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Effects of System Design and Co-product Treatment Strategies on the Life Cycle Performance of Biofuels from Microalgae

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Abstract

This study presents a life cycle greenhouse gas and energy assessment for two algal biofuel production pathways: biodiesel produced through lipid extraction (LE) and renewable diesel produced through hydrothermal liquefaction (HTL). The two production pathways generate different co-products, which are handled through allocation in life cycle assessment-based analyses. The method and assumptions used for co-product allocation effect the performance of the analyzed fuels, and were thus examined through scenario analysis; five co-product allocation strategies were tested for the LE pathway and six were tested for the HTL pathway. After allocation, the carbon intensity of renewable diesel varied from 36 gCO_2e/MJ to 54 gCO_2e/MJ, while the carbon intensity of biodiesel ranged, remarkably, from -59 gCO_2e/MJ to 125 gCO_2e/MJ. The optimal algal oil production pathway is determined by comparing open-loop and closed-loop systems, considering not only the

estimated net environmental impacts, but also the confidence or uncertainty of those outcomes.

Keywords

Hydrothermal liquefaction, Lipid extraction, Close loop system, Displacement, LCA

1. Introduction

Interest in biofuels derived from microalgae as an alternative to traditional energy crops is growing because it may avoid some of the consequential effects of terrestrial oil crops (Chisti, 2007). Besides high productivity and oil content, microalgae require significantly less land area and do not require fertile cropland. However, microalgae require a large amount of fertilizer during cultivation to achieve high oil productivity. And the energy input during harvesting and dewatering of the biomass is intensive. Many life cycle assessment (LCA) studies of algal oil production have been done to evaluate environmental impacts and identify energy intensive processes of the system with various assumptions for growth parameters and oil extraction or conversion technologies. Results from these studies show greenhouse gas (GHG) emissions from algae biodiesel vary from 20 to 500 g CO_2e /MJ, while the energy return on energy investment (EROI) of algae biodiesel ranges from 0.2 to 6 (Quinn & Davis, 2015). This range of values is the result of both method- and model-induced variability and real variability in the performance of current and simulated future systems (Yuan, Kendall, & Zhang, 2014).

The sources of method and model-induced variability are many, and among them the methods used to treat co-products stand out as requiring additional study and guidance. Most biofuel production processes are multi-functional systems that produce biofuel products along with economically valuable co-products, such as algal biomass residual (algal cake) that may be used as animal feed and fertilizers. Instead of assigning environmental burdens solely to the biofuel, some methods are required to represent impacts attributable solely to the biofuel, or distribute the environmental impacts between the biofuel and co-products. In the LCA of a biofuel production system, practitioners often face the challenge of co-product allocation, because more than one method can be used to handle co-products and there is no commonly shared understanding on when different methods are applicable or preferable (Flysjö, Cederberg, Henriksson, & Ledgard, 2011).

The allocation methods used for partitioning environmental burdens to primary products such as biofuels and co-products and the assumption of how co-products are utilized can significantly affect the results of a LCA (Hoefnagels, Smeets, & Faaij, 2010). Moreover, different allocation methods might be favored by different co-product utilization assumptions, meaning the choice of allocation method might be affected by utilization choices (Zaimes & Khanna, 2014). While harmonizing allocation methods across different studies could address this, due to differences in system boundaries, pathway designs, and the quantities and quality of products, this is often impossible. Numerous studies have tested the weaknesses and advantages of each allocation method, and sometimes a hybrid allocation approach is employed to present a realistic utilization of the energy products and co-products. However, there is no agreement on which allocation method is the best for biofuel LCA, and comparing several allocation approaches is recommended for case studies (Cherubini, Strømman, & Ulgiati, 2011; ISO14040, 2006).

This research explores the real, method-induced, and model-induced variability of algal biofuels by comparing two algal fuel pathways: renewable diesel from hydrothermal liquefaction (HTL) and biodiesel from a solvent-based lipid extraction (LE) process. Each of these pathways generates different co-products that can be utilized in different ways.

