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Life Cycle Energy and Carbon Footprints of Microalgal Biodiesel Production in Western Australia: A Comparison of Byproducts Utilization Strategies

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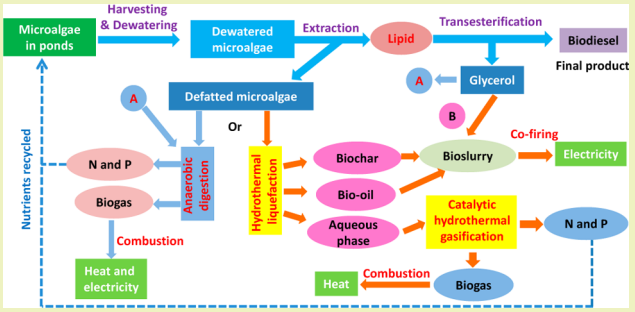
Supporting Information

ABSTRACT: This study compares the performances of anaerobic digestion and hydrothermal liquefaction as byproducts (defatted microalgae and glycerol) utilization strategies to offset overall life cycle energy and carbon footprints of microalgal biodiesel production in Western Australian (WA). Utilization of byproducts via anaerobic digestion or hydrothermal liquefaction enables the production of electricity and process heat, as well as the recovery of inherent nutrients. As a result, the anaerobic digestion route and hydrothermal liquefaction route substantially reduce life cycle energy inputs for producing 1 MJ biodiesel from 4.3 MJ (without byproducts utilization) to 1.3 and 0.7 MJ, yielding carbon footprints of ~80 and ~33 g CO_2-eq/MJ biodiesel, respectively. The results indicate that hydrothermal liquefaction, which shows better life cycle performance and requires smaller reactor footprint than anaerobic digestion, can be another potential strategy to recover energy embedded in defatted microalgae. It is also evident that while vast coastal areas are available in WA for marine microalgae cultivation, further technological advances are required to realize a truly sustainable biodiesel production from microalgae. Sensitivity analyses suggest that key R&D areas are improvement of microalgae biological properties (e.g., growth rate and lipid content) and innovations in engineering designs (e.g., culture circulation velocity, methane yield during anaerobic digestion, and bio-oil yield during hydrothermal liquefaction).



KEYWORDS: *Biomass, Microalgae, Biodiesel, Life cycle analysis, Anaerobic digestion, Hydrothermal liquefaction, Bioslurry, Biochar, Bio-oil, Glycerol*

INTRODUCTION

Challenges in meeting energy security and reducing greenhouse gas (GHG) emissions associated with fossil fuel use have led to significant interests in renewable energy such as biofuels.[1] Development of liquid alternative transport fuels is particularly important for Australia because of the nation's high consumption of transport fuels[2] and low proven petroleum reserves.[3] Microalgae is considered as a promising feedstock for liquid biofuel (e.g., biodiesel) production.[4] It offers several potential advantages, including its higher oil productivity (compared with other land-based oil plants),[5] ability to grow on nonarable land with saline water,[6] potential applications in wastewater management,[7] and efficient utilization of CO_2 in flue gas from power stations.[8]

Australia, particularly Western Australia (WA), has several geographic advantages for marine microalgae cultivation and subsequent biodiesel production.[9] These advantages include abundant coastal land for marine microalgae farming, high levels of sunlight per unit area (higher than many other countries), and suitable ambient temperature for microalgae growth.[9] Considering these advantages, pilot-scale microalgae plants have been established for evaluating the viability of microalgal biodiesel production. It is known that microalgal biodiesel production involves several processes that can be energy intensive such as cultivation, harvesting and dewatering, and lipid extraction.[10] Therefore, understanding the life cycle energy and carbon footprints of these processes is essential to assessing the viability and sustainability of microalgal biodiesel production at an industrial scale in WA.

Table 1 lists the details of some previous reports on the life cycle analysis (LCA) of microalgal biodiesel production in different regions such as France,[11,12] the United Kingdom,[8,13] The Netherlands,[14] the United States,[6,10,15−19] China,[20] Brazil,[21] and Singapore.[22] Because of the region-dependent nature of LCA studies, results from those LCA studies are unlikely applicable to WA's conditions. Meanwhile, little has been reported on LCA of microalgal biodiesel production in WA. It is also known that wet lipid extraction, which avoids energy-intensive drying of microalgae slurry, is essential to achieving net energy gain over the whole life cycle.[6,8,11,19] The

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Table 1. Benchmarking of Life Cycle Energy and Carbon Footprints with Other Published Studies

authors	country/ region	algae strain (growth rate, g/m^2/day; lipid content, wt % dry weight)	cultivation system	energy inputs[a] MJ/MJ biodiesel	GHG emissions[a] g CO_2-eq/MJ biodiesel	notes
this study	WA	*Pleurochrysis carterae* (22/14.6%)	open ponds	1.3	80	scenario A[b]
				0.7	33	scenario B[c]
Lardon et al. (2009)[11]	France	*Chlorella vulgaris* (19.25/38.5%, low N; 24.75/17.5%, normal N)	open ponds	5.3	58.9	normal N; dry[d]
				4	8.0	normal N; wet[d]
				2.3	24.1	low N; dry[d]
				1.7	−16.1	low N; wet[d]
Delrue et al. (2012)[12]	France	not specified (20−30/20%−50%)	open ponds	0.8−1.1	69.0−105.6	reference system[e]
			hybrid system	0.4−0.5	29.8−47.3	innovative system[f]
Stephenson et al. (2010)[8]	U.K.	*Chlorella vulgaris* (30/40%)	open ponds	0.17	19.3	values from figure(s)[g,h]
			bioreactor	5.4	319.9	values from figure(s)[g,h]
Shirvani et al. (2011)[13]	U.K.	*Chlorella vulgaris* (20/18%)	open ponds	2.3	118.0	main considerations[i]
Clarens et al. (2011)[15]	US	not specified (26.7/17.4%)	open ponds	0.7	71.7	derived from Liu et al. (2012)[50] [j,k]
Batan et al. (2010)[16]	U.S.	*Nannochloropsis salina* (25/50%)	bioreactor	0.9	−75.3	main considerations[l]
Brentner et al. (2011)[17]	U.S.	not specified	open ponds and bioreactor	7.8	534.0	base case[m]
				1.1	80.5	best case[n]
Chowdhury et al. (2012)[10]	U.S.	*Schizochytrium limacinum* (25/50%)	open ponds	0.5	27.8	main considerations[o]
Frank et al. (2012)[18]	U.S.	not specified (25/25%)	open ponds	2.8	20.4	main considerations[p]
Vasudevan et al. (2012)[6]	U.S.	*Not specified* (20/25%)	open ponds	3.3	278.0	dry lipid extraction[q]
				0.4	53.0	wet lipid extraction[q]
Sills et al. (2012)[19]	U.S.	not specified (25/34%, base case)	hybrid system	2.9[g]	201.9[g]	dry pathway[r]
				0.7	70.0	wet pathway[s]
Liao et al. (2012)[20]	China	*Chlorella vulgaris* (35/40%)	open ponds	0.7	160.0	main considerations[t]
Jorquera et al. (2010)[21]	Brazil	*Nannochloropsis sp.* (11/29.6%)	open ponds and bioreactor	1.8	not analyzed	derived from Liu et al. (2012)[50] [j]
Khoo et al. (2011)[22]	Singapore	*Nannochloropsis sp.*	hybrid system	4.4	344.3[g]	main considerations[u]

