J., Tran, M., Rasala, B., Mayfield, S., 2010. Biofuels from algae:
 challenges and potential. Biofuels. 5, 763–784.
- Holma, A., Koponen, K., Antikainen, R., Lardon, L., Leskinen, P., Roux, P., 2013.
 Current limits of life cycle assessment framework in evaluating environmental
 sustainability e case of two evolving biofuel technologies. J. Clean. Prod. 54, 215–228.
 Humbert S., De Schryver A., Bengoa X., Margni M., Jolliet O., 2012. IMPACT 2002+:
 User guide.
 - 18

- ISO 2006a. Environmental Management-Life Cycle Assessment-Principles and
 Framework, second ed., ISO 14040; 2006-07-01; ISO: Geneva, Switzerland.
- ISO, 2006b. Environmental Management-Life Cycle Assessment-Requirements and
 Guidelines, first ed., ISO 14040; 2006–07-01; ISO: Geneva, Switzerland.
- Jorquera, O., Kiperstok, A., Sales, E.A., Embiruçu, M., Ghirardi, M.L., 2010.
 Comparative energy life-cycle analyses of microalgal biomass production in open
 ponds and photobioreactors. Bioresource Technol. 101, 1406–1413.
- 457 Khoo, H.H., Sharratt, P.N., Das, P., Balasubramanian, R.K., Naraharisetti, P.K., Shaik,

S., 2011. Life cycle energy and CO₂ analysis of microalgae-to-biodiesel: Preliminary
results and comparisons. Bioresource Technol. 102, 5800–5807.

- 460 Kumar, A., Ergas, S., Yuan, X., Sahu, A., Zhang, Q., Dewulf, J., Malcata, F. X., Van
- Langenhove, H., 2010. Enhanced CO₂ fixation and biofuel production via microalgae:
 recent developments and future directions. Trends Biotechnol. 28, 371–380.
- Lardon, L., Helias, A., Sialve, B., Steyer, J. P., Bernard, O., 2009. Life Cycle
 Assessment of Biodiesel Production from Microalgae. Environ. Sci. Technol. 43, 6475–
 6481.
- 466 Lee, A.K., Lewis, D.M., Ashman, P.J., 2009. Microbial flocculation, a potentially low-
- 467 cost harvesting technique for marine microalgae for the production of biodiesel. J. Appl.
 468 Phycol. 21, 559–567.
- Liew, W.H., Hassim, M.H., Ng, D.K.S., 2014. Review of evolution, technology and sustainability assessments of biofuel production. J. Clean. Prod. 71, 11–29.
- 471 Lü, J., Sheahan, C., Fu, P., 2011. Metabolic engineering of algae for fourth generation
 472 biofuels production. Energy Environ. Sci. 4, 2451–2466.
- 473 Mendes, R.L., Fernandes, H.L., Coelho, J.P., Reis, E.C., Cabral, J.M.S., Novais, J.M.,
- 474 Palavra, A.F., 1995. Supercritical CO₂ extraction of carotenoids and other lipids from
- 475 Chlorella vulgaris. Food Chem. 53, 99–103.

