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Highlights

- The environmental aspects of milking of microalgae for renewable hydrocarbon production have been analysed.
- Milking process have negative GHG emissions indicating that the process consumes more CO_2 onsite than those produced on the upstream.
- The renewable energy return on investment of fossil energy is slightly higher than 1.
- The energetic feasibility and carbon balance of milking process are highly dependent on the hydrocarbon contents of *B. braunii*.

Life cycle analysis of milking of microalgae for renewable hydrocarbon production

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Abstract

Botryococcus braunii is a unique microalga which can repeatedly produce the hydrocarbons after their non-destructive extraction – the process called milking. *Botryococcus braunii* hydrocarbons can be converted to high-quality fuel or used as other high-value products. In this study, we conduct the life cycle analysis of the milking process for renewable hydrocarbon production focusing on the GHG emissions, the fossil energy consumption, the freshwater consumption and the land use of the process. The total-CO_2 emissions and the GHG emissions over 100-year time span for production of *B. braunii* hydrocarbons were estimated to be -0.39 kg CO_2-eq/kg hydrocarbons and -0.90 kg CO_2-eq/kg hydrocarbons, respectively. The fossil energy ratio of the process was found to be 1.04 MJ produced/MJ fossil energy consumed. The fresh water consumption of the process and the land use were estimated to be 1802 kg/kg hydrocarbons and 0.85m^2/kg of hydrocarbons, respectively.

Keywords: Renewable fuel, *Botryococcus braunii*, Microalgae, CO_2 sequestration

1 Introduction

Carbon dioxide is a constituting component of the carbon cycle of the earth. Human activities have disturbed the natural cycle of emission and absorption of CO_2 between the atmosphere, oceans, and soil, plant, animals and microorganisms by not only emitting more CO_2 into the atmosphere but also by reducing the sinks of CO_2 such as by deforestation (Salam & Noguchi, 2005; U. B. Singh & Ahluwalia, 2013). The use of fossil fuel for power generation, transportation, and industrial processes is the major source of CO_2 emissions by human activities (EPA). Substituting biofuels for fossils is anticipated to lower the GHG emissions generated by the transportation sector. However, the conventional biofuels (first generation biofuels) use some specific food crops (such as rapeseed, palm and sugarcane) and compete with the other food crops for arable land, fertilizer and fresh water resources. Hence, they have raised many concerns over the increased food market prices and food security (A. Singh et al., 2011), and the indirect GHG emissions caused by the land-use change (Searchinger et al., 2008). The second generation biofuels which are produced from dedicated energy crops and wastes (Antizar-Ladislao & Turrion-Gomez, 2008) are not sufficient to fulfil the rising energy demand, and also associated with many technical barriers (Naik et al., 2010). Third generation biofuels are produced from microalgae. Microalgae are fast growing single cellular species which require sunlight, water, CO_2 and some other nutrients (mainly nitrogen and phosphorous) to produce organic compounds (Chisti, 2007). Unlike the higher plants, microalgae do not need arable land to grow, and can be utilized to produce biofuel, human and animal nutrients, cosmetics and pharmaceutical products without any adverse effect on the food supply (Brennan & Owende, 2010). Microalgal fuels recycle the CO_2 (Campbell et al., 2011). Based on the Redfield ratio ($C_{106}H_{263}O_{110}N_{16}P$), carbon is the most important nutrition for microalgae growth, and up to 50 % of algal biomass is made of carbon (Moheimani, Matsuura, et al., 2013). To achieve high biomass productivity, almost all algal culture requires the addition of CO_2 (Fon Sing et al., 2013; Moheimani, 2016). Some microalgal species including *Scenedesmus* and *Botryococcus braunii* can be grown efficiently by utilizing the direct flue gases from the power plant as the C source (Brennan & Owende, 2010). The use of flue gases for the growth of microalgae fixes the CO_2 resulted from the combustion of fossil fuels in the power plants before it goes to the atmosphere and the fast growth of microalgae absorbs the CO_2 at a faster rate than higher plants (U. B. Singh &

Ahluwalia, 2013). Hence, microalgae are one of the potential resources, which offer a solution for CO_2 mitigation and global energy demand without disturbing the food supply. However, the energy and cost-intensive nature of the process are the major barriers to the commercial production of algae-based biofuels. The selection of microalgal species with higher oil contents and fast growth rate, recycling of nutrients in the process, and pathways of wet processing of microalgae instead of using dried biomass are some of the major sustainability drivers of the process (Chaudry et al., 2015a).

Amongst the known microalgal species, *Botryococcus braunii* is the highest oil producing but a slow-growing alga. *Botryococcus braunii* is known to produce long-chain hydrocarbons in the extracellular matrix in contrast to the other microalgal species that produce intracellular lipids. The types of hydrocarbons produced depend on the race of *B. braunii*. Race A produces n-alkadienes (C23-C33), race B produces triterpenoids such as Botryococcenes (C30-C37) and methylated squalenes (C31-C34), and race L produces single tetraterpenoids (Lycopadienes) (Eroglu & Melis, 2010). The elemental composition of *B. braunii* hydrocarbons (86.38 % C, 11.96 % H, 0.17 % N, 1.1 % O and <1 % S) and their higher heating value (49MJ/kg) are very close to those of fossil crude oil (Chaudry et al., 2015a; Dote et al., 1994). These hydrocarbons can not only be converted to high-quality fuel such as jet fuel, gasoline and diesel by catalytic cracking (Hillen et al., 1982; Jin et al., 2016; Murata et al., 2014) but also can be used in other industries such as cosmetics (Huang et al., 2009). However, in spite of producing hydrocarbons similar to the fossil fuel, the low productivity of *B. braunii* makes it an unsuitable source of raw material for the low-grade biofuel production (e.g. renewable diesel). It is to be noted that due to the high cost associated, even fast growing, high oil producing algal to biofuel production is currently not feasible. However, besides producing the extracellular hydrocarbons, *B. braunii* has some other unique properties. The extracellular hydrocarbons of *B. braunii* can be extracted without destructing the microalgae cells and colonies using biocompatible solvents – the process called non-destructive extraction or milking. After non-destructive extraction, if returned under growth conditions, *B. braunii* can reproduce the hydrocarbons without any extra supply of fertilizers (Chaudry et al., 2015a; Frenz et al., 1989; Moheimani, Cord-Ruwisch, et al., 2013; Moheimani, Matsuura, et al., 2013). The milking of *B. braunii* does not only significantly reduce the fertilizer requirement of the process (by 90 %) (Chaudry et al., 2015b) but also reduces the requirement of the fast growth of microalgae, a bottleneck of using slow growing *B. braunii* in the conventional single extraction process. This makes milking a potential process for the renewable hydrocarbon production whose feasibility should be determined. Resource assessment, techno-economic analysis, and life cycle analysis have been used as the foundational tools for evaluating the feasibility of the algae-based biofuels. The technical and economic feasibility and the constraints of the milking process for the hydrocarbon production have been determined in the previous studies based on the energetic feasibility and the techno-economic analysis (Chaudry et al., 2017b, 2018). The energetic feasibility analysis of the milking process estimated its onsite energy ratio around 2 MJ produced/MJ consumed (Chaudry et al., 2017b). The techno-economic study of the milking process estimated the minimum sales price of the *B. braunii* hydrocarbons as $\$3.20L^{-1}$, and revealed that in spite of using slow-growing alga, the economics of the milking process is comparable to any other algal fuel production pathway utilizing fast-growing algal species (Chaudry et al., 2018). It should be noted here that our previous studies (Chaudry et al., 2017b, 2018) calculated the onsite material (CO_2, fertilizer, fresh water, and solvent) and energy consumptions of the milking process, however, any indirect material and fossil energy consumption other than associated with the fertilizer and the CO_2 emissions were not taken into consideration. Therefore, they do not give an indication of the total fresh water used, net

C balance, and energy gain over the total fossil energy used for the generation of algal hydrocarbons, hence, do not determine the environmental viability of the process.