[a]Functional units converted (if necessary) using the biodiesel lower heating value (LHV) and density reported, or 37.2 MJ/kg and 0.88 kg/L respectively if not reported. [b]Scenario A: open ponds, autoflocculation, dissolved air flotation, centrifugation, wet lipid extraction, transesterification, and anaerobic digestion. [c]Scenario B: open ponds, autoflocculation, dissolved air flotation, centrifugation, wet lipid extraction, transesterification, and hydrothermal liquefaction. [d]Main considerations: system infrastructure; nutrients−fertilizer; CO_2 source−flue gas; harvesting and dewatering−flocculation, thermal drying; lipid conversion−transesterification; and system boundary−well to pump. [e]Reference pathway: raceways, centrifugation, thermal drying, n-hexane lipid extraction, transesterification, and anaerobic digestion. [f]Innovative pathway: Bioreactor and raceway, belt filter press, dimethyl ether lipid extraction, hydrotreating, and anaerobic digestion. [g]Data taken from figures in the reference. [h]Main considerations: system infrastructure; nutrients−fertilizer; CO_2 source−flue gas; harvesting and dewatering−flocculation, centrifugation; wet lipid extraction; lipid conversion−transesterification; product transport and distribution; byproducts utilization−anaerobic digestion; and system boundary−well to wheels. [i]Main considerations: system infrastructure; nutrients−fertilizer; CO_2 source−flue gas; harvesting and dewatering−flocculation, thermal drying; dry lipid extraction; lipid conversion−transesterification; product transport and distribution; byproducts utilization−animal feed, combustion; and system boundary−well to wheels. [j]Data normalized to the function unit in Liu et al. (2012).[50] [k]Main considerations: system infrastructure; nutrients−fertilizer, wastewater; CO_2 source−flue gas, liquid CO_2; harvesting and dewatering−autoflocculation, gravity thickening; wet lipid extraction; lipid conversion−transesterification; byproducts utilization−anaerobic digestion, combustion; and system boundary−well to wheels. [l]Main considerations: nutrients−fertilizer; CO_2 source−flue gas; harvesting and dewatering−centrifugation, filtration; dry lipid extraction; lipid conversion−transesterification; product transport and distribution; byproducts utilization−animal feed; and system boundary−well to pump. [m]Base case: open ponds, centrifugation, thermal drying, hexane lipid extraction, esterification, and landfilling. [n]Best case: flat-plate bioreactor, flocculation, supercritical methanol extraction and esterification, and anaerobic digestion. [o]Main considerations: nutrients−fertilizer; CO_2 source−flue gas; harvesting and dewatering−filter press, thermal drying; dry lipid extraction; lipid conversion−transesterification; byproducts utilization−anaerobic digestion; and system boundary−well to pump. [p]Main considerations: nutrients−fertilizer; CO_2 source−flue gas; harvesting and dewatering− autoflocculation, dissolved air flotation, centrifugation; wet lipid extraction; lipid conversion−transesterification; product transport and distribution; byproducts utilization−anaerobic digestion; and system boundary−well to wheels. [q]Main considerations: system infrastructure; nutrients−fertilizer; CO_2 source−flue gas; harvesting and dewatering−dissolved air flotation, centrifugation, thermal drying; dry and wet lipid extraction; lipid conversion−transesterification; product transport and distribution; byproducts utilization−anaerobic digestion; and system boundary−well to wheels. [r]Dry pathway: hybrid cultivation, centrifugation, thermal drying, hexane extraction, transesterification, and animal feed. [s]Wet pathway: hybrid cultivation, belt filter press, hydrothermal liquefaction, hydrotreatment, and anaerobic digestion. [t]Main consideration: nutrients−fertilizer; CO_2 source−flue gas; harvesting and dewatering−flocculation, centrifugation, thermal drying; dry lipid extraction; lipid conversion−transesterification; product transport and distribution; byproducts utilization−anaerobic digestion; and system boundary−well to wheels. [u]Main considerations: nutrients−fertilizer; CO_2 source−compressed air; harvesting and dewatering−flocculation, centrifugation; wet lipid extraction; lipid conversion−transesterification; and system boundary−well to pump.