- 476 Mendes, R.L., Nobre, B.P., Cardoso, M.P., Pereira, A.P., Palavra, A.F., 2003.
- 477 Supercritical carbon dioxide extraction of compounds with pharmaceutical importance
- 478 from microalgae. Inorg. Chim. Acta. 356, 328-334.
- 479 Mortensen, L.M., Gislerød, H.R., 2014. The effect on growth of Chlamydomonas
- 480 *reinhardtii* of flue gas from a power plant based on waste combustion. AMB Express, 4,
- **481 49–54**.
- 482 Pagliaro, M., Ciriminna, R., Kimura, H., Rossi, M., Della Pina, C., 2007. From Glycerol
 483 to value-added products. Angew. Chem. Int. Edit. 46, 4434–4440.
- 484 Pagliaro, R., Rossi, M., 2010. Future of Glycerol: 2nd Edition. Royal Society of
 485 Chemistry, London, UK.
- 486 Pedroni, P., Davison, J., Beckert, H., Bergman, P., Benemann, J., 2001. A proposal to
- 487 establish an international network on biofixation of CO2 and greenhouse gas488 abatement with microalgae. J. Energy Environ. Res. 1, 136–150.
- 489 PE International, 2007. GaBi Professional Database. http://documentation.gabi490 software.com (accessed October 2013).
- 491 Pittman, J.K., Dean, A.P., Osundeko, O., 2011. The potential of sustainable algal
 492 biofuel production using wastewater resources. Bioresource Technol. 102, 17–25.
- 493 Polak, J.T., Balaban, M., Peplow, A., Philips, A.J., 1989. Supercritical carbon dioxide
- 494 extraction of lipids from algae, in: Johnston, K.P., Penninger, J.M.L. (Eds.), ACS
- 495 Symposium Series:406. Supercritical Fluid Science and Technology. American
 496 Chemical Society, Washington D.C., pp. 449-467.
- Razon, L.F., Tan, R.R., 2011. Net energy analysis of the production of biodiesel and
 biogas from the microalgae: *Haematococcus pluvialis* and *Nannochloropsis* sp. Appl.
- 499 Energ. 88, 3507–3514.
- 500 Ribeiro, K.S., Kobayashi, S., Beuthe, M., Gasca, J., Greene, D., Lee, D.S., Muromachi,
- 501 Y., Newton, P.J., Plotkin, S., Sperling, D., Wit, R., Zhou, P.J., 2007. Transport and its
- 502 infrastructure. In Climate Change 2007: Mitigation. Contribution of Working Group III to

- 503 the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [B.
- 504 Metz, O.R. Davidson, P.R. Bosch, R. Dave, L.A. Meyer (eds)], Cambridge University
- 505 Press, Cambridge, United Kingdom and New York, NY, USA.
- 506 Rodolfi, L., Chini Zittelli, G., Bassi, N., Padovani, G., Biondi, N., Bonini, G., Tredici, M.
- 507 R., 2009. Microalgae for Oil: Strain Selection, Induction of Lipid Synthesis and Outdoor
- 508 Mass Cultivation in a Low-Cost Photobioreactor. Biotechnol. Bioeng. 102, 100–112.
- 509 Sander, K., Murthy, G.S., 2010. Life cycle analysis of algal biodiesel. Int. J. Life Cycle
- 510 Assess. 15, 704–714.
- 511 Santana, A., Jesus, S., Larrayoz, M. A., Filho, R. M., 2012. Supercritical carbon dioxide
- 512 extraction of algal lipids for the biodiesel production. Procedia Eng. 42, 1755–1761.
- 513 Schenk, P.M., Thomas-Hall, S.R., Stephens, E., Marx, U., Mussgnug, J.H., Posten, C.,
- 514 Kruse, O., Hankamer, B., 2008. Second generation biofuels: high-efficiency microalgae
- 515 for biodiesel production. Bioenerg. Res. 1, 20–43.
- 516 Scott, S.A., Davey, M.P., Dennis, J.S., Horst, I., Howe, C.J., Smith, D.J.L., Smith, A.G.,
- 517 2010. Biodiesel from algae: challenges and prospects. Curr. Opin. Biotech. 21, 277–
 518 286.
- 519 Sevigné-Itoiz, E., Fuentes-Grunewald, C., Gasol, C. M., Garces, E., Alacid, E., Rossi,
- 520 S., Rieradevall, J., 2012. Energy balance and environmental impact analysis of marine
- 521 microalgal biomass production for biodiesel generation in a photobioreactor pilot plant.
- 522 Biomass. Bioenerg. 39, 324–335.
- 523 Singh, A., Nigam, P.S., Murphy, J.D., 2011. Mechanism and challenges in 524 commercialisation of algal biofuels. Bioresour. Technol. 102, 26–34.
- Singh, A., Pant, D., Olsen, S.I., Nigam, P.S, 2012. Key issues to consider in microalgae
 based biodiesel production. Int. J. Energ. Res. 29, 687–700.
- 527 Singh, A., Olsen, S.I., 2012. Comparison of algal biodiesel production pathways using
- 528 Life Cycle Assessment tool, in: Singh, A., Pant, D., Olsen, S.I. (Eds.), Life Cycle
- 529 Assessment of Renewable Energy Sources. Springer-Verlag, London, pp. 145–168.