2. Materials and Methodology

2.1. Goal and Scope

The objective of this study is to evaluate and compare the life cycle GHG emissions and energy performance of biodiesel and renewable diesel produced from microalgae through two technology pathways under different co-product treatment strategies using a process-based, prospective LCA approach. LCA is a technique for evaluating the environmental aspects and potential environmental impacts of a product throughout its life cycle, considering the full supply chain of inputs (ISO14040, 2006). Life cycle energy and GHG assessments are a narrow application of the LCA method, since full LCA considers a suite of impact categories.

The research presented here applies this narrow form of LCA, accounting for energy, direct water consumption (meaning indirect and upstream water use are not accounted for) and global warming potential (GWP). Energy and water consumption are reported simply as inventory values (e.g. MJ of energy and liters of water). GHGs are reported in units of CO_2-equivalent (CO_2e). The IPCC's 100-year GWPs are used to convert non-CO_2 emissions into CO_2e (28 for biogenic CH_4, 30 for fossil CH_4, and 265 for N_2O) (IPCC, 2013). This means that 1 kg of methane released is equivalent to 30 kg of CO_2 released when assessed over a 100 year period.

2.2. System Definition and Boundary

The system boundary of the two pathways (the LE pathway and HTL pathway) is illustrated in Figure 1. The scope of this analysis is "cradle-to-gate," meaning that the analysis stops at the biorefinery gate. Thus, the life cycle stages included in the analysis are microalgae cultivation in open raceway ponds (ORPs), algae harvesting and dewatering, biocrude production via LE or HTL, conversion of bio-crude oil into the final energy product (biodiesel or renewable diesel), and utilization of co-products. Figure 1 describes the steps in each of the considered pathways.

The processes of algae cultivation, harvesting and dewatering, drying, oil extraction, and utilization of algal cake occur within the same facility. From there the crude oil is transported to a nearby refinery for conversion to biodiesel or renewable diesel. Construction, repair and maintenance of infrastructure, production of equipment and waste management are excluded from the system boundary. The functional unit of analysis is 1 MJ of algal biofuel, although 1 kg of dry biomass is used as a modeling unit of analysis to assess the material and energy consumption in each unit process in the life cycle inventory (LCI) assessment.

2.3. The Microalgae Cultivation, Harvesting and Dewatering

The cultivation model of the microalgae Scenedesmus *dimorphus,* grown in ORPs, is adopted from previous work (Yuan et al., 2014). The production facility of 400 acres of open raceway ponds are assumed to be located in southern New Mexico (which determines water quality, groundwater depth for water pumping and evaporation rates), with pond dimensions of 100 meters by 10 meters and a water depth of 0.3 meters.

In previous research (Yuan et al., 2014), four combinations of technologies for harvesting and dewatering were considered, including bioflocculation followed by dissolved air flotation (DAF) and centrifugation, flocculation with polymer followed by DAF and centrifugation, flocculation with alum followed by DAF and centrifugation, and centrifugation only. The most efficient harvesting and dewatering technology route was found to be bioflocculation following DAF and centrifugation, because bioflocculation required no chemical inputs. These are used in the current model as the default harvesting and dewatering route. We assume no chemicals are used for bioflocculation. After dewatering, the density of microalgae biomass is assumed to be 180 g/L. Table 1 summarizes key parameter assumptions, material inputs, and energy inputs during the algae cultivation and harvesting stage.

2.4. Algae Renewable Diesel Production through HTL Pathway

HTL is a thermochemical process involving the reaction of biomass in water at subcritical temperatures (below 374 °C) and high pressure (10–25 MPa) for a certain reaction time with or without the use of a catalyst (Ross et al., 2010). HTL yields a product typically referred to as bio-crude or bio-oil along with gaseous, aqueous (liquid) phase, and solid phase (char) streams. In order to model the HTL process under different operation conditions, a mathematical kinetic HTL model was employed (P. J. Valdez, Tocco, & Savage, 2014). The LCA model includes nutrient recycling and six co-product allocation strategies.