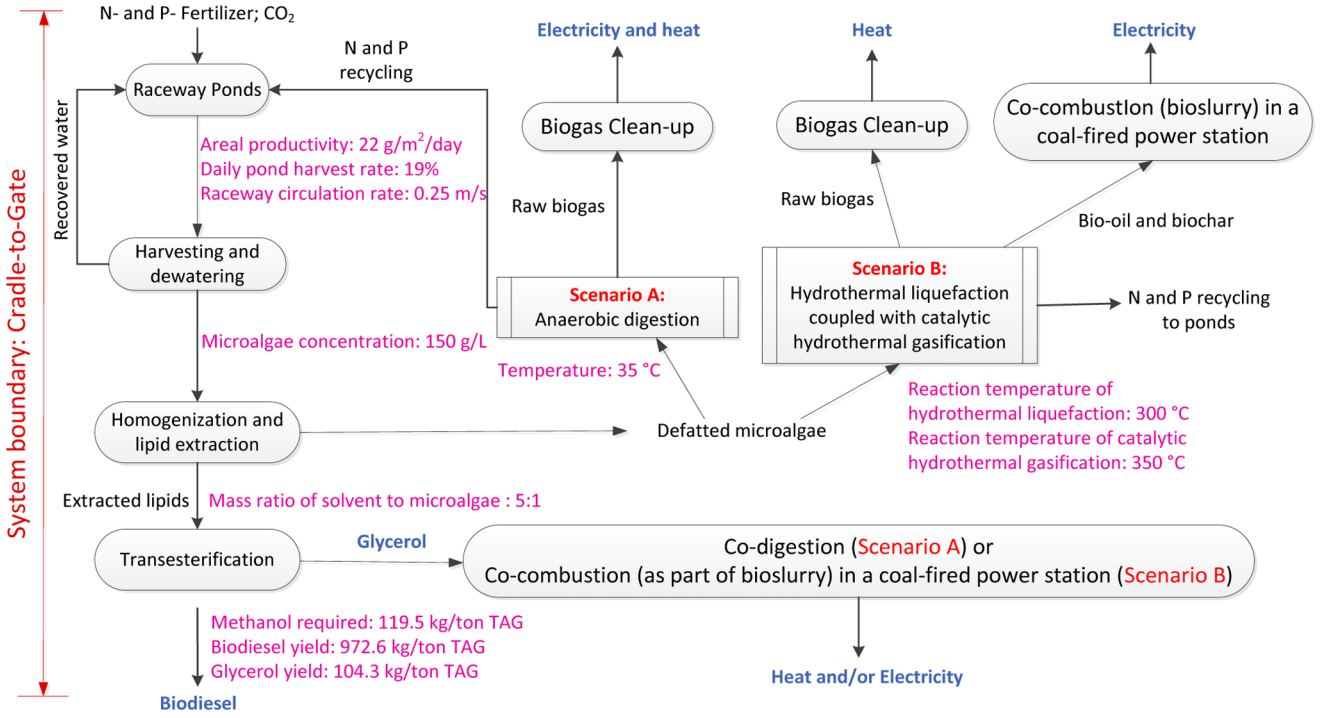

Figure 1. Process chain and scenarios for biodiesel production from marine microalgae in WA.

microalgae residue slurry after wet lipid extraction can also be considered as an important energy source.[11,17] Its expected that its utilization may have significant effect on overall LCA performance and can enhance the sustainability of biodiesel production. There are at least two utilization options for feedstock with high moisture contents (generally ~85%[23]), i.e. anaerobic digestion[24] and hydrothermal liquefaction.[25] Most previous studies[6,8,10,12,17,19] focused on anaerobic digestion for producing biogas (mainly CH_4) and recycling nutrients (mainly N and P). Biogas can be burned for heat and electricity production (Table 1). Hydrothermal liquefaction converts biomass into bio-oil,[25] which can be updated to liquid transport fuels,[26] directly burned in stationary engines,[27,28] and/or co-combusted in coal-fired power stations.[29−31] Little work has been done on the LCA considering hydrothermal liquefaction of defatted microalgae residues.

Therefore, this study aims to carry out a systematic and comprehensive LCA on energy and carbon footprints for microalgal biodiesel production under the conditions in WA. Such analysis provides essential information for assisting government policy setting and identifying further research and development (R&D) priorities. Particular efforts were taken to assess the ability of byproducts utilization strategies (i.e., anaerobic digestion and hydrothermal liquefaction) in offsetting the overall energy and carbon footprints. Sensitivity analyses were also conducted to identify the key process aspects requiring further R&D for realizing truly sustainable production of microalgal biodiesel.

METHODOLOGY

The systematic LCA on energy and carbon footprints of microalgal biodiesel production is based on a hypothetical production system in Karratha, WA. The main focus is on byproducts utilization strategies and their impacts on the system's overall life cycle performance. A LCA model is established based on the data reported in open literature and first-principles engineering calculations. A brief description is given in this section, and more details can be found in the Supporting Information (SI).

Method Overview. This study considers the overall process chain and scenarios (Figure 1, description given in next subsection) with a system boundary being set as "Cradle-to-Gate". The plant has a lifetime of 30 years, except for the plastic pond liners (10 years). The functional unit for this study is *1 MJ Biodiesel*. The life cycle energy footprint is defined as the total nonrenewable energy inputs per MJ of biodiesel produced. It is calculated based on the equation employed in a previous study.[29] The total nonrenewable energy inputs include direct (process heat and electricity, etc.) and indirect (fertilizers, process chemicals, and system construction, etc.) energy inputs involved in the whole process chain, considering the total accumulated energy during the full process from production, delivery, and utilization of each item. The life cycle carbon footprint is calculated as the total direct and indirect GHG emissions per MJ of biodiesel produced. The calculation considers the three main GHGs (i.e., CO_2, CH_4, and N_2O) in terms of their carbon dioxide equivalent (CO_2-eq) via multiplying the estimated mass of emissions by their 100-year global warming potentials.[32] A substitution allocation method[8,33] is used to estimate the energy and carbon credits from byproducts utilization, which may produce and is thereby able to displace process heat, electricity, and/or fertilizers. The credits from byproducts utilization are therefore equal to the primary energy requirements and GHG emissions associated with production of the displaced process heat, electricity, and/or fertilizers.