The life cycle analysis (LCA) has been used as a premier tool to assess the environmental impacts of algal fuels for various production pathways in previous studies. For example, Bennion et al. (2015) presented the life cycle comparison of HTL and pyrolysis pathways on the metrics of net energy ratio and the GHG emissions (Bennion et al., 2015). Quinn et al. (2014) conducted the environmental assessment of lipid extraction pathway on the metrics of net energy ratio and the GHG emissions (Quinn et al., 2014). Yang et al. (2011) conducted the life cycle analysis of biodiesel production from microalgae focusing on water footprints and the nutrient balance (Yang et al., 2011). Clarens et al. (2010) presented the comparison of environmental impacts of algae feedstock with switchgrass, canola and corn farming for biofuel production on the metrics of energy consumption, GHG emissions, water and land use, and eutrophication potential (Clarens et al., 2010). Life cycle analysis strategy has also been used previously for the optimum design of the algal biorefinery. For example, Gong & You (2014a) conducted multi-objective optimization to simultaneously optimize the cost and the global warming potential of algal fuel production process (Gong & You, 2014a). Gong & You (2014b) proposed a biorefinery design for zero direct GHG emissions (Gong & You, 2014b). Gong & You (2015) presented the comprehensive superstructure in an LCA study focusing on the coproduction of biodiesel and bioproducts (Gong & You, 2015). Gong & You (2017) developed a consequential life cycle optimization framework to account for the impacts of the markets and the related processes influenced by the target process in the life cycle analysis, and applied the proposed framework to the algal biorefinery (Gong & You, 2017).

In this study, environmental assessment of the milking process has been performed using the life cycle analysis approach. – accounting for all the direct and indirect emissions, and fossil energy and fresh water consumption occurring along the production chain. As mentioned earlier, *B. braunii* hydrocarbons are similar to the fossil hydrocarbons and can be used as the green alternate of the fossil fuels. Although, the *B. braunii* hydrocarbons still need to be refined to attain the properties required for fuel; however, the energy requirement for refining of *B. braunii* hydrocarbons into fuel would be minimal due to the lack of nitrogen and oxygen contents (Nagano et al., 2012). Therefore, the emissions of raw algal hydrocarbons produced via the milking process have been compared with those of crude oil. For a more holistic approach, the GHG emissions, the fossil energy and the fresh water consumption, and the land use of the milking process have also been compared with those of other biofuels reported in the literature.

2 Methods

2.1 Process model

The process engineering models developed in Aspen Custom Modeler V8.4 consisting of mass and energy balances for the different stages of the process (presented in our previous study, (Chaudry et al., 2018)) formed the basis for the life cycle analysis model. Milking of *B. braunii* comprises of 4 main stages; 1) growth of microalgae, 2) harvesting and dewatering, 3) oil extraction and 4) solvent recovery similar to the conventional oil extraction process (Fig. 1). However, unlike the conventional process, milking does not involve any cell disruption before oil extraction, and the extraction is carried out with biocompatible solvents (such as heptane and hexane) only to keep the process non-destructive for algal cells and colonies. The algal biomass after the oil extraction in milking is recycled for the repetitive production of hydrocarbons. This is also in contrast to the conventional process in which after extracting the oil from algae only once, the leftover biomass is used either in anaerobic digestion to produce gaseous fuel to generate heat and electricity or sold as animal/aquatic feed. *B. braunii* can be recycled multiple times and do not need any extra fertilizer to reproduce the hydrocarbons (Moheimani, Cord-Ruwisch, et al., 2013; Moheimani, Matsuura, et al., 2013).

In this study, the engineering models (presented in detail in our previous study (Chaudry et al., 2018)) considered open ponds for the growth of fresh microalgae and for the hydrocarbon production from the recycled microalgae. The productivity and hydrocarbon contents of *B. braunii* were estimated to be 9 g m^{-2} d^{-1} and 40 % DW (dry weight), respectively. Each batch of culture grown was considered to replenish the hydrocarbon contents in five days in hydrocarbon production ponds after each extraction up to nine times. The culture was assumed to be concentrated (dewatered) using rotating filters from 0.5 g/lit to 75 g/lit before oil extraction. Oil extraction was considered using heptane as the solvent in KARR column extractor with 50 % extraction efficiency, and a distillation column was used for the process of solvent recovery. The raw hydrocarbons were assumed to be sent to the refinery for the upgradation process. After nine extractions, the leftover algal biomass was considered to be sold as aquaculture feed. The other option for the leftover biomass usually considered in the conventional algal fuel production process (single extraction) is to use it in anaerobic digestion to produce energy onsite as well as to recycle the nutrients. However, in case of milking, the continuous supply of leftover biomass is not available as it is recycled for the repeated production of hydrocarbons and anaerobic digestion may not be economical for the process (Chaudry et al., 2018). A simple block diagram of the milking process is shown in Fig. 1. The onsite material and energy consumption of the process is given in Table 1. A detailed block diagram with the flow rates of each stream can be found in the supplementary data of this article. Further details of the engineering model are presented in our previous study (Chaudry et al., 2018).

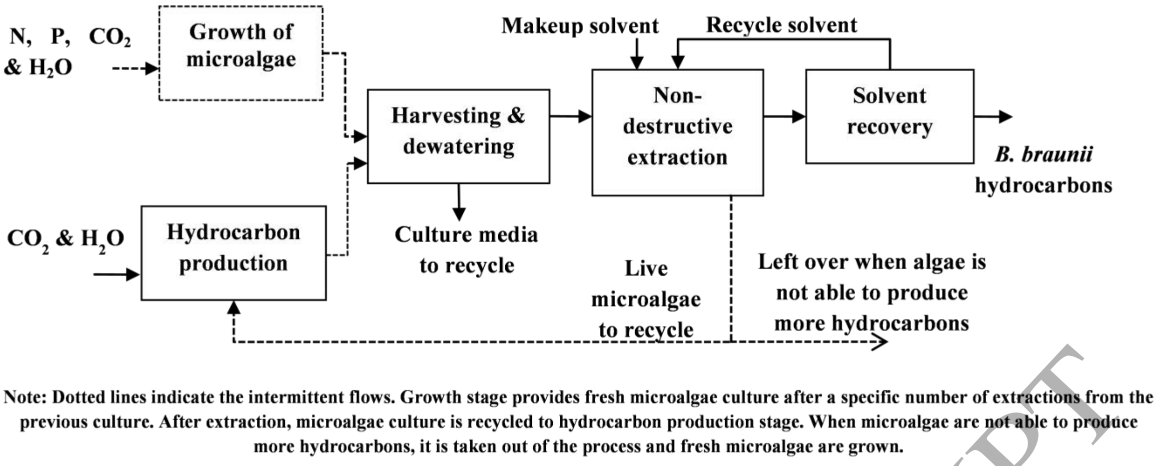

Fig. 1: The block diagram of milking process for renewable hydrocarbon production taken from (Chaudry et al., 2018)

Table 1: Onsite material and energy consumption of the milking process for the production of 1 kg of *B. braunii* hydrocarbons

Energy consumption		
Operation	Electricity* (kWh)	Heat (kWh)
Open pond mixing	1.23	
Fresh water supply	0.42	
CO_2 supply and distribution	0.40	
Culture pumping	0.42	
Dewatering	3.67	
Oil extraction and recovery	0.04	0.66
Material consumption	(kg)	
Nitrogen fertilizer ($NaNO_3$)	0.23	
Phosphorous fertilizer (DAP)	0.03	
CO_2 supply	11.22	
Makeup solvent	0.03	

*Note: All electricity consumption includes 10 % line losses (Peters & Timmerhaus, 1991).

2.2 Life cycle analysis model

The outputs of the engineering model were the inputs for the life cycle analysis model. The data of the life cycle emissions, upstream fossil energy and fresh water consumption was obtained from GREET 2016 (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) developed by Argonne National Laboratory (see https://greet.es.anl.gov/). The total-CO_2 emissions, the GHG-100 emissions over the 100-year life span, the life cycle fossil energy, and the freshwater consumption were calculated. The total-CO_2 emissions are the total amount of CO_2 including the equivalents from VOC (volatile organic carbon) and CO (carbon monoxide). GHG-100 emissions are the total emissions for CO_2, methane and nitrous oxide with their global warming potentials (1, 25, and 298 kg CO_2-eq respectively, based on a 100-year time window) (Weinberg et al., 2012).