2.4.1 HTL modeling

The kinetic HTL model developed by Valdez et al. (2014) estimates product quantities including crude oil, aqueous phase, gas phase and solid phase as a function of the characteristics of the algae feedstock (P. J. Valdez et al., 2014). The model provides four operating conditions, 250°C, 300°C, 350°C and 400°C, with retention times ranging from 1 to 90 minutes. The HTL product yields reflect the biochemical composition of microalgae and the operating conditions of the HTL system. Unfortunately, this kinetic model is not capable of defining the properties of each product. Instead the C and N content in each product are estimated from empirical data in the literature (as described in section 2.6.). Below some of the key features and assumptions beyond the kinetic modeling of the HTL technology pathway are described:

- *HTL Process Model:* The HTL process energy demand is assumed to be equal to the energy needed to heat the medium to operation temperature from ambient temperature at 20°C (Fortier, Roberts, Stagg-Williams, & Sturm, 2014). A spiral tube heat exchanger is integrated in the system, to re-heat the incoming biomass with the outgoing streams from HTL reactor, assuming 80% of HTL heat can be recovered with 85% efficiency (Delrue et al., 2013). Additional energy is needed to meet process energy demands; grid electricity is used for pumping, and natural gas (NG) is used for the remaining heat demand not met by heat re-circulation. NG is assumed to be combusted in a boiler with 85% efficiency.
- *HTL Products Separation.* There is currently no consistent method used for separation of the HTL products (Xiu & Shahbazi, 2012). Various methods including water separation, solvent separation, filtration, vacuum and centrifugation were

reported to separate solid and oil under lab conditions (Huang et al., 2013; Zacher, Olarte, Santosa, Elliott, & Jones, 2014). Due to the inconsistency and lack of data for scaled application, the separation process is omitted in this analysis.

- *Bio-crude Upgrading.* Bio-crude from HTL has high potential for co-processing with petroleum crude oil in conventional refineries to produce renewable transportation fuels such as renewable diesel, which has the identical properties as conventional diesel (Jensen, Hoffmann, & Rosendahl, 2016). However, the bio-crude has higher oxygen, nitrogen and sulfur content than conventional crude oil. Because of the high oxygen content, an additional process for removing oxygen from the bio-crude, deoxygenation, is recommended before the co-processing (Xiu & Shahbazi, 2012). We assume biocrude oil can be co-processed directly with petroleum crude in a refinery (Jensen et al., 2016). The upgrading process of biocrude oil to renewable diesel is modeled using the refinery process of crude oil from the GREET model (Palou-Rivera & Wang, 2010). Inputs and outputs of the HTL pathway are summarized in Table 2.

2.4.2 Co-products from HTL

When using HTL as the oil conversion technology, co-products including the nutrient-rich aqueous phase, gaseous phase and bio-char, can all be reused within the production system to reduce the primary fertilizer, CO_2 and energy inputs demand by the system

(Fortier et al., 2014; Frank, Elgowainy, Han, & Wang, 2013; Grierson, Strezov, & Bengtsson, 2013; Liu et al., 2013; Ponnusamy, Reddy, Muppaneni, Downes, & Deng, 2014). Energy recovery may occur through the combustion of char and bio-crude to generate heat. The nutrient-rich liquid stream can be recycled into the cultivation pond as a nutrient supply for microalgae growth, while the gaseous fraction is composed mostly of CO_2 which can be reused for algae cultivation. Detailed modeling assumptions for each co-product are described in the supplementary material.

2.5. Algae Biodiesel Production through the LE Pathway

Lipid extraction is a widely modeled microalgal biodiesel production pathway. In contrast to lipid extraction from dry biomass, a wet lipid extraction technology is preferred for microalga because it avoids extensive thermal input for drying while still yielding relatively high crude oil. The extracted lipid is assumed to be transported and processed in a biorefinery. The algal biomass remaining after LE (algal cake) and glycerol co-produced from transesterification are two co-products that can be used in various applications.

2.5.1 LE Pathway Modeling

The model of lipid extraction from wet algae biomass using hexane extraction is adopted from a previous study (Yuan et al., 2014). Transesterification is the conversion technology used to convert crude algal oil to biodiesel. With production of 1 kg dry algae biomass, the yields of biodiesel, glycerol and algal cake are 5.75 MJ, 17 g and 0.84 kg, respectively.