Process Chain and Scenarios. As depicted in Figure 1, the system includes the processes from microalgae cultivation to the production of biodiesel as a main product. The main inputs for the process chain and scenarios, including those for the base, low and high cases, and the justifications of using these values are summarized in Table 2. Briefly, marine microalgae (*Pleurochrysis carterae*) are cultivated in open raceway ponds in a semicontinuous mode. This

Table 2. Main Inputs for the Process Chain and Scenarios

inputs parameters	low case	base case	high case
Cultivation			
areal productivity ($g/m^2/day$)[a]	10	22	34
daily pond harvest rate (% of total pond volume)[b]	10	19	29
total lipid content[c] (wt % dry basis (db))		36.5	
TAG fraction (wt % of total lipid)[d]	30	40	90
raceway evaporation rate (m/day)[e]		0.01	
raceway circulation rate (m/s)[f]	0.2	0.25	0.3
CO_2 utilization efficiency (%)[g]		82	
distance between CO_2 source to farm (km)[h]	2.5	5	20
distance between water source and farm (km)[i]	2	5	20
Harvesting and dewatering[j]			
algae concentration after bioflocculation (g/L) and its harvest efficiency		10 (90%)	
algae concentration after dissolved air flotation (g/L) and its harvest efficiency		60 (90%)	
algae concentration after centrifugation (g/L) and its harvest efficiency		150 (95%)	
overall harvest efficiency[k]		95	
Lipid extraction			
fraction of algae cell homogenized after two passes (%)[l]		90	
recovery rate of cell homogenization (wt %)[m]		95	
solvent (hexane) loss (g/kg lipid extracted)[l]		5.2	
TAG extraction efficiency (%)[l]		95	
Transesterification			
biodiesel yield (kg/ton algae TAG)[n]		972.6	
crude glycerol yield (kg/ton algae TAG)[n]		104.3	
methanol (kg/ton algae TAG)[n]		119.5	
KOH (kg/ton algae TAG)[n]		10	
lower heating value (LHV) of biodiesel (MJ/kg)[o]		37.2	
density of biodiesel (kg/L)[o]		0.88	
Anaerobic digestion			
methane yield (L-CH_4/g total solid)[p]	0.1	0.3	0.4
efficiency of CHP for electricity production (%)[q]	28	33	38
efficiency of total CHP (%)[q]		76	
N recycled for algae cultivation (wt % of N in feedstock)[r]	41	61	86
P recycled for algae cultivation (wt % of P in feedstock)[r]	20	52	89
Hydrothermal liquefaction			
higher heating value (HHV) of bio-oil (MJ/kg)[s]		38.3	
bio-oil yield from HTL of lipid-extracted algae biomass (wt %, daf)[t]	30	41	50
reaction temperature (°C)[u]	250	300	350
reaction time (min)[u]		60	
distance between the coal-fired power plant to farm[v]	10	50	200
carbon (C) fraction in bio-oil (wt % of bio-oil)[w]		74.5	
hydrogen (H) fraction in bio-oil (wt % of bio-oil)[w]		10.4	
nitrogen (N) fraction in bio-oil (wt % of bio-oil)[w]		5.3	
oxygen (O) fraction in bio-oil (wt % of bio-oil)[x]		9.9	
conversion rate of organic carbon to CH_4 and CO_2 (% of total organic carbon conversed)[y]		90	
volume percentage of CH_4 in biogas produced from catalytic hydrothermal gasification (vol %)[u]		60	
volume percentage of CO_2 in biogas produced from catalytic hydrothermal gasification (vol %)[u]		40	
N recycled for algae cultivation (wt % of N in feedstock)[z]	10	35	73
P recycled for algae cultivation (wt % of P in feedstock)[z]	36	54	72

[a]Data taken from Moheimani et al. (2006)[34] as base case value (see Section 3.1 in the SI for details). [b]Calculated as 50% × specific growth rate, based on the data reported by Moheimani et al. (2006)[34] (see Section 3.1 in the SI). [c]Data taken from Moheimani et al. (2006).[34] [d]See Section 3.1 in the SI for justification. [e]Data taken from Luke et al.(1988).[51] [f]Based on data reported by Norsker et al. (2011).[52] [g]Data taken from Frank et al. (2012).[18] [h]Estimated value (see Section 3.5 in the SI). [i]Estimated value (see Section 3.3 in the SI). [j]Data taken from Davis et al. (2012).[46] [k]As suggested by Davis et al. (2012),[46] supernatants of autoflocculation and DAF is recycled back to ponds. Microalgae lost during these steps can be eventually recovered and only overflow from centrifuges is subjected to byproducts utilization. Thus, a net harvested efficiency of 95%, equal to centrifuge loss, is considered. [l]Data taken from Frank et al. (2011).[36] [m]Data taken from Stephenson et al. (2010).[8] [n]Calculated based on mass balance. [o]Data taken from Sturm et al. (2011).[7] [p]Estimated based on review of some previous studies[10,15,17,19,24,46,53−64] (see Section 5.2 in the SI). [q]Data taken from Frank et al. (2011).[36] [r]Estimated, based on review of some previous studies[24,62,65−67] (see Section 5.2 in the SI). [s]Calculated based on Dulong's formula: HHV (MJ/kg)= 0.338 × C + 1.428 × (H−O/8), where C, H, and O are mass percentage based on dry microalgae mass. [t]Base case bio-oil yield estimated based on Valdez et al. (2012)[25] while high case and low case values estimated based on the review of some previous studies.[40,42−44,68−74] [u]Data taken from Frank et al. (2012).[18] [v]Estimated value (see Section 5.3.3 in the SI). [w]Estimated based on Valdez et al. (2012).[25] [x]Calculated by difference. [y]Estimated based on Frank et al. (2012).[18] [z]Estimated based on some previous studies[25,67] (see Section 5.3.4 in the SI).

study considers 25 cultivation ponds (4 ha each), with an effective cultivation area of 100 ha. The annual average growth rates (areal growth rate: 22 g/m^2/day; specific growth rate: 0.38 day^{-1}) are taken from a local study[34] and used as base case values. The harvest manner of a semicontinuous mode is well-documented in a recent study by Murphy and Allen.[35] For a semicontinuous system, 50% of microalgae in cultivation media needs to be harvested at a rate equal to the specific growth rate. The base case daily harvest rate is estimated as 19% (50% × 0.38) of pond volume. A combination of autoflocculation, dissolved air flotation, and centrifugation is used as harvesting and dewatering method.[18] Dewatered microalgae (solid concentration: 150 g/L[18]) is subsequently subjected to pressure homogenization and wet lipid extraction. The extracted lipids (mainly triacylglycerols, TAG) are then converted to biodiesel via transesterification reaction with methanol. Hereafter in this paper, biodiesel produced from marine microalgae is denoted as "biodiesel" unless otherwise specified.