2.2.1 System boundary

The goal of this study was to estimate the emissions related to the production of *B. braunii* hydrocarbons via milking and their transport to a U.S. refinery. The GHG emissions of these renewable hydrocarbons are compared with the fossil crude oil with the same system boundary. The well-to-wheel life cycle stages for any liquid fuel comprises of oil production/extraction of oil, transport to the refinery, refinery treatment, transport and distribution to pumps, and combustion in the vehicle (shown in Fig. 2). However, as this study focuses on the process of hydrocarbon extraction from microalgae, the system boundary was defined from well-to-use (also shown in Fig. 2). The algal hydrocarbons can be upgraded to the fuel in the refinery or utilized to produce the other fuel based products; therefore, the upgrading stage was intentionally excluded from the system boundary. The system boundary considered for the analysis in this study includes 1) the complete hydrocarbon production process (milking) comprising of growth of microalgae/ hydrocarbon production from the recycled microalgae, harvesting and dewatering of microalgae, and hydrocarbon extraction and recovery (as shown in Fig. 1) and 2) transport of algal hydrocarbons to the refinery. For the reference system, the same system boundary was considered, i.e. crude oil recovery and transport to the refinery.

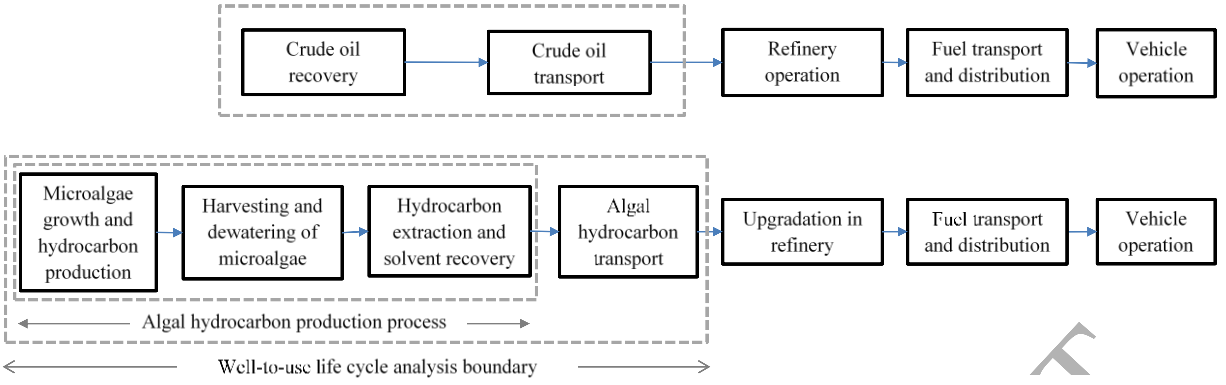

Fig. 2: Well-to-wheel Life Cycle boundary of fuel. The dashed lines show the boundaries considered for the analysis in this study. The detailed algal hydrocarbon production process is shown in Fig. 1.

The total well-to-use emissions for the system were calculated as the sum of the net emissions for the hydrocarbon production process and the emissions of the hydrocarbons transport to U.S. refineries. The net emissions calculation for the *B. braunii* hydrocarbon production process is shown in Fig. 3.

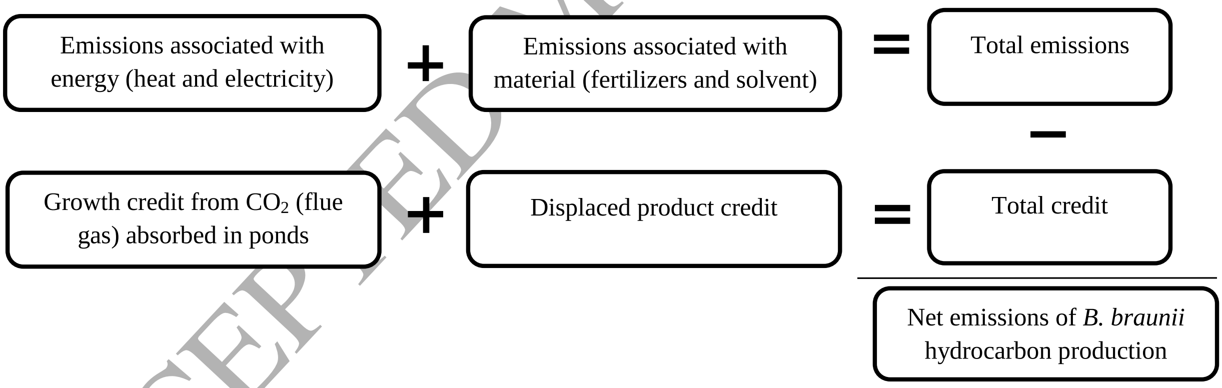

Fig. 3: Net emission calculations for *B. braunii* hydrocarbon production process from growth to oil extraction

All the upstream emissions associated with the acquisition of energy and materials required for the production of hydrocarbons are included in the analysis. No construction-related emissions are included within the scope of this study. Moreover, the environmental effects related to the human force involved (transport, food, living) were not considered. The displaced product credit and the growth credit are explained in sections 2.2.2 and2.2.3, respectively. The transportation of *B. braunii* hydrocarbons to the refinery was considered 600 miles by rail, similar to that used in the model of transportation of algal oil to U.S. refinery in GREET 2016. The results for the hydrocarbon production process (this boundary is also shown in Fig. 2) have been reported in detail.

2.2.2 Co-product credit

In life cycle analysis, co-products can be treated with the allocation method based on mass, energy, volume or market value or the displacement method. The allocation method allocates the feedstock use, energy use and the emissions between the primary product and the co-products on the basis of mass, energy content or the economic revenue (Huo et al., 2009). Each allocation method is associated with the benefits and disadvantages (Cherubini, 2010). The other method of considering the co-product is the displacement method which expands the system boundary to include the production of the co-products by other means that would theoretically be avoided as a result of the production of the co-products by the primary process being modeled (Cherubini, 2010; Huo et al., 2009). The International Organization for Standardization (ISO) suggests avoiding the allocation method for the co-products by expanding the system boundary when possible (Cherubini, 2010; Ekvall & Finnveden, 2001). Therefore, this study considered the displacement method. The leftover microalgae after the specific number of extractions was considered to replace the soybean meal (SBM) for the aquatic life. The displaced product credit was calculated as

$$Credit_{dis-product} = r_{dp}.m_{LEA}.Em_{SBM} \tag{1}$$

Where, $m_{LEA,}$ is the amount of co-product produced per functional unit and, r_{dp}, is the displacement ratio of the product. The displacement ratio (r_{dp}) of the SBM to the lipid extracted algae depends upon the nutritious value of the lipid extracted algae (LEA) as the aquatic feed (Huo et al., 2009). There is limited data available on the use of LEA in aquaculture in general and no data is available for the use of *B. braunii* left over after milking, in particular. This study assumed 0.68 Kg of SBM is replaced with each Kg of LEA based on a previous study which estimated the price of LEA as $ 200/ton as compared to $294/ton for SBM based on the performance of LEA as aquatic feed with the soybean meal (Ivey & Wilkersham, 2014). A sensitivity analysis is performed around this parameter.

2.2.3 Growth credit

The flue gas from the power plant is utilized as C source for microalgae growth and hydrocarbon production from recycled algae. This CO_2 will be emitted into the atmosphere if not captured in microalgal biomass and can be considered as a credit to the emissions of the process. The onsite carbon balance is shown in Fig. 4.