2.5.2 Co-products from LE Pathway

Algal cake and glycerol are co-products from the LE and transesterification route. The modeled algal cake is composed of 8% lipid, 39% protein, 43% carbohydrate and 10% ash (dry weight based). This nutrient rich algal cake has great potential to be used for animal feed, fish feed or organic fertilizer; the energy and nutrients can also be recycled and reused in the microalgae cultivation processes through energy recycling technologies. Glycerol can displace synthetic glycerol with a 1:1 mass ratio (Yuan et al., 2014), though currently glycerol from biodiesel production is the dominant source in the U.S. market.

2.6. Co-product Treatment Methods

Allocation methods include partitioning methods and system expansion that expands the product system to include the displacement effects of a co-product on substitutable products in the market (ISO14044, 2006), where the displacement method and economic allocation are more recommended by several studies and economists than energy and mass based allocation methods (Lardon, Hélias, Sialve, Steyer, & Bernard, 2009; Wang, Huo, & Arora, 2011). An alternative to utilizing co-products in the market is the reuse and recycling co-products within the production system to reduce material inputs, leading to a closed-loop production system. A closed-loop system avoids uncertainties from co-product allocation issues and is advocated under the concept of circular economy (Murray, Skene, & Haynes, 2017). We have considered potential applications of co-products from the two algae biofuel pathways, and investigated different treatment methods in the following section.

2.6.1 Co-product Treatment - HTL

Six co-product utilization scenarios and four co-product allocation strategies based on co-products of the HTL process are investigated (Table 3). Recycled nutrients are assumed to displace synthetic fertilizers. Recycled CO_2 gas for algae cultivation displaces CO_2 that would otherwise be piped in. The biochar is the only co-product that requires allocation strategies. System expansion methods are the default co-product allocation approach, but economic allocation and energy allocation are also included.

Scenario 1: Economic Allocation

Economic allocation is an alternative approach to displacement calculations; it partitions the impacts of a production system among co-produced products based upon the economic value of each product. In this study, the price of renewable diesel is assumed to have the same market value of conventional diesel of $2.96/gallon (DOE, 2018).

The price of biochar is assumed to be equal to or less than agrichar and charcoal, reported in a large range from $0.08/kg to $13.5/kg. A mean value of $2.65/kg of biochar was used (Jirka & Tomlinson, 2013; Kulyk, 2012).

Scenario 2: Energy Allocation

Energy allocation is similar to economic allocation, but partitions the impacts based on the energy value of each product. The higher heating value (HHV) of biochar and crude oil are used to calculate the energy content in each. In this scenario, the environmental impacts are allocated based on energy content divided between crude oil and biochar, and upgrading of crude oil to renewable diesel is included separately.

HHV of biochar is reported to range from 5 to 15 MJ per kg (Barreiro, Prins, Ronsse, & Brilman, 2013; Jena, Vaidyanathan, Chinnasamy, & Das, 2011; Neveux et al., 2014), the HHV of crude oil ranges from 33.6 to 37.3 MJ per kg (Barreiro et al., 2013; Biller, Ross, Skill, & Llewellyn, 2012; Vardon, Sharma, Blazina, Rajagopalan, & Strathmann, 2012), and the HHV of renewable diesel is assumed to be the same as conventional diesel at 37 MJ/kg. A conservative value as 7 MJ/kg is used for HHV of biochar and 35.7 MJ/kg is used for crude oil.

Scenario 3: Mass Allocation

The mass allocation method partitions environmental impacts based on mass of biochar and biodiesel. The mass of biochar and crude oil resulting from HTL varies under different operation conditions as modeled. The renewable diesel mass is estimated using bio-crude upgrading efficiency at 99% (Palou-Rivera & Wang, 2010).

Scenarios 4: System Expansion

Biochar is used as a soil amendment that can reduce 10% of fertilizer application and 30% of N_2O emission from the field as described previously. Fertilizer inputs for California corn production are used for evaluating the environmental benefits of biochar as soil amendment. The GHG emission from fertilizer application on a typical California corn farm is 270 kg CO_2e per hectare with 4.54 kg N_2O emission per hectare (Zhang & Kendall, 2016). Fertilizer input data are adopted from University of California–Davis (UCD) cost and return studies (Brittan, Munier, Klonsky, & Livingston, 2004; Brittan, Schmierer, Munier, Klonsky, & Livingston, 2008; Frate, Marsh, Klonsky, & De Moura, 2008; Vargas et al., 2003). The potential for long-term carbon sequestration is not considered.