- 530 Thana, P., Machmudah, S., Goto, M., Sasaki, M., Pavasanta, P., Shotipruka, A., 2008.
- 531 Response surface methodology to supercritical carbon dioxide extraction of 532 astaxanthin from *Haematococcus pluvialis*. Bioresour. Technol. 99, 3110–3115.
- 533 Vasudevan, V., Stratton, R. W., Pearlson, M. N., Jersey, G. R., Beyene, A. G.,
- 534 Weissman, J. C., Rubino, M., Hileman, J. I., 2012. Environmental Performance of Algal
- 535 Biofuel Technology Options. Environ. Sci. Technol. 46, 2451–2459.
- 536 Weinberg, J., Kaltschmitt, M., Wilhelm, C., 2012. Analysis of greenhouse gas 537 emissions from microalgae-based biofuels. Biomass Conv. Bioref. 2, 179–194.
- 538 Wijffels, R.H, Barbosa, M.J., 2010. An outlook on microalgal biofuels. Science. 329,
- 539 **796–799**.
- 540 Xu, L., Brilman, D.W.F., Withag, J.A.M., Brem, G., Kersten, S., 2011. Assessment of a
- 541 dry and a wet route for the production of biofuels from microalgae: Energy balance 542 analysis. Bioresour. Technol. 102, 5113–5122.
- Yang, Q., Chen, G.Q., 2012. Nonrenewable energy cost of corn-ethanol in China.
 Energ. Policy. 41, 340–347.
- 545 Zhang, L.X., Wang, C.B., Song, B., 2013. Carbon emission reduction potential of a
- 546 typical household biogas system in rural China. J. Clean. Prod. 47, 415–421.
- 547

548 Web References

- 549 All-gas, 2012. Available at: <u>http://www.all-gas.eu/Pages/default.aspx</u>. (accessed 550 15.03.2015).
- 551 Baskette, R., 2015. Supercritical carbon dioxide extraction of microalgae oils for
- 552 biodiesel production. Supercritical Fluid Technologies, INC. Available at:
- 553 <u>http://www.supercriticalfluids.com/wp-content/uploads/TN-115-Supercritical-Carbon-</u>
- 554 <u>Dioxide-Extraction-of-Microalgae-Oils-for-Biodiesel-Production.pdf</u> (accessed
- 555 15.03.2015).

- 556 BFS Bio Fuel Systems. Available at: <u>http://www.biopetroleo.com/</u>. (accessed
- 557 15.03.2015).
- 558 Biofuel.org.uk, 2010. Third Generation Biofuels. Available at: <u>http://biofuel.org.uk/third-</u>
- 559 <u>generation-biofuels.html</u> (accessed 15.07.2015).
- 560 Danish Meteorological Institute, 2013. Available at: http://www.dmi.dk/en/vejr/
- 561 (accessed 15.03.2015).
- 562 Dorminey, B., 2013. A new win-win? CO2-eating microalgae as a biofuel feedstock.
- 563 GENI Global Network Energy Institute. Available at:
- 564 <u>http://www.geni.org/globalenergy/library/technical-articles/</u> (accessed 15.03.2015)
- 565 US EIA (US Energy Information Administration), 2015. International Energy Statistics.
- 566 Available at: <u>http://www.eia.gov/</u> ((accessed 15.07.2015).
- 567