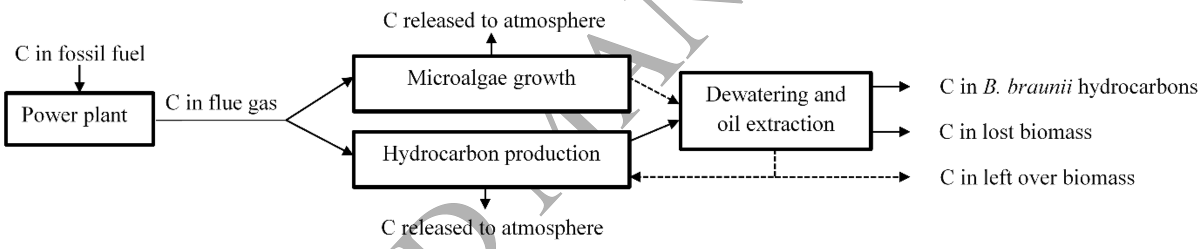

Fig. 4: Onsite carbon balance

The carbon credit by CO_2 absorbed in algal biomass and hydrocarbon were measured by calculating the C fixed in all the products and by products including losses (see equation 2).

$$Credit_{growth} = \left(\sum_{p \in P} X_{c,p} A_p + X_{c,loss} A_{loss} \right) * M_{CO2}/M_C \qquad (2)$$

where, P represents the group of products and coproducts, $X_{c,p}$ and $X_{c,loss}$ are the mass fractions of C in the product/coproduct and lost biomass, A_p and A_{loss} are the amounts of product/coproduct and the lost biomass, M_{CO2} and Mc are the molecular/atomic weights of CO_2 and C.

2.2.4 Fossil energy ratio

Fossil energy ratio is a variant of net energy return on investment commonly used for the renewable fuel (Murphy et al., 2011). The life cycle fossil energy consumptions for the hydrocarbon production process was calculated in a similar way as the emissions; including all the upstream fossil energy consumption associated with the acquisition of energy (electricity and heat) and material (fertilizer and solvent) required for the hydrocarbon production process as shown in Fig. 5.

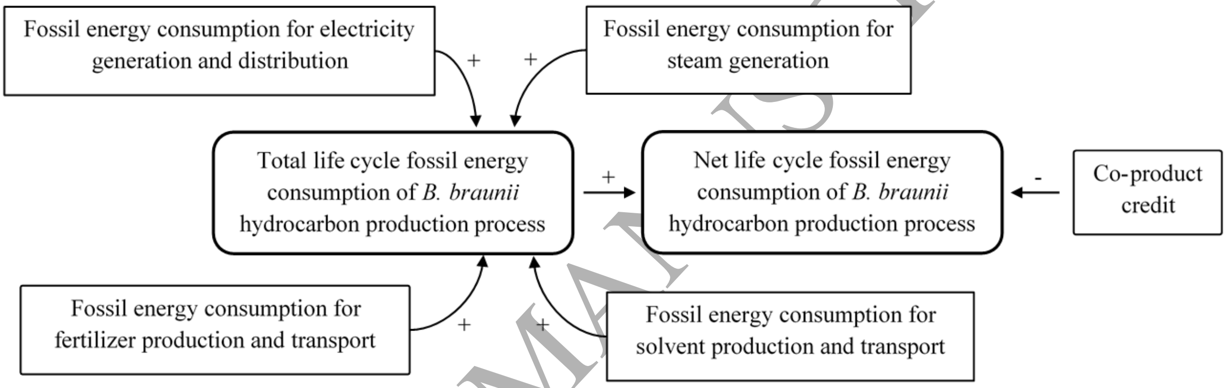

Fig. 5: Calculation of the life cycle fossil energy consumption of the milking process

Co-product credit for fossil energy consumption was calculated in the similar way as the emission credit i.e. fossil energy avoided by the coproduct replacement otherwise consumed for the production of the replaced product was considered as credit. The fossil energy ratio (FER) was calculated as follows.

$$FER = \frac{HHV\ of\ the\ B.braunii\ hydrocarbons\ produced}{Net\ life\ cycle\ fossil\ energy\ consumption\ of\ the\ process} \quad (3)$$

The *HHV* (higher heating value) of the *B. braunii* hydrocarbons was reported to be 49 MJ/Kg hydrocarbons (Chaudry et al., 2015a; Jin et al., 2016).

2.2.5 Fresh water consumption and land use

Botryococcus braunii is a fresh water alga. The total onsite water consumption is derived by the evaporation in open ponds, drying of leftover biomass and the harvest losses. The recycle of process water is necessary for algae fuel production process especially if fresh water algae is utilized, to keep the water footprints of the fuel low (Yang et al., 2011). In case of milking, there are no considerable losses and the whole culture is recycled after the extraction making 100 % recycle of the culture water possible. In this study, however, 10 % harvest losses are assumed (Chaudry et al., 2018). The evaporation in open ponds depends upon the ambient conditions and vary with the location. This study assumed 0.3 cm d^{-1} evaporation rate (Chaudry et al., 2018; Davis et al., 2011).

The other life cycle water consumption arises from the upstream water consumption associated with the material and energy utilized onsite. The net life cycle water consumption was calculated in a similar way as the net life cycle energy consumption. The land use of the milking process was calculated as 120 % of the total open pond area required for the growth of fresh microalgae and the hydrocarbon production from the recycled microalgae (Chaudry et al., 2018). No indirect land use was considered in this analysis.

3 Results and discussion

3.1 GHG emissions

The net CO_2 emissions and the GHG-100 emissions for the production of *B. braunii* hydrocarbons, after considering the growth and displaced product credit, were found to be -0.39 kg CO_2/kg hydrocarbons and -0.90 kg CO_2-eq/kg hydrocarbons, respectively. The CO_2 absorbed by the biomass in the growth and hydrocarbon production ponds is nearly 35 % of the total CO_2 fed to the ponds (calculated by onsite carbon balance). It was assumed that 80 % of the CO_2 is taken up by the algae in growth ponds. For the hydrocarbon production, the similar amount of CO_2 was assumed to be supplied to maintain the performance of microalgae cells, and hydrocarbon production, however, the theoretical requirement of carbon for hydrocarbon production is lower causing the release of the higher percentage back into the atmosphere. The emissions of the process and the credits are shown in Table 2. The distribution of the net total-CO_2 emissions and the GHG-100 emissions for the *B. braunii* hydrocarbon production process are shown in Fig. 6. Dewatering energy contributes the most to the emissions of the process. GHG-100 credit for the replacement of soybean meal with the lipid extracted algae is significantly higher than the total-CO_2 credit.

Table 2: The total-CO2 and GHG-100 emissions for *B. braunii* hydrocarbon (HC) production process

	Total emissions	Growth credit	Displaced product credit	Net emissions
Total-CO_2, kg CO_2/kg HC	3.59	-3.93	-0.05	-0.39
GHG-100, kg CO_2-eq/kg HC	3.82	-3.93	-0.79	-0.90

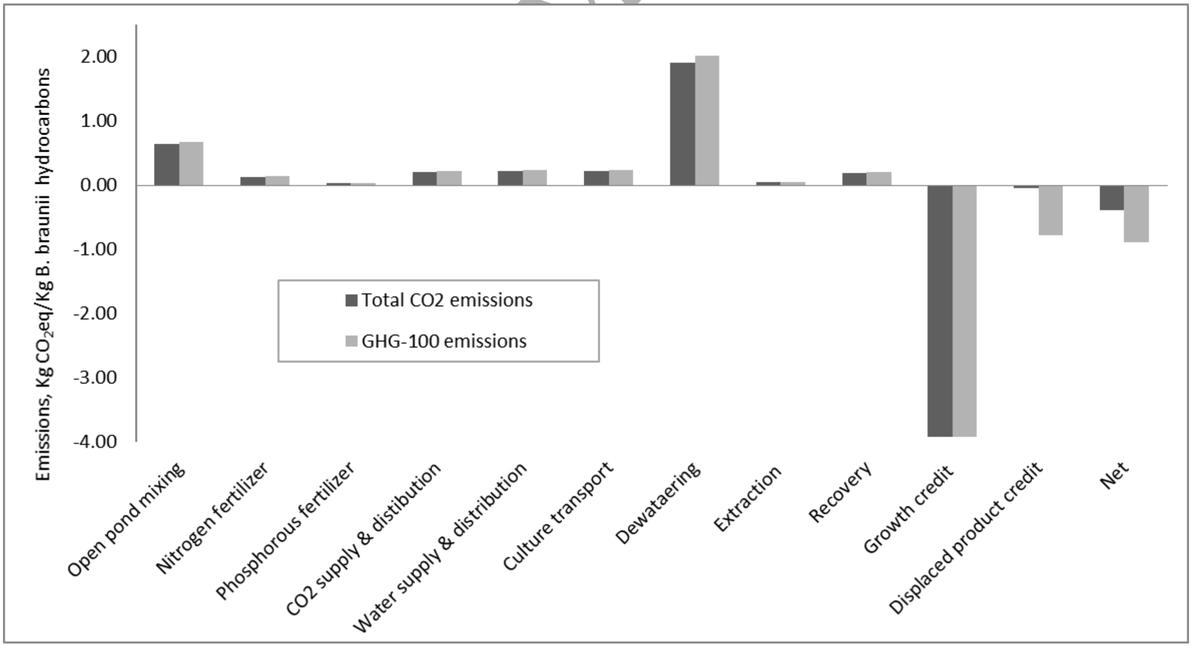

Fig. 6: Contribution to total-CO_2 emissions and GHG emissions over the 100-year time frame for *B. braunii* hydrocarbons production process