Scenario 5: Closed-loop co-product utilization

Biochar is combusted in a combined heat and power (CHP) unit and displaces natural gas and grid electricity. The efficiency of CHP to convert biochar into electricity and heat is 36% and 50%, respectively. The energy content in biochar is estimated using the HHV of biochar at 7 MJ/kg (Barreiro et al., 2013; Jena et al., 2011; Neveux et al., 2014).

Scenario 6: Closed-loop co-product utilization

Biochar is combusted in a boiler to produce heat and displace natural gas use on site. The boiler operates at 85% efficiency.

2.6.2 Co-product Treatment - LE

As described in table 3, four utilizations of algal cake are modeled: displacement of dairy cattle feed, displacement of fishmeal, on-site anaerobic digestion (AD) for energy and nutrient recycling, and on-site HTL of biomass residual for energy and nutrient recycling.

Glycerol is treated simply in these scenarios; either through economic allocation in Scenario 1, or displacement assuming one to one substitution for synthetic glycerol. The treatment of algal cake is described for each scenario below.

Scenario 1: Economic Allocation

Economic allocation is based on the market price of biodiesel and glycerol, which are biodiesel and glycerol use \$3.48/gallon (DOE, 2018) and \$0.11/kg (Yuan et al., 2014), respectively. The market price of algal cake is estimated based on the Feed Value Calculator developed by Saskatchewan Ministry of Agriculture assuming the algal cake is used as cattle feed (2012). The Feed Value Calculator calculates the relative value of crude protein, total digestible nutrients (TDN), phosphorus, calcium and moisture content based on the market price of reference feeds. In the current estimation, the 2017 average price of canola meal and barley grain in US were used as reference. The algal cake was assumed to be sun dried to 40% moisture content before transportation and use. A TDN value for algal cake of 78% was used for price estimation (MišurCoVá, KráčMar, Klejdus, & Vacek, 2010). The market value of algal cake is estimated as $175 per metric tonne based on its biomass substrate characteristics.

Scenario 2: System Expansion - Displacement of California Dairy Cow Feedstuffs

Based on review of the existing literature, no research or assessment of the displacement value for algal cake in California exists. To conduct this calculation a feed optimization tool tailored to California is identified, PCDAIRY_2015_USA (Least Cost and Ration Analysis Programs for Dairy Cattle), referred to hereafter as PCDAIRY (Robinson & Ahmadi, 2015). PCDAIRY uses an economic optimization based on the price of available feeds to recommend a balanced ration at lowest cost. To identify feedstuffs likely to be displaced by the introduction of algal cake, PCDAIRY is run with and without algal cake. By doing so, the consequential change induced by introducing algal cake into the feed market in California can be estimated. Of course if algal cake is introduced in very large volumes, the price of algal cake and competing feeds could change; these displacement calculations implicitly assume that the introduction of algal cake from the simulated facility will not have a significant effect on the price of other feeds. Assumptions and operating parameters that were used in the PCDAIRY tool can be found in supplementary material.

Table 4 was calculated using PCDAIRY, it reflects a model run with an optimization goal of milk sale profit given fixed nutrient composition and prices for each feed. Based on PCDAIRY calculations, the addition of algal cake in a standard dairy cattle feed ration would result in small changes to all ration constituents but notable increases in corn silage, and decreases in alfalfa hay and dry distiller's grains and soluble (DGS). These changes constitute the effects of adding algal cake to a dairy feed ration and will be used to calculate its displacement value.

Scenario 3: System Expansion- Displacement of Fishmeal

Lipid-extracted algal biomass is a suitable candidate to partially replace the use of fishmeal in fish farming. It is found that replacing up to 10 percent of the crude protein in fishmeal and soybean protein by lipid-extracted algal biomass (including species *Navicula sp*., *Chlorella sp*. and *Nannochloropsis salina*) residual does not lower the growth rate or the feed efficiency in fish farming applications (Patterson & Gatlin, 2013). The displacement ratio of algal biomass to fishmeal in this study is estimated at 0.975 based on protein content (39% for algal cake and 40% for fishmeal). Based on previous LCAs, a primary energy requirement of 19.85 MJ and emissions of 1.35 kg CO_2e are associated with the production of 1 kg of fishmeal (Patterson & Gatlin, 2013; Pelletier et al., 2009).