Table 1 569

- Summary of the inventory data for producing 1 MJ of algal biodiesel 570
- (HHV=39.35 MJ/kg of biodiesel). 571

FRESHWATER CULTIVATION	AMOUNT	UNIT	NOTES
Carbon dioxide	0.61	kg	Calculated from 1
Tap water	0.47	m ³	Calculated from 2
Electricity consumption	0.78	kWh	Calculated from 2
Ammonium nitrate	0.08	kg	Calculated from 3
Monocalcium phosphate	0.03	kg	Calculated from 3
WASTEWATER CULTIVATION			
Carbon dioxide	0.61	kg	Calculated from 1
Wastewater	0.47	m ³	Calculated from 2
Electricity consumption	0.78	kWh	Calculated from 2
FLOCCULATION			
Electricity consumption	0.05	kWh	Calculated from 2
Aluminium sulphate	0.04	kg	Calculated from 4
Lime	0.15	kg	Calculated from 5
CENTRIFUGATION			
Electricity consumption	0.11	kWh	Calculated from 6
DRYING			
Heat	1.12	MJ	Calculated from 7
EXTRACTION WITH HEXANE			
Electricity consumption	0.01	kWh	Calculated from 2
Heat	0.10	MJ	Calculated from 2
Hexane	0.39	g	Calculated from 5
SUPERCRITICAL CO ₂			
EXTRACTION			
CO ₂ liquid	3.7	g	Calculated from 8
Electricity consumption	0.18	kWh	Calculated from 9
TRANSESTERIFICATION			
Electricity consumption	0.001	kWh	Calculated from 2
Heat	0.02	MJ	Calculated from 2
Methanol	2.9	g	Calculated from 5

589 1: Wijffels and Barbosa, 2010

- 590 2: Brentner et al., 2011
- 591 3: Grobbelaar, 2004
- 592 4: Grima et al., 2003
- 593 5: Lardon et al., 2009
- 594 6: Foley et al., 2011 595
- 7: Xu et al., 2011
- 596 8: Mendes et al., 1995 597 9: Singh and Olsen, 2012
- 598

600 Table 2

601 Parameters and processes used in the study adapted to the Danish situation.

PARAMETERS	AMOUNT	UNIT	REFERENCES
Denmark's electricity mix	-	-	Ecoinvent 2.2
Reference year of electricity mix	2004		Ecoinvent 2.2
Denmark's carbon intensity	0.2	kg CO ₂ /2005 US \$	US EIA, 2015
Average solar irradiation in Denmark	3730	MJ/m2/y	Danish Meteorological Institute, 2013
Productivity days	200	n°	Danish Meteorological Institute, 2013
CO ₂ emission from Danish cement industry	1420067	t/y	Singh and Olsen, 2012

606 **Table 3**

607 Summary of cultivation systems and technologies used for each analysed

608 scenario.