Two main byproducts are produced, i.e. defatted microalgae and glycerol. In this study, the main processes (i.e., cultivation, harvesting and dewatering, lipid extraction, and transesterification) are kept the same, with two byproducts unitization scenarios being considered. Scenario A (i.e., the anaerobic digestion route) employs anaerobic digestion of the defatted microalgae and glycerol to produce biogas that is further cleaned and burned in a combined heat and power (CHP) unit for electricity and heat production. The supernatant, rich in C, N and P nutrients, is recycled to the cultivation ponds for microalgae growth. Scenario B (i.e., the hydrothermal liquefaction route) produces bio-oil, biochar, and aqueous phase via hydrothermal liquefaction of the defatted microalgae. The bio-oil and biochar are mixed with glycerol to prepare a bioslurry fuel for further transport and subsequent co-combustion in coal-fired power plants for electricity production. The aqueous phase containing C, N, and P is subjected to catalytic hydrothermal gasification to produce biogas and recover nutrients.[18] The biogas is cleaned and burned in a natural gas boiler to produce process heat consumed on-site. The nutrients (N and P) in liquid are recycled to the cultivation ponds.

RESULTS AND DISCUSSION

Life Cycle Energy Flow without Byproducts Utilization. Figure 2 illustrates the life cycle energy inputs associated with production of defatted microalgae, glycerol, and 1 MJ biodiesel, without allocation of credits from byproducts utilization. Therefore, the data reveal life cycle energy inputs and distribution of energy among the three outputs. Three observations can be made from Figure 2. First and most important, ~84% of total energy outputs is in the forms of byproducts (primarily defatted microalgae). Therefore, it is clear that if the byproducts are not utilized, biodiesel production is not sustainable because energy inputs (4.3 MJ) are more than that produced in biodiesel (1 MJ). This highlights strong needs for effectively utilizing byproducts (including defatted microalgae and glycerol) in order to produce biodiesel sustainably. Second, cultivation is the most energy-intensive process, accounting for ~64% of the total energy inputs. Energy inputs associated with pressure homogenization and wet lipid extraction are also considerable (~30% of the total inputs). Last, electricity is the most significant energy input, followed by embodied energy of fertilizers. These two contribute to ~62% of the total energy inputs. In addition, ~35% of the total energy inputs is associated with process heat and energy embedded in infrastructure construction materials. Clearly, burdens associated with system infrastructure cannot be offset by byproducts utilization. Electricity and process heat production and nutrients recovery are the key objectives of byproducts utilization.

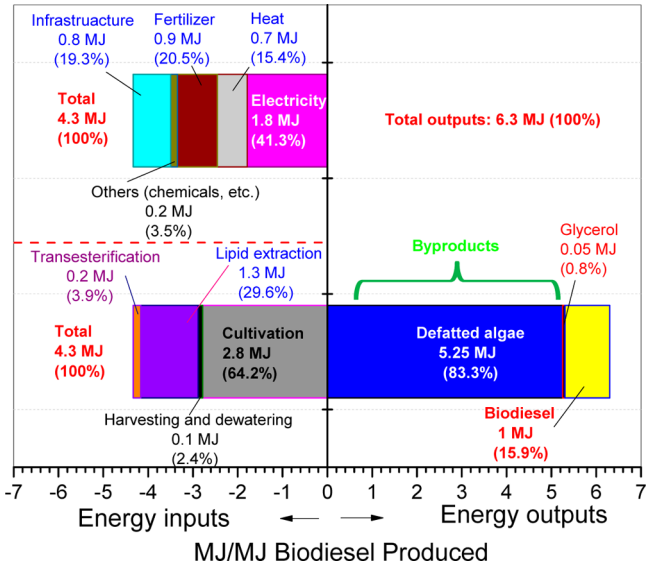

Figure 2. Life cycle energy inputs and outputs associated with production of 1 MJ biodiesel (base case), without byproducts allocation.

Life Cycle Energy and Carbon Credits from Byproducts Utilization. Figure 3 presents the base case energy and carbon footprints for both the anaerobic digestion route and hydrothermal liquefaction route, benchmarking against the energy and carbon credits from byproducts utilization. Details (values and rationale) of the base case inputs for byproducts utilization are given in Section 5 of the SI. The energy and carbon credits from the two byproducts utilization approaches broadly include three groups: (1) electricity produced from biogas or bioslurry combustion, (2) process heat generated by biogas combustion, and (3) recycled N and P fertilizers. The recycled carbon (CO_2 in flue gas and/or carbon in digested liquid) produced from anaerobic digestion or hydrothermal liquefaction is also introduced to the cultivation ponds for reducing the demands of flue gas CO_2 delivered from Yurralyi Maya Power Station (see Section 3.5 of the SI). However, the effect of the recycled carbon on the overall life cycle performance is insignificant. As the upstream burdens for flue gas CO_2 are not considered, only electricity consumed for CO_2 delivery (i.e., transport from the power plant to the microalgae farm and transfer into the cultivation ponds) contributes to the life cycle energy and carbon footprints. In addition, the majority (>70%) of electricity is consumed to transfer CO_2 into the cultivation ponds,[36] which is not saved by recycling CO_2 from biogas combustion. In other words, the recycled CO_2 also needs to be transferred into the cultivation ponds. Therefore, the recycled carbon has little effect on the overall energy and carbon footprints.

For scenario A, the anaerobic digestion route, the major energy and carbon credits are from biogas combustion, which offsets ~100% of on-site consumption of process heat and electricity (panels a and b of Figure 3). Nutrients recovery is also a considerable credit, with ~61% of N and ~52% of P recycled to the cultivation ponds.

Attempts were made to upgrade or refine the bio-oil produced from the hydrothermal liquefaction of raw microalgae into diesel-like via hydrotreating.[19] However, the N content (e.g., ~2%) in product fuel[37] is considerably higher than fossil diesel,[38] which could hinder its direct application as a transport fuel due to nitrogen oxides (NO_x) emission during combustion.