The well-to-use emissions of the process (all the upstream emissions of the *B. braunii* hydrocarbons at the refinery gate) and the reference process are shown in Fig. 7. Transport of algal hydrocarbons to the refinery has no significant contributions to the emissions. Production of algal hydrocarbons recycles the CO_2 in contrast to the extraction of fossil crude oil which emits CO_2. It is worth to mention that the actual GHG emission savings by the use of *B. braunii* hydrocarbons are not only those mitigated by the algal hydrocarbons (-0.89 kg CO_2-eq/kg hydrocarbons – well-to-use emissions of algal hydrocarbons) but also those avoided otherwise generated by the crude oil extraction (0.36 kg CO_2-eq/kg crude oil). For the well-to-wheel life cycle emissions, the downstream emissions associated with the upgradation of hydrocarbons, transport and distribution and vehicle operation would be included. Anticipating that the transport and distribution and the vehicle operation will generate the same emissions for the both (crude oil and *B. braunii* hydrocarbons), the final GHG emission savings by the use of algal hydrocarbons will be determined by the upgradation process (mainly its energy consumption). The previous studies have shown that the conversion of algae oil to fuel does not contribute much to the total energy consumption of the process (Clarens et al., 2010; Weinberg et al., 2012). In particular, the *B. braunii* hydrocarbons have the very low concentration of nitrogen and oxygen and contain no sulphur, and the types of hydrocarbons present in *B. braunii* oil are limited as mentioned earlier. Therefore, it can be anticipated that the conversion of *B. braunii* hydrocarbons to the high-quality fuel will be less energy consuming than the refining of fossil crude oil containing significant impurities and a complex mixture of hydrocarbons.

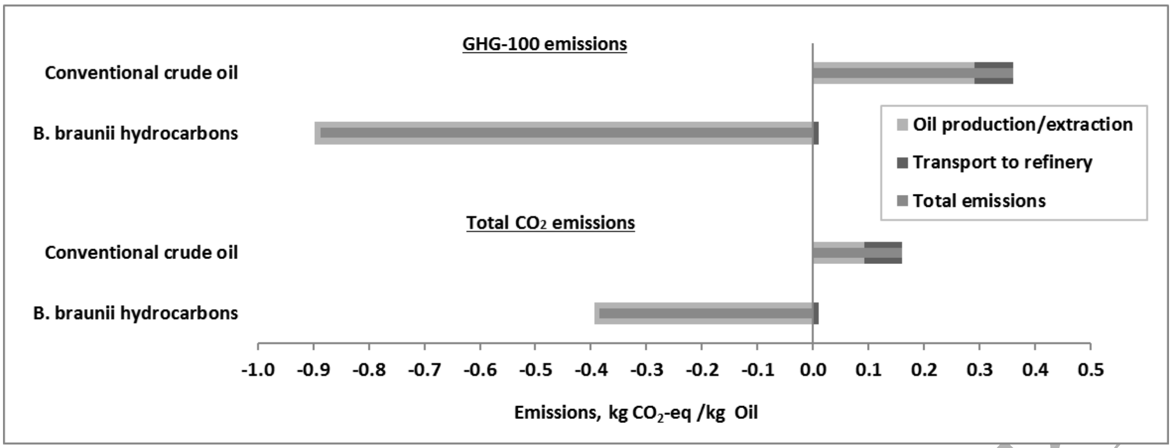

Fig. 7: Well-to-use emissions of the *B. braunii* hydrocarbon production process and the reference process

Milking process yields a different product (hydrocarbons) than other algal fuel production processes (such as conventional wet extraction, hydrothermal liquefaction, and pyrolysis, etc.) which produce algal lipids that are converted to biodiesel. Therefore, due to the different types of product produced and the difference in the system boundaries considered for the analysis, the GHG emissions presented in this study cannot be directly compared with the well-to-pump GHG emissions of the other algal fuel products presented in the literature. However, keeping in mind that conversion of algal lipids to fuel and their transport and distribution does not contribute significantly towards the total emissions of the process, and growth of microalgae and oil recovery are the major influencing stages of the processes (Bennion et al., 2015), it is worth to compare the GHG emissions of algal hydrocarbons to other biofuels. The well-to-pump GHG emissions reported in the literature for the other algal fuel production processes vary from -100 g CO_2-eq/MJ renewable diesel to 230 g CO_2-eq/MJ renewable diesel (Bennion et al., 2015). It should be noted that GHG emissions of the milking process (-18.4 g CO_2-eq /MJ of *B. braunii* hydrocarbons, converted from -0.90 kg CO_2-eq/kg *B. braunii* hydrocarbons) are comparable with those of other algal fuel production processes reported in the literature. It is worth to mention here that milking process has low emissions without onsite energy generation which is a key to low GHG emissions for the conventional algal fuel production process (E. D. Frank et al., 2011). The well-to-pump emissions for the soybean biodiesel production have been reported as -62 g CO_2-eq/MJ (an average of all cases of reference study) without considering any land use change (Huo et al., 2009). As mentioned earlier, the land use change can have a significant effect on the GHG emissions of biofuel produced from the crops grown on arable land.

3.2 Fossil energy ratio

The total direct and indirect (life cycle) fossil energy consumption for the *B. braunii* hydrocarbon production process is shown in Table 3. The fossil energy ratio for the *B. braunii* hydrocarbons was found to be 1.04 MJ produced/MJ of fossil energy consumed. It should be noted here that the onsite energy return of the process is almost double (nearly 2 calculated in our previous study (Chaudry et al., 2017b)) than the life cycle energy return calculated in this study. The major indirect fossil energy consumption is associated with the electricity obtained from the grid. The energy consumption for the transport of the process is negligible as compared to the energy consumption of the hydrocarbon production process. The distribution of the total life cycle fossil energy consumption excluding any co-product credit for the *B. braunii* hydrocarbon production process is shown in Fig. 8.

Table 3: Life cycle fossil energy consumption for the algal hydrocarbon (HC) production via milking process

Total life cycle fossil energy consumption, MJ/Kg HC	Displaced product credit, MJ/Kg HC	Net life cycle fossil energy consumption, MJ/kg HC
47.96	0.69	47.27