CODE			HARVESTING	EXTRACTION
CODE		WATER SOURCE	MODE	MODE
Sc1-CO ₂	Pure CO ₂	Tap water	Aluminum sulfate	With hexane
Sc1-wCO ₂	Waste CO ₂	Tap water	Aluminum sulfate	With hexane
Sc2-CO ₂	Pure CO ₂	Tap water	Lime	With hexane
Sc2-wCO ₂	Waste CO ₂	Tap water	Lime	With hexane
Sc3-CO ₂	Pure CO ₂	Tap water	Centrifugation	With hexane
Sc3-wCO ₂	Waste CO ₂	Tap water	Centrifugation	With hexane
Sc4-CO ₂	Pure CO ₂	Tap water	Aluminum sulfate	Supercritical CO ₂
Sc4-wCO ₂	Waste CO ₂	Tap water	Aluminum sulfate	Supercritical CO ₂
Sc5-CO ₂	Pure CO ₂	Tap water	Lime	Supercritical CO ₂
Sc5-wCO ₂	Waste CO ₂	Tap water	Lime	Supercritical CO ₂
Sc6-CO ₂	Pure CO ₂	Tap water	Centrifugation	Supercritical CO ₂
Sc6-wCO ₂	Waste CO ₂	Tap water	Centrifugation	Supercritical CO ₂
Sc7-CO ₂	Pure CO ₂	Wastewater	Aluminum sulfate	With hexane
Sc7-wCO ₂	Waste CO ₂	Wastewater	Aluminum sulfate	With hexane
Sc8-CO ₂	Pure CO ₂	Wastewater	Lime	With hexane
Sc8-wCO ₂	Waste CO ₂	Wastewater	Lime	With hexane
Sc9-CO ₂	Pure CO ₂	Wastewater	Centrifugation	With hexane
Sc9-wCO ₂	Waste CO ₂	Wastewater	Centrifugation	With hexane
Sc10-CO ₂	Pure CO ₂	Wastewater	Aluminum sulfate	Supercritical CO ₂
Sc10-wCO ₂	Waste CO ₂	Wastewater	Aluminum sulfate	Supercritical CO ₂
Sc11-CO ₂	Pure CO ₂	Wastewater	Lime	Supercritical CO ₂
Sc11-wCO ₂	Waste CO ₂	Wastewater	Lime	Supercritical CO ₂
Sc12-CO ₂	Pure CO ₂	Wastewater	Centrifugation	Supercritical CO ₂
Sc12-wCO ₂	Waste CO ₂	Wastewater	Centrifugation	Supercritical CO ₂

611 Table 4

612 Parameters used for modelling the *Nannochloropsis* cultivation in PBRs.

PARAMETERS	AMOUNT	UNIT	REFERENCES
Nannochloropsis productivity	0.27	kg/m³/day	Jorquera et al., 2010
Biomass productivity	37.8	t/ha/year	Singh and Olsen, 2012
Number of PBR	2667	per hectare	Brentner et al., 2011
PBR lenght	2.5	m	Brentner et al., 2011
PBR height	1.5	m	Brentner et al., 2011
PBR thick	0.070	m	Brentner et al., 2011
PBR volume	0.263	m ³	Brentner et al., 2011
Residence time	2.6	days	Brentner et al., 2011
Area	3.75	m²	Brentner et al., 2011
LDPE sheet	0.011	kg/kg biomass	Brentner et al., 2011
Life time	50	years	Brentner et al., 2011
Steel	0.00085	kg/kg biomass	Brentner et al., 2011
Life time	50	years	Brentner et al., 2011

615 **Table 5A**

Results of the sensitivity analysis for GWP (kg CO2-eq). Basic case (91% extraction efficiency and 29% lipid content) compared to the increase of extraction efficiency (95%) and lipid content (60%). The functional unit is 1 MJ

of biodiesel.