Scenario 4 and 5: Recycling and Reuse in a Closed-loop System

Two recycling technologies, AD and HTL, are tested for scenarios 4 and 5. AD produces biogas, suitable for use in a CHP unit, and digestate, from which the liquid fraction is recovered and fed into the ORPs for water and nutrient recycling, and the solid fraction is composted and used off-site as a nutrient-rich soil amendment.

Just as when HTL is used to process whole algae, HTL applied to algal cake produces a CO_2-rich gaseous stream, a nutrient-rich aqueous stream, a biochar and a biocrude product. The nutrient rich stream is used for nutrient recycling while biocrude and biochar are combusted in a boiler for heat generation. The results for Scenario 4 and 5 are adopted from previous study by Zhang et al. (Zhang, Kendall, & Yuan, 2014).

2.7. Data Sources

The primary data for modeling parameters such as the algae growth model, energy inputs for cultivation, harvesting and HTL and upgrading inputs, are based on peer-reviewed literature as described in each section. The reference LCI data including fertilizer production, gasoline production, grid electricity and natural gas production and related emissions come from the ecoinvent Database, the Gabi Professional database and the U.S. LCI database accessed through Gabi 6 software (Ecoinvent, 2011; National Renewable Energy Laboratory & PE International, 2012). LCI data are provided in supplementary material.

3. Results and Discussion

3.1. Effects of HTL Operation Conditions without Co-product Allocation

The effects of operation conditions on renewable diesel yield, primary energy consumption and GWP100 of the system before allocation are shown in figure 2. Among all tested conditions, the yield of renewable diesel is the highest at temperatures of 350°C for 15 minutes. The lowest primary energy consumption and life cycle GHG emissions from 1 MJ renewable diesel production occurred at temperatures of 300°C and 350°C with retention time from 15 minutes to 60 minutes. Operating at 350°C for 15 minutes is used as the optimal condition because a shorter retention time is preferred for lower cost at industrial facilities. The following sections report results using this operation condition as default.

Table 5 shows process based contributions to energy and GWPs. Cultivation and harvesting of microalgae is the most energy intensive stage for renewable diesel production, predominately due to the electricity use for pumping. These values reflect reduced fertilizer inputs due to nutrients recycling from the aqueous phase. The upgrading stage has higher GHG emissions and energy use than HTL processing. Before allocation of co-products, the GWP100 and total primary energy input for renewable diesel is 0.056 kg CO_{2e}/MJ and 0.96 MJ/MJ, respectively.

3.2. Effects of Co-product Treatment on the HTL Pathway and LE Pathway

Figure 3 reports the results for un-allocated energy and emissions from the HTL pathway and Le pathway along with results from different co-products treatment scenarios.

For the case of HTL pathway, economic allocation leads to the lowest energy and life cycle GHG intensity (or carbon intensity) for renewable diesel among all allocation approaches because of the high value estimated for biochar. When the price of biochar is set at $0.5/kg instead of $2.65/kg (default value), the economic allocation results in approximately equal carbon intensity of biochar to other allocation methods. Second to economic allocation in terms of favorable carbon intensity is the substitution of biochar for soil amendments. Depending on the long term carbon sequestration potential of biochar in soils, this use could result in even lower carbon intensity. In terms of closed-loop utilization, combustion in a CHP is slightly preferable to combustion in a boiler for heat generation only. Overall, the allocation approach has relatively small effects on the final results due to the small yield of biochar from HTL. This suggests the findings for renewable diesel produced through the HTL pathway are reasonably robust to changes in the value of co-products and the allocation method chosen.

Without allocation of co-products, biodiesel production from LE requires much higher energy (3.52 MJ/MJ) than renewable diesel from HTL, because the yield of crude oil from 1 kg biomass under the LE pathway is less than the crude oil produced under HTL. However, biodiesel is very sensitive to the treatment of