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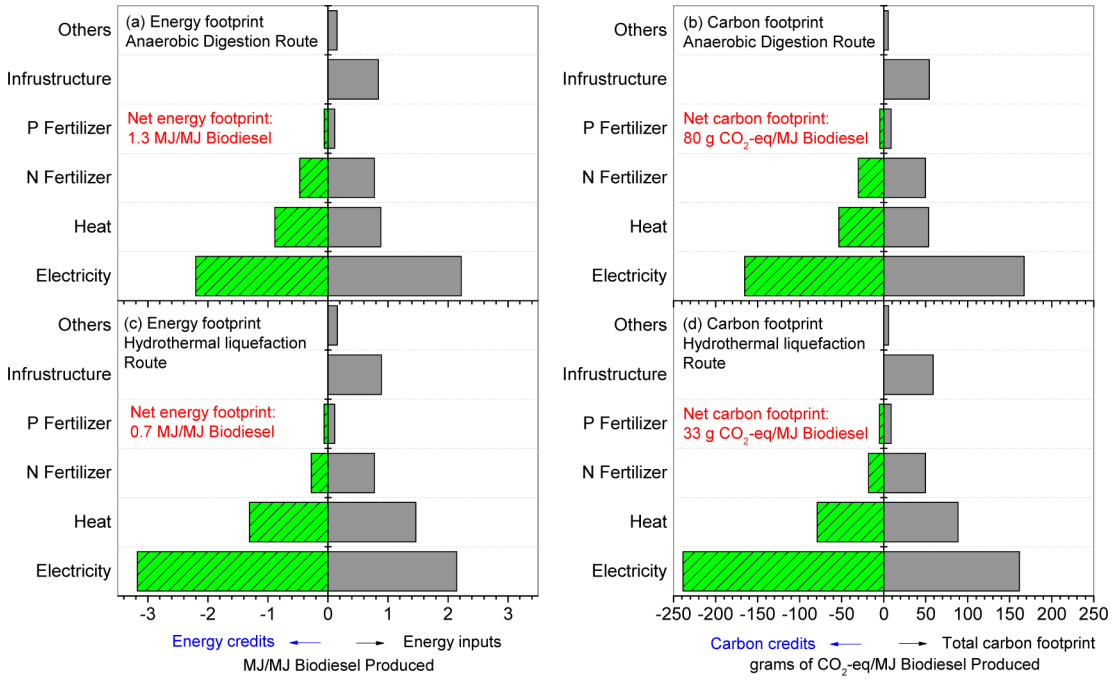

Figure 3. Life cycle energy and carbon credits from scenario A (anaerobic digestion route, panels a and b), and scenario B (hydrothermal liquefaction route, panels c and d).

On the other hand, the biodiesel produced from the conventional transesterification process is suitable for direct combustion in diesel engines. Therefore, in scenario B, the hydrothermal liquefaction route of this study, the bio-oil and biochar produced from defatted microalgae via hydrothermal liquefaction are mixed with glycerol to produce a bioslurry fuel. Bioslurry fuel is suitable for co-firing in coal-based power plants for electricity production.[28−31] High content of N in bioslurry is unlikely to be problematic because most coal-fired power plants are equipped with NO_x control devices.[39] Therefore, the key advantage of this technical route is to produce high-quality biodiesel (via transesterification) as a final product and bioslurry fuel for electricity production. Indeed, bioslurry combustion produces ∼48% more electricity than that is consumed during the whole process. This surplus electricity contributes to WA's electricity grid and therefore is able to offset the overall life cycle burdens for biodiesel production. The carbon balance (see Section 5.3 of the SI) during hydrothermal liquefaction of defatted microalgae suggests that ∼45% of carbon is present in the aqueous phase. This means that a significant amount of energy is retained in the aqueous phase. Catalytic hydrothermal gasification is thus employed to convert carbon in the aqueous phase to biogas that is combusted on-site for process heat production. As shown in panels c and d of Figure 3, ∼89% of the consumed process heat can be provided by biogas combustion. After catalytic hydrothermal gasification, ∼36% of N and ∼54% of P (see Section 5.3 of the SI) can be recycled from the aqueous phase, offsetting upstream burdens for the production of these fertilizer production.

A comparison between the hydrothermal liquefaction and anaerobic digestion routes leads to four interesting findings. First, the hydrothermal liquefaction route produces more electricity and process heat than anaerobic digestion route. This is apparently because that during hydrothermal liquefaction more carbon is converted for direct energy production (i.e., electricity and heat) than anaerobic digestion. In the hydrothermal liquefaction route, ∼53.8% and ∼17.1% of carbon in defatted microalgae carbon is retained in bio-oil and converted to CH_4, respectively (see Figure S11 of the SI). The bio-oil and CH_4 are then used for electricity and heat production. On the contrary, only ∼31.4% of carbon in the defatted microalgae is converted to CH_4 for electricity and heat production in the anaerobic digestion route (see Figure S9 of the SI). Second, less N is recovered from hydrothermal liquefaction route because ∼23% of N is retained in bio-oil (see Section 5.3 of the SI). Clearly, electricity production from bioslurry is at the expense of losing some N nutrient retained in it. It is also known that process heat can only be consumed on-site, and therefore, no additional credits are obtained from surplus heat (if any). Therefore, electricity production and nutrients (N and P) recycling are two criteria to be considered in selecting byproducts utilization strategies. Third, more process heat is required for the hydrothermal liquefaction route because a higher reaction temperature (∼300 °C) is required compared to that (∼35 °C) in the anaerobic digestion route. This however is not a problem as the majority (∼89%) of the process heat can be provided by the combustion of biogas produced from catalytic hydrothermal liquefaction. Finally, the reaction time of hydrothermal liquefaction (e.g., typically less than 60 min[40−44]) is much shorter than anaerobic digestion (e.g., generally longer than 20 days[24]). This considerably reduces reactor footprint for easy scale-up.

Overall, the anaerobic digestion route and the hydrothermal liquefaction route can substantially reduce life cycle energy inputs for biodiesel production from 4.3 (without byproducts utilization) to 1.3 and 0.7 MJ/MJ biodiesel, respectively. Their corresponding carbon footprints are 80 and 33 g of CO_2-eq/MJ, respectively. Compared with the "standard" anaerobic digestion route, the hydrothermal liquefaction route offers much lower energy and carbon footprints hence can be considered as another attractive byproducts utilization strategy.