CODE	BASIC CASE	EXTRACTION EFFICIENCY 95%	LIPID CONTENT 60%
Sc1-CO ₂	5.95E+00	5.70E+00	2.90E+00
Sc1-wCO ₂	3.11E+00	2.98E+00	1.53E+00
Sc2-CO ₂	6.23E+00	5.97E+00	3.04E+00
Sc2-wCO ₂	3.39E+00	3.25E+00	1.67E+00
Sc3-CO ₂	6.71E+00	6.43E+00	3.28E+00
Sc3-wCO ₂	3.88E+00	3.72E+00	1.90E+00
Sc4-CO ₂	4.60E+00	4.41E+00	2.25E+00
Sc4-wCO ₂	1.77E+00	1.69E+00	8.83E-01
Sc5-CO ₂	4.88E+00	4.68E+00	2.39E+00
Sc5-wCO ₂	2.05E+00	1.96E+00	1.02E+00
Sc6-CO ₂	5.37E+00	5.14E+00	2.62E+00
Sc6-wCO ₂	2.54E+00	2.43E+00	1.25E+00
Sc7-CO ₂	4.01E+00	3.84E+00	1.97E+00
Sc7-wCO ₂	1.18E+00	1.13E+00	5.96E-01
Sc8-CO ₂	4.29E+00	4.11E+00	2.10E+00
Sc8-wCO ₂	1.46E+00	1.40E+00	7.32E-01
Sc9-CO ₂	4.78E+00	4.58E+00	2.34E+00
Sc9-wCO ₂	1.94E+00	1.86E+00	9.67E-01
Sc10-CO ₂	2.66E+00	2.55E+00	1.32E+00
Sc10-wCO ₂	-1.67E-01	-1.60E-01	-8.32E-02
Sc11-CO ₂	2.94E+00	2.82E+00	1.45E+00
Sc11-wCO ₂	1.13E-01	1.08E-01	5.61E-02
Sc12-CO ₂	3.43E+00	3.29E+00	1.69E+00
Sc12-wCO ₂	5.99E-01	5.74E-01	3.02E-01

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623 **Table 5B**

- 624 Results of the sensitivity analysis for non-renewable energy consumption (MJ).
- 625 Basic case (91% extraction efficiency and 29% lipid content) compared to the
- 626 increase of extraction efficiency (95%) and lipid content (60%). The functional
- 627 unit is 1 MJ of biodiesel.

CODE	BASIC CASE	EXTRACTION EFFICIENCY 95%	LIPID CONTENT 60%
Sc1-CO ₂	8.27E+01	7.92E+01	4.03E+01
Sc1-wCO ₂	6.51E+01	6.24E+01	3.18E+01
Sc2-CO ₂	8.36E+01	8.01E+01	4.08E+01
Sc2-wCO ₂	6.60E+01	6.33E+01	3.23E+01
Sc3-CO ₂	9.27E+01	8.88E+01	4.52E+01
Sc3-wCO ₂	7.51E+01	7.20E+01	3.67E+01
Sc4-CO ₂	6.26E+01	6.00E+01	3.06E+01
Sc4-wCO ₂	4.50E+01	4.32E+01	2.21E+01
Sc5-CO ₂	6.36E+01	6.09E+01	3.11E+01
Sc5-wCO ₂	4.60E+01	4.41E+01	2.26E+01
Sc6-CO ₂	7.26E+01	6.96E+01	3.55E+01
Sc6-wCO ₂	5.51E+01	5.28E+01	2.70E+01
Sc7-CO ₂	5.93E+01	5.69E+01	2.91E+01
Sc7-wCO ₂	4.18E+01	4.00E+01	2.06E+01
Sc8-CO ₂	6.03E+01	5.78E+01	2.95E+01
Sc8-wCO ₂	4.27E+01	4.09E+01	2.10E+01
Sc9-CO ₂	6.94E+01	6.65E+01	3.39E+01
Sc9-wCO ₂	5.18E+01	4.96E+01	2.54E+01
Sc10-CO ₂	3.93E+01	3.77E+01	1.94E+01
Sc10-wCO ₂	2.17E+01	2.08E+01	1.09E+01
Sc11-CO ₂	4.02E+01	3.86E+01	1.98E+01
Sc11-wCO ₂	2.26E+01	2.17E+01	1.13E+01
Sc12-CO ₂	4.83E+01	4.73E+01	2.42E+01
Sc12-wCO ₂	3.17E+01	3.04E+01	1.57E+01

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631 Figure captions

Fig. 1 System boundaries of biodiesel production and the most important flowsused for each stage.

Fig. 2 GWP (kg CO₂-eq) of all 24 scenarios. CO₂ indicates the use of 'pure' CO₂

(grey column) for algae cultivation whereas wCO₂ specifies the use of waste CO₂ (white column) in microalgae cultivation stage. All scenarios have been compared to fossil diesel (black column, Ecoinvent Centre, 2007).