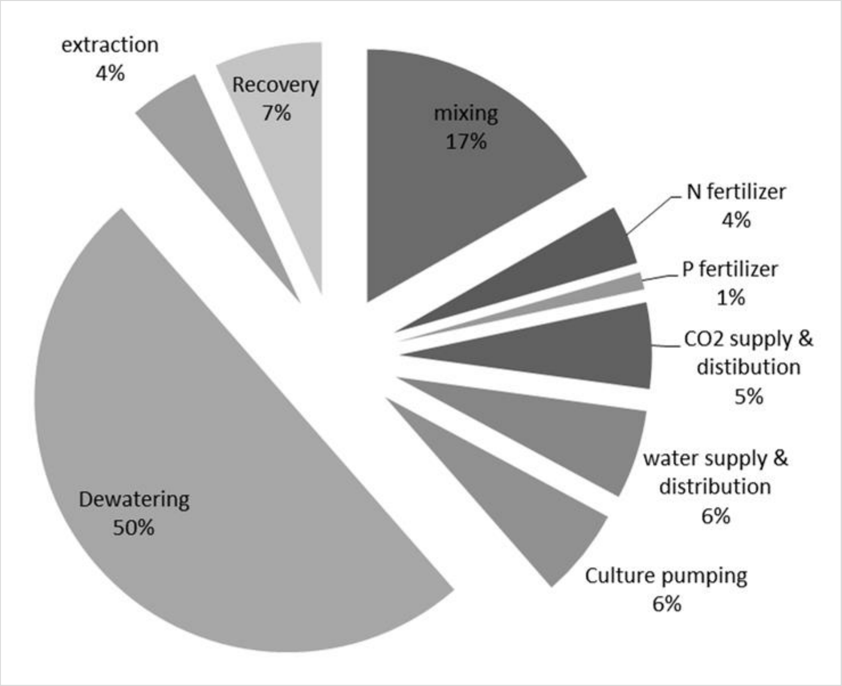

Fig. 8: Distribution of total life cycle energy consumption of algal hydrocarbon production via milking process

Dewatering is the most energy consuming step of the process. Some of the *B. braunii* strain has the tendency to float on the surface (Chaudry et al., 2017b). The natural floating phenomenon can be used as the first dewatering step (prior to the filtration) to reduce the energy of filtration. Experimental investigation of floating phenomenon of *B. braunii* strains suitable for milking is recommended. If applicable, floating phenomenon can significantly improve the fossil energy ratio and the GHG emission savings of the process by reducing the energy requirement for dewatering.

The well-to-pump energy ratio (output/input) of different pathways of conventional algal fuel production process (utilizing fast-growing algal species) reported in the literature vary between 0.4-2 (Bennion et al., 2015). This variation in the literature is not only because of the difference of pathways but also due to the difference in process model assumptions for the similar pathways. The fossil energy consumption of the conventional algal fuel processes is significantly affected by the onsite renewable energy generation using leftover algal biomass after the oil extraction either in anaerobic digestion or catalytic gasification (E. Frank et al., 2013; E. D. Frank et al., 2011). For example, the lipid extraction pathway has the energy ratio (output/input) of 0.39 based on the total energy consumption and 1.82 based on the fossil energy consumption (total minus renewable energy mainly from leftover biomass) (E. D. Frank et al., 2011). On the other hand, this study did not consider any onsite energy generation mainly because milking does not produce the leftover biomass continuously due to its recycling and an only a small amount is available after multiple uses. This indicates that the milking process is overall less energy consuming than the conventional process, but its fossil energy consumption is higher due to the absence of onsite renewable energy. The fossil energy ratio of algal fuel, in general, is significantly lower than that (3.2) estimated for the soybean biodiesel (Sheehan et al., 1998). In future, it would be beneficial to analyse the milking process coupled with some other renewable energy source, for example, fast growing algae dedicated to generating onsite energy as an option for the better fossil energy consumption scenario. Moreover, alternate technologies, such as, the growth of *B. braunii* on biofilm that can significantly reduce the energy consumption of the process (Chaudry et al., 2017a), should be investigated.

3.3 Fresh water consumption and land use

The life cycle fresh water consumption for the milking process was estimated to be 1802 kg /kg hydrocarbons (equivalent to 37 L/MJ of hydrocarbons) mainly arising from the onsite water consumption (see Table 4) which is very high than the fresh water consumption of the crude oil (0.07 L/MJ). The fresh water consumption of the milking process is comparable to that reported for the conventional algal fuel production process in the literature (10 L/MJ and 16 L/MJ for seawater and fresh water algae, respectively with 100 % recycle of culture media after harvest, and 99 L/MJ in absence of recycle) (Chisti, 2013). On the other hand, the fresh water consumption of the milking process is lower than those of the other biofuels which is, for example, 383 L/MJ for biodiesel and bioethanol derived from soybean and 50 L/MJ and 396 L/MJ for bioethanol derived from sugarcane and jatropha respectively (A. Singh et al., 2011).

The land use for the production of algal hydrocarbons via milking process was estimated to be 0.85m^2/kg (17.26 m^2/GJ). This is comparable to the open pond area required for the algal biodiesel (by the conventional process) (2-13 m^2/GJ) and in contrast to very high crop-land use for the production of soybean biodiesel (689 m^2/GJ) (A. Singh et al., 2011).

Table 4: Life cycle fresh water consumption for the algal hydrocarbon (HC) production via milking process

Onsite water consumption, kg/kg HC	Total life cycle water consumption, kg/kg HC	Displaced product credit, kg/kg HC	Net life cycle water consumption, kg/kg HC
1815.49	1831.96	30.22	1801.74

3.4 Sensitivity analysis

The sensitivity analysis was performed to quantify the effect of the assumptions of the productivity and hydrocarbon contents of *B. braunii* used in the process models on the emissions, fossil energy ratio, freshwater consumption and the land use of the milking process. The productivity of *B. braunii* does not have any significance influence on the milking process (see Fig. 9). The hydrocarbon contents of *B. braunii* have more influence on the environmental impacts of the process (see Fig. 10). The milking of *B. braunii* with 50 % lower hydrocarbon contents than the base case (40 % dry weight) will emit more CO_2 and GHG gases than the CO_2 sequestrated by the microalgae grown during the process resulting in positive net emissions.

The effect of variation in the displacement ratio used in the calculation of displaced product credit on the emissions and fossil energy ratio of the process was also studied in the sensitivity analysis. The displacement ratio of displaced product (SBM) does not affect the total-CO_2 emissions and fossil energy ratio of the process significantly as the life cycle energy consumption and CO_2 emissions of soybean meal are not very high. However, the GHG-100 emissions of the process are significantly affected by the assumption of the displacement ratio indicating that the credit added by displacing the soybean meal with the co-product of the process (lipid extracted algae) plays a significant role in determining the GHG saving potential of renewable hydrocarbons (see Fig. 11). The actual displacement ratio for displacing the aquatic feed with the *B. braunii* biomass after the repeated hydrocarbon extraction should be determined in the future for a more realistic co-product credit of the process.