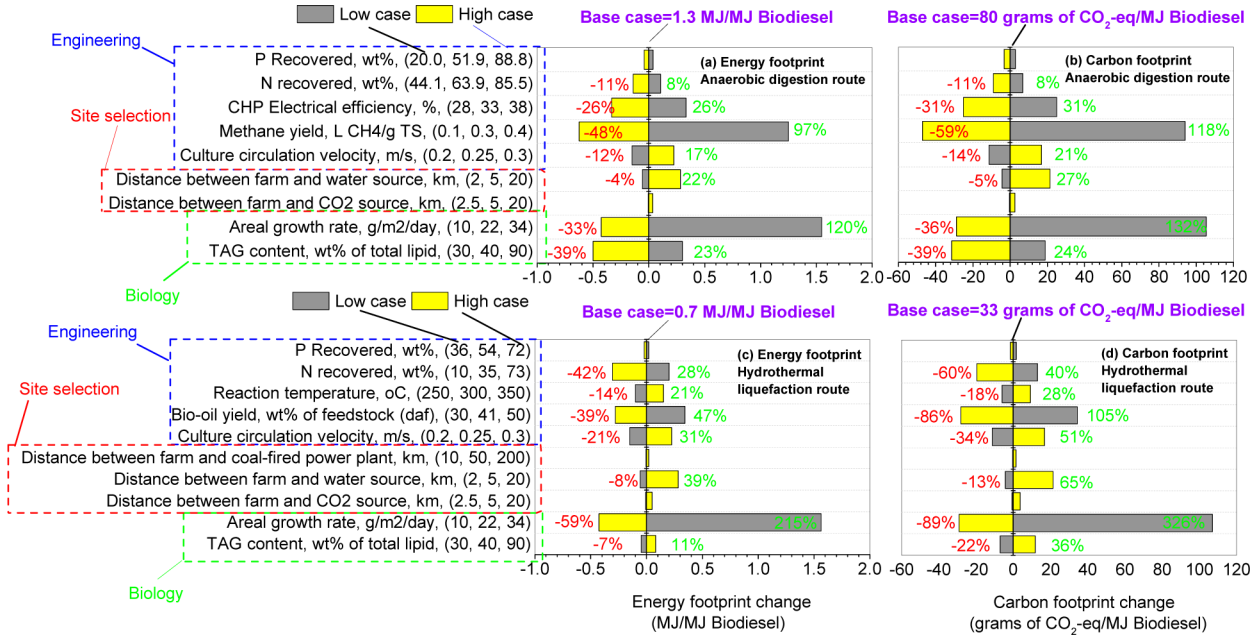

Figure 4. Sensitivity analysis for life cycle energy and carbon footprints of biodiesel production from scenario A (anaerobic digestion route) and scenario B (hydrothermal liquefaction route). Percentage values shown are calculated as relative differences to those of the base case.

However, the energy footprints of 1.3 MJ/MJ biodiesel (anaerobic digestion route) and 0.7 MJ/MJ biodiesel (hydrothermal liquefaction route) are considerably higher than the maximum sustainable energy footprint ~0.3 MJ/MJ[45] that is required for a renewable liquid transport fuel to be sustainable. Therefore, further R&D is required to achieve biodiesel production in a truly sustainable manner.

Sensitivity Analysis. Because of the uncertainties of input parameters associated with commercial-scale production of biodiesel,[19] sensitivity analysis is then conducted to reflect such effect on the overall energy and carbon footprints. Sensitivity analysis also identifies key parameters to which the energy and carbon footprints are most sensitive. This further provides guidance to selection of microalgae strain and farm site and improvement of engineering design. These key parameters can be broadly grouped into three categories, i.e., biological, farm site selection, and engineering parameters. Table 2 lists the base case values and those for sensitivity analysis, along with justifications on selection of these values. The results of sensitivity analysis are presented in Figure 4.

Figure 4 shows that microalgae growth rate and TAG content are two important biological parameters for strain selection. Indeed, the net energy and carbon footprints for both the anaerobic digestion route and the hydrothermal liquefaction route are highly sensitive to growth rate. Increasing growth rate from 22 to 34 g/m^2/day reduces the energy and carbon footprints by 33−59% and 36−89%, respectively, depending on the scenarios analyzed. A low growth rate of 10 g/m^2/day is clearly not favored because of the high energy and carbon footprints. Increasing TAG content from 40% to 90% of total lipid (i.e., 14.6% to 32.9% of dry microalgae, see Section 3.1 of the SI) decreases 39% of the energy and carbon footprints for the anaerobic digestion route. This is apparently because more biodiesel can be produced at a higher TAG content. Surprisingly, a low TAG fraction (30 wt % of the total lipid) results in ~7% and ~22% reduction in the energy and carbon footprints for the hydrothermal liquefaction route. When the TAG fraction is as low as 30%, the energy distributed in byproducts (defatted microalgae and glycerol) slightly increases from ~84% to ~88% of the total energy outputs. Therefore, more energy and carbon credits can be produced from hydrothermal liquefaction of the defatted microalgae and subsequent utilization of the products, including bioslurry (produced from bio-oil, biochar, and glycerol) co-firing for electricity and CH_4 combustion for process heat. Hydrothermal liquefaction of the defatted microalgae is more energetically efficient than biodiesel production. As shown in Figure S4 and Figure S12 in the SI, only ~16% of energy in microalgae is converted to biodiesel while ~83% of energy in the defatted microalgae is converted to bio-oil and biogas. From an energetic point of view, hydrothermal liquefaction favors microalgae with low TAG contents. However, a low TAG content may not be economically favorable if biodiesel is the final product.[46] This is evidenced by a ~25% reduction in the biodiesel productivity when the TAG content decreases from 40% to 30%.