Fig. 3 Non-renewable energy consumption (MJ) of all 24 scenarios. CO_2 indicates the use of industrial CO_2 (grey column) for algae cultivation whereas w CO_2 specifies the use of waste CO_2 (white column) in microalgae cultivation stage. All scenarios have been compared to fossil diesel (black column, Ecoinvent Centre, 2007).

Fig. 4 Relative contribution of each stage of the worst scenario, which assumed the use of freshwater and 'pure' CO₂ for algae cultivation, centrifugation for algal harvesting and algal oil extraction with hexane. (Read the legend from top to bottom)

Fig. 5 Relative contributions of each stage of the best scenario, which assumed the use of wastewater and waste CO_2 for algae cultivation, flocculation with aluminium sulphate for algal harvesting and sCO_2 extraction in algal oil extraction. (Read the legend from top to bottom)











Supporting information for "Application of LCA approach to Energy and Greenhouse Gas Emission impact of biodiesel production from microalgae cultivated in PBRs: a case study in Denmark" submitted by Monari et al. (2013)

1. Detailed description of LCI data

The following detailed tables describe which flows are used and their correspondent processes in Gabi and which database has been used. The processes considered are cultivation (Table 1.1), harvesting and drying (Table 1.2), algal oil extraction (Table 1.3), transesterification (Table 1.4), anaerobic digestion (Table 1.5) and glycerol use (Table 1.6).

FLOWS USED FOR CULTIVATIO		
Flows	Process in Gabi	Database
Carbon dioxide (CO ₂)	RER: carbon dioxide liquid at plant	Ecoinvent
Water	RER: tap water at user	Ecoinvent
Total electricity consumption in cultivation	DK: electricity production mix	Ecoinvent
LDPE sheet	RER: polyethylene LDPE, granulate at plant	Ecoinvent
Steel	RER: reinforcing steel at plant	Ecoinvent
Ammonium nitrate	RER: ammonium nitrate, as N, at regional storehouse	Ecoinvent
Mono calcium phosphate	RER: single superphosphate, as P ₂ O ₅ , at regional storehouse	Ecoinvent
WASTEWATER CULTIVATION		
Water	Water (wastewater, untreated) [Production residues in life cycle]	Ecoinvent
Nitrogen	Nitrogen (N-compounds) [Inorganic emissions to air]	Ecoinvent
Phosphorus	Phosphorus [Inorganic emissions to air]	Ecoinvent

 Table 1.1: cultivation phase

HARVESTING		
Flows used for harvesting	Process in Gabi	Database
Electricity consumption in flocculation	DK: Electricity production mix	Ecoinvent
Aluminium sulphate	RER: aluminium sulphate powder at plant	Ecoinvent
Lime	CH: lime hydrated packed at plant	Ecoinvent
CENTRIFUGATION		
Electricity consumption in centrifugation	DK: Electricity production mix	Ecoinvent
DRYING		
Heat	RER: heat, unspecific at chemical plant	Ecoinvent

Table 1.2: harvesting and drying phases

EXTRACTION WITH HEXANE		
Flows for algal oil extraction	Process in Gabi	Database
Electricity consumption in hexane extraction	DK: electricity production mix	Ecoinvent
Heat	RER: heat unspecific at plant	Ecoinvent
Hexane	RER: hexane at plant	Ecoinvent
SCO ₂ EXTRACTION		
CO ₂ liquid	RER: carbon dioxide liquid at plant	Ecoinvent
Electricity	DK: electricity production mix	Ecoinvent

Table	1.3:	algal	oil	extra	actic	n	phase

TRANSESTERIFICATION		
Flow	Process in Gabi	Database
Electricity consumption	DK: Electricity production mix	Ecoinvent
Heat	RER: Heat unspecific at plant	Ecoinvent
Methanol	GLO: methanol at plant	Ecoinvent