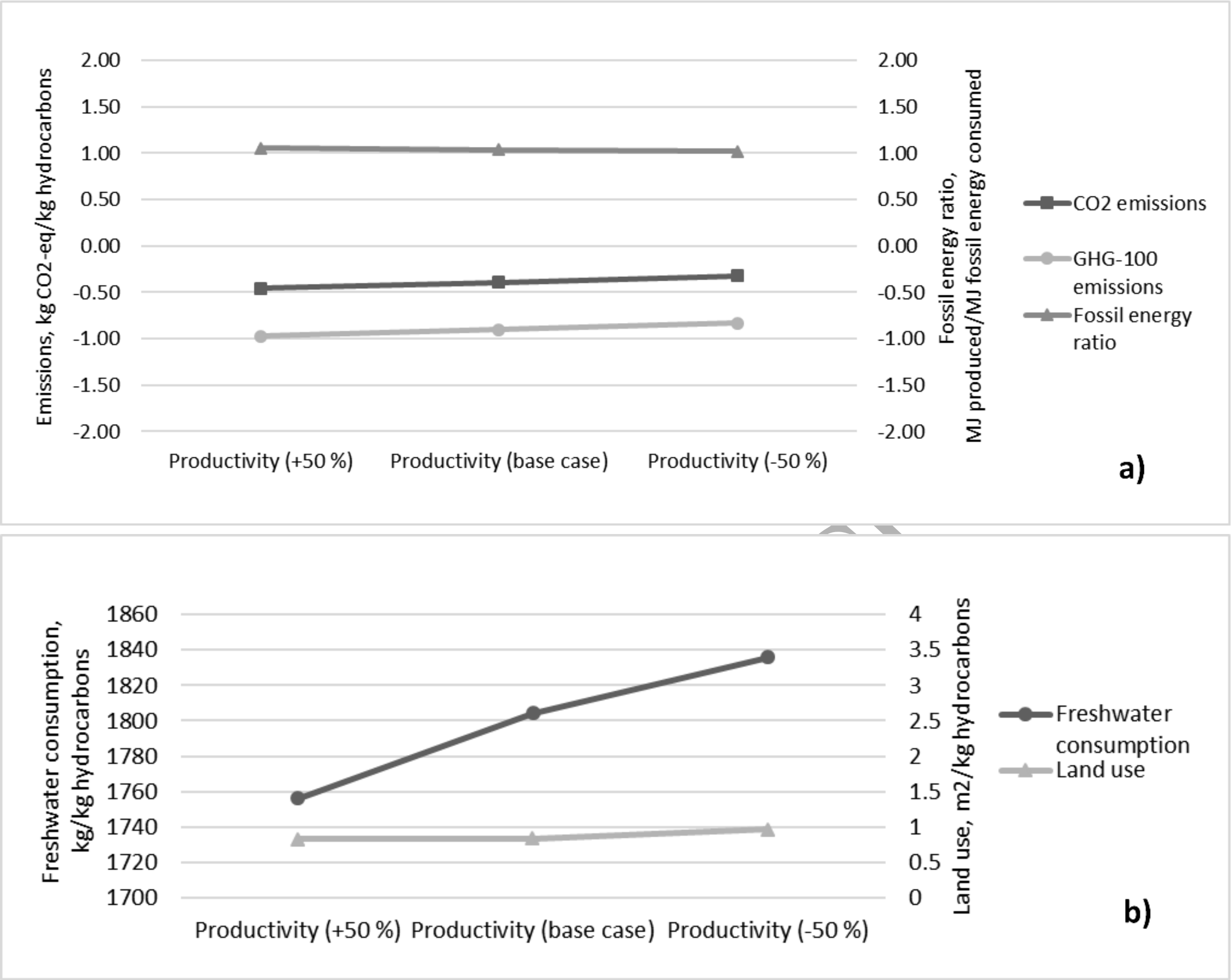

Fig. 9: Effect of productivity of *B. braunii* on emissions and fossil energy ratio (a), and freshwater consumption and land use (b) of hydrocarbon production process via milking with base case productivity of 9 g m^{-2}d^{-1}

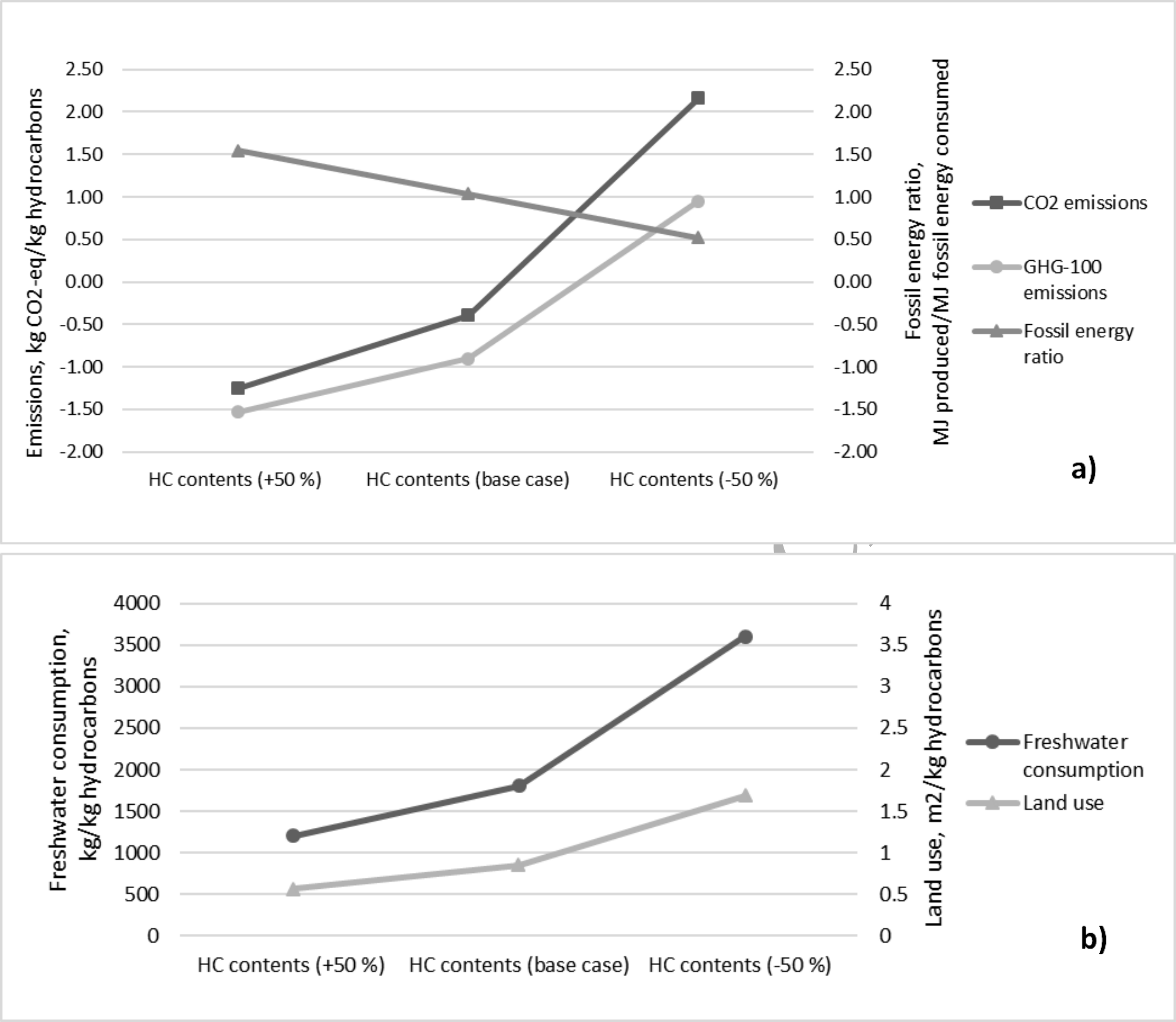

Fig. 10: Effect of hydrocarbon contents of *B. braunii* on emissions and fossil energy ratio (a) and freshwater consumption and land use (b) of hydrocarbon production process via milking with base case hydrocarbon contents of 50 % on dry weight basis

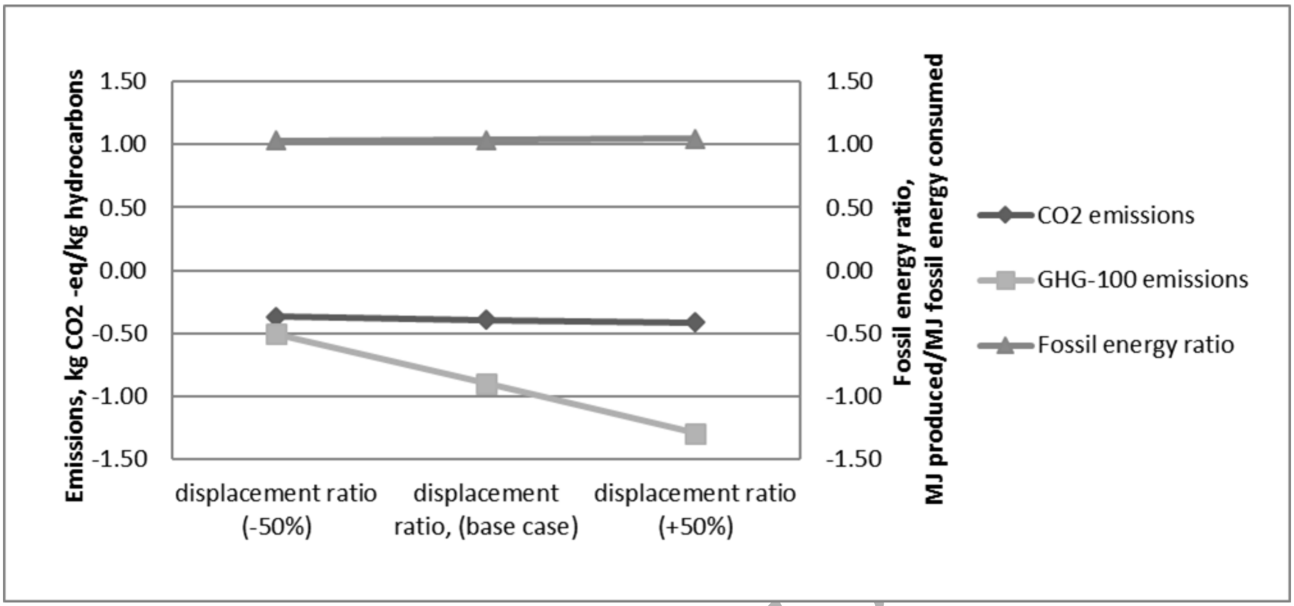

Fig. 11: The sensitivity analysis for the effect of changes in the displacement ratio used in the calculation of displaced product credit on the emissions and fossil energy ratio of the hydrocarbon production process with the base case displacement ratio of 0.68