Sensitivity analysis on farm site selection parameters suggests that the distance from the microalgae farm to the intake point of seawater (if seawater is used to cultivate microalgae) is the most important consideration. Increasing the distance from 5 to 20 km leads to more electricity consumption in delivering water from the intake point to the microalgae farm. The energy and carbon embedded in construction materials of water pipelines are also increased. As a result, the energy footprint increases ~22−39% and the carbon footprints increases ~27−65%, depending on the scenarios studied. On the other hand, the life cycle performance of biodiesel production is less sensitive to the distance between the CO_2 source and the microalgae farm. This is because that the majority of electricity (>70%) consumed for CO_2 delivery is to transfer flue gas into the cultivation ponds, if using a low-pressure transport pipeline. Changing in the distance between bioslurry combustion site (i.e., a coal-based power plant) and the microalgae farm from 10 to 200 km also shows negligible effect on the net energy and carbon footprints. This is because that the transport of bioslurry using diesel vehicles is not energy intensive.[47]

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Engineering parameters such as circulation velocity of culture media, fertilizers (N and P) recovery rate, product yields, electrical efficiency of the CHP unit, and reaction conditions are also examined to assess their effect on the energy and carbon footprints. If microalgae strain is able to achieve good mixing at a low culture circulating velocity of 0.2 m/s, a reduction of ∼12−21% on the energy footprint and ∼14−34% on the carbon footprints is expected, depending on the scenarios analyzed. Alternatively, this highlights the importance of altering culture media circulation velocity, e.g., at a high speed during day time and a low speed at night. Nutrients (particularly N) recycling rates can also considerably affect the overall life cycle performance. Increasing the N recycling rate results in ∼11−42% reduction in the energy footprint and ∼11−60% reduction in the carbon footprint, which is also dependent on the scenarios analyzed. This is consistent with the finding in Figure 3 that the nutrients recycling rates significantly affect the overall life cycle performance. The effect of the P recovery rate on the energy and carbon footprints is insignificant because P fertilizer contributes little to the total inputs. Changes in CH_4 yield substantially affects the energy and carbon footprints (up to ∼118%) when the anaerobic digestion route is considered, showing the great importance of improving CH_4 yields. Changes of electrical efficiency of the CHP unit also results in ∼26% and ∼31% variations in the energy and carbon footprints, respectively, suggesting that electrical efficiency of the CHP unit is also important. Variations in bio-oil yield lead to a ∼39−47% change in the energy footprint and a ∼86−105% change in the carbon footprint when the hydrothermal liquefaction route is employed. It should be noted that the current hydrothermal liquefaction model fixes carbon fraction in biochar and gas phase. Decreasing bio-oil yield means that more carbon is partitioned into aqueous phase that is converted to biogas via catalytic hydrothermal gasification. The biogas produced is able to generate process heat that partly offsets the effect of bio-oil yields on the overall life cycle performance. Increasing the reaction temperature from 300 to 350 °C results in ∼21% and ∼28% increases in the energy and carbon footprints, respectively, for the hydrothermal liquefaction route.

Further Discussion. This section discusses the scalability of microalgal biodiesel production in WA and benchmarks the energy and carbon footprints in this study with those reported in other published papers. The base case annual energy productivity of biodiesel in WA is ∼296 GJ/ha, which is ∼15 time higher than that of canola biodiesel production in the State.[47] It is estimated that ∼12.24−24.08 PJ biodiesel would be produced from microalgae in order to displace 10−20% of total diesel fuel consumed in WA's transport sector in 2010.[48] Given the energy productivity of ∼296 GJ/ha, ∼50,280−97,000 ha of farm land would be required, at an effective cultivation land fraction of 85%. According to a study on identification of microalgae cultivation sites in WA,[49] the suitable land areas include south of Geraldton, southeast of Exmouth, and coastal land between Karratha and Port Hedland. A close estimation reveals that only the area between Karratha and Port Hedland is ∼630,000 ha, indicating that WA has great potential in microalgal biodiesel production because of its large coastal land area, abundant sunshine and unlimited seawater source.[49]

Table 1 benchmarks the energy and carbon footprints obtained from this study against some studies reported in the literature. It can be seen that the life cycle energy and carbon footprints in this study are in a broad range of the previously reported values. However, significant discrepancies are observed for the energy footprint (from ∼0.17 MJ/MJ biodiesel[8] to 7.8 MJ/MJ biodiesel[17]) and also for the carbon footprint (from ∼19.3[8] to 534.0 g CO_2-eq/MJ biodiesel[17]). Such discrepancies can be due to various reasons such as differences in system boundaries and methods of byproducts allocation.[50] For example, in Stephenson et al.,[8] defatted microalgae were subjected to anaerobic digestion. However, in the base case of Brentner et al.,[17] defatted microalgae were directly filled in land without energy recovery, leading to the considerably higher energy and carbon footprints reported. Additionally, the overall energy and carbon footprints are also sensitive to the process chains selected, particularly the cultivation system and lipid extraction method. Open raceway ponds generally yield lower energy and carbon footprints than bioreactors, as shown in Stephenson et al.[8] Wet lipid extraction also leads to lower energy and carbon footprints than dry lipid extraction as a result of omitting energy-intensive drying process, as demonstrated by Vasudevan et al.[6] and Sills et al.[19] (Table 1). Overall, the results in the published LCA studies differ considerably, apparently due to discrepancies in system boundaries, byproducts allocation methods, and process chains. Consequently, care must be taken for direct comparisons among these results in different publications.

CONCLUSIONS

This study reports the life cycle energy and carbon footprints of biodiesel produced from marine microalgae in WA, focusing on the comparison between anaerobic digestion and hydrothermal liquefaction for byproducts utilization. The net energy footprints are 1.3 and 0.7 MJ/MJ biodiesel for the anaerobic digestion route and hydrothermal liquefaction route, respectively. The corresponding carbon footprints are 80 and 33 g CO_2-eq/MJ biodiesel, respectively. Compared with the anaerobic digestion route, the hydrothermal liquefaction route offers much lower energy and carbon footprints and therefore is another attractive byproducts utilization approach. It is true that WA has great potential in biodiesel production from microalgae because of its vast coastal areas in the state and the high annual energy productivity of biodiesel (i.e., ∼296 GJ/ha). However, the relatively high energy footprints (i.e., 1.3 and 0.7 MJ/MJ biodiesel for the two routes, respectively) imply that considerable further R&D is required for truly sustainable production of microalgal biodiesel. Particularly, efforts should be focused on improvement of microalgae biological properties (e.g., growth rate and lipid content) and innovations in engineering design (e.g., culture circulation velocity, nutrients recycling rates, CH_4 yield during anaerobic digestion, and bio-oil yield during hydrothermal liquefaction, etc.).

ASSOCIATED CONTENT

Supporting Information

Data as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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