 Table 1.4: transesterification phase

ANAEROBIC DIGESTION		
PRODUCTION OF BIOGAS		
Flow	Process in Gabi	Database
Electricity	CH:electricity, low voltage, at grid	Ecoinvent
Plant for Anaerobic digestion	CH: anaerobic digestion plant, biowaste	Ecoinvent
Transport	CH: transport, lorry 20-28t, fleet average	Ecoinvent
Transport for municipal waste	CH: transport, municipal waste collection, lorry 21t	Ecoinvent
Heat	RER: heat, natural gas, at boiler condensing modulating >100kW	Ecoinvent
Municipal solid waste	CH: disposal, municipal solid waste, 0 % water, to municipal incineration [municipal incineration]	Ecoinvent
Biogas from biowaste	CH: biogas, from biowaste, at storage [fuels]	Ecoinvent
ELECTRICITY FROM BIOGAS		
Lubricating oil	RER: lubricating oil, at plant	Ecoinvent
Cogen unit for electricity	RER: cogen unit 160kWe, components for electricity only	Ecoinvent
Disposal of oil	CH: disposal, used mineral oil, 10% water, to hazardous waste incineration	Ecoinvent
Cogen unit for electricity and heat	RER: cogen unit 160kWe, common components for heat+electricity	Ecoinvent
Biogas	CH: biogas, production mix, at storage [fuels]	Ecoinvent

Table 1.5: anaerobic digestion

USE OF GLYCERINE TO PRODUCE PROPYLENE GLYCOL		
Flow	Process in Gabi	Database
Electricity use	UCTE: electricity, medium voltage, production UCTE, at grid [production mix]	Ecoinvent
Heat	RER: heat, natural gas, at industrial furnace >100kW	Ecoinvent
Transport in street	RER: transport, lorry >16t, fleet average [Street]	Ecoinvent
Transport in railway	RER: transport, freight, rail [Railway]	Ecoinvent
Chemical plant	RER: chemical plant, organics	Ecoinvent

Table 1.6: glycerol use phase

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2. LCIA: the relative contributions of each unit process in cultivation phase

In this section, it is possible to observe the different processes used for cultivation and their relative weights to GWP and non renewable energy consumption for each case: freshwater cultivation and "pure CO_2 ", wastewater cultivation and "pure CO_2 ", freshwater cultivation and waste CO_2 , wastewater cultivation and waste CO_2 .



Figure 2.1: contribution of each process unit in freshwater cultivation when "pure" CO_2 is used. In this case the unit processes considered are: tap water in which phosphate, ammonium nitrate and CO_2 are added, electricity for mixing and pumping CO_2 and LDPE for PBR construction



Figure 2.2: contribution of each process unit in wastewater cultivation when "pure" CO_2 is used. In this case the unit processes considered are: wastewater (already enriched by phosphorus and nitrogen) in which CO_2 is added, electricity for mixing and pumping CO_2 and LDPE for PBR construction. In this case, the nutrients are not added to the water



Figure 2.3: contribution of each process unit in freshwater cultivation when waste CO_2 from a nearby cement industry is used for algal flow. In this case the unit processes considered are: tap water in which phosphate, ammonium nitrate and CO_2 are added, electricity for mixing and pumping CO_2 and LDPE for PBR construction. Since CO_2 is a waste flow, the negative contribution of CO_2 indicates that the flow does not take into account its production process



Figure 2.4: contribution of each process unit in wastewater cultivation when waste CO_2 from a nearby cement industry is considered. In this case the unit processes considered are: wastewater (already enriched by phosphorus and nitrogen) in which CO_2 is added, electricity for mixing and pumping CO_2 and LDPE for PBR construction. In this case, the nutrients are not added to the water and since CO_2 is a waste flow, the negative contribution of CO_2 indicates that the flow does not take into account its production process