Milking of *B. braunii* was also compared with the single extraction (no recycling of biomass as in case of conventional extraction) with all other assumptions similar to the base case of milking. Milking has higher fossil energy ratio, and lower freshwater consumption and land use than single extraction (see Fig. 12). Single extraction with base case assumptions is more beneficial than milking in terms of CO_2 sequestration (see Fig. 12). In case of single extraction, more biomass is grown leading to the higher amount of carbon fixed in the biomass and more co-product is produced adding higher displaced product credit to the emissions of the process. However, realistically the market for the big amount of leftover algae after every single extraction is another challenge that needs to be considered. Another option is to use the leftover algae for onsite heat/power generation via anaerobic digestion instead of selling it as aquatic feed. This will increase the fossil energy ratio of the single extraction and reduce the carbon fixed onsite. The emissions generated onsite will be considered as the biogenic emissions, and the emissions associated with the purchased power will be avoided and the C fixed will be only present in the extracted oil and the anaerobic digestate.

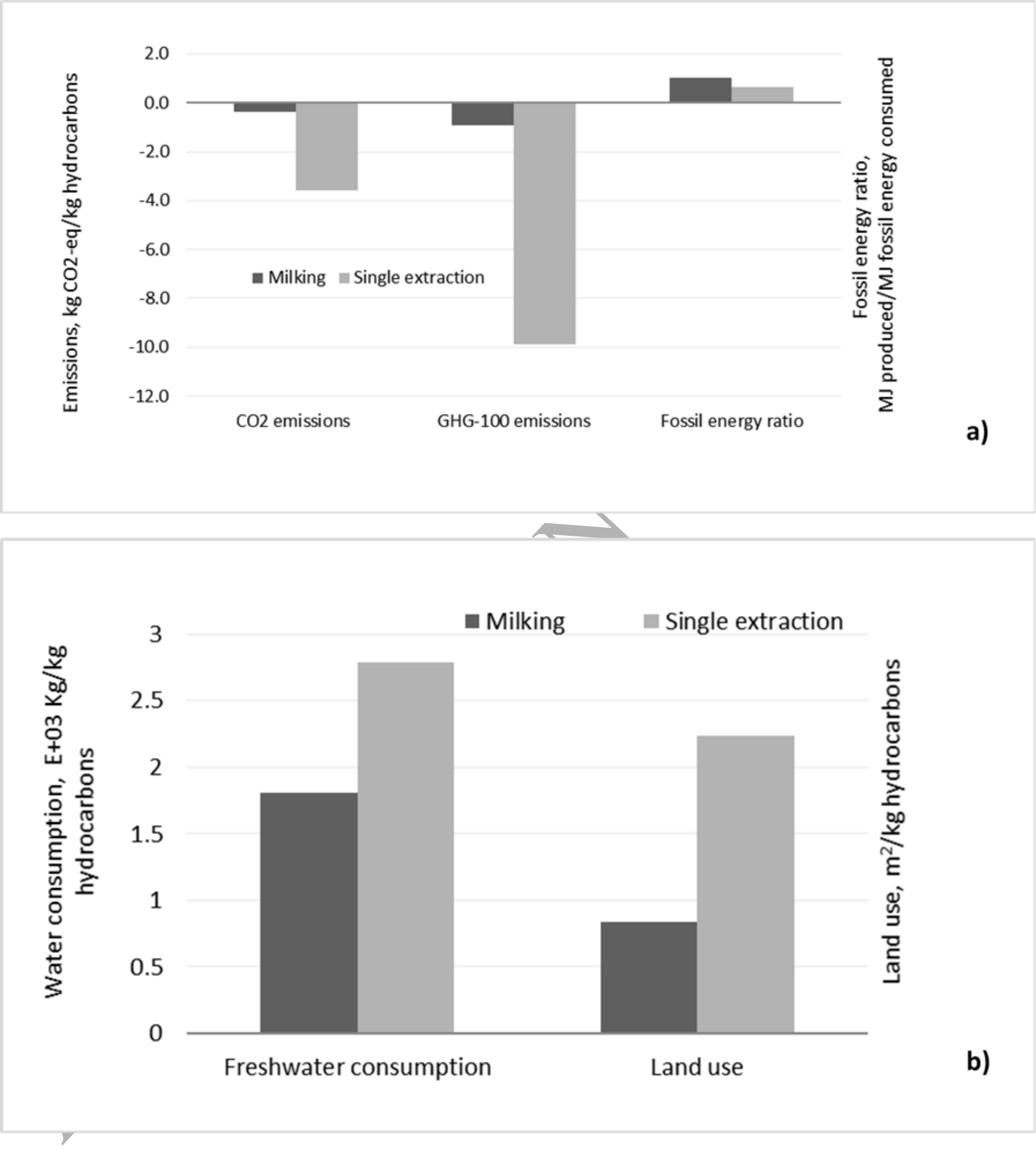

Fig. 12: Comparison of environmental impacts of algal hydrocarbon production via milking and single extraction processes

4 Conclusion

This study aimed to analyse the environmental benefits of the renewable hydrocarbons produced by milking of *B. braunii*. The total-CO_2 emissions and GHG-100 emissions for the production of *B. braunii* hydrocarbons were estimated to be -0.39 kg CO_2-eq/kg hydrocarbons and -0.90 kg CO_2-eq/kg hydrocarbons, respectively. The fossil energy ratio, the freshwater consumption and the land use of the process were found to be 1.04 MJ produced/MJ fossil energy consumed, 1802 kg/kg hydrocarbons and 0.85m^2/kg hydrocarbons, respectively. For the production of hydrocarbons, the milking process has the clear advantage over the extraction of fossils in terms of the GHG emissions. The conversion of algal hydrocarbons to the useful form of energy was intentionally excluded from this study. However, it is anticipated that the conversion of algae oil to fuel is relatively less energy demanding than the conventional crude oil due to the narrow range of hydrocarbons, and low nitrogen and sulphur contents, making it likely to further increase the environmental benefits of algal fuel over the fossil fuel.

Microalgal fuel, in general, have advantage over the first generation biofuels in terms of the freshwater consumption and the land use. In spite of utilizing the freshwater microalgae, the freshwater consumption of the *B. braunii* hydrocarbons (produced via milking) is significantly lower than that of the first generation biofuels. Milking, also, has the advantage over the conventional algal fuel process (utilizing fast-growing algal species) in terms of effective utilization of fertilizer, the production of hydrocarbons instead of lipids, and lower total energy consumption. However, due to the high energy consumption and the lack of the biomass for the onsite energy generation, the fossil fuel consumption of the milking process is high. Optimizing the milking process for the fossil energy consumption and/or coupling it with another renewable energy source would be beneficial in the future studies. Furthermore, as the dewatering of microalgae is the major contributor to the total energy consumption and the emissions of the process, the natural floating phenomenon of *B. braunii* should be tested for the strains selected for the milking to reduce the energy requirement of the process. Moreover, the higher hydrocarbon contents are the key to energetically positive and environmentally beneficial milking process. *B. braunii* strains able to repeatedly produce higher hydrocarbon contents after milking should be identified to get the advantage of the process. Furthermore, the algal hydrocarbons can not only be used as fuel but also as an alternative raw material for the other fossil-based products. A complete cradle-to-grave analysis for the final product along with the careful consideration of the co-product should be performed to anticipate the clearer picture of the environmental benefits of the use of algal hydrocarbons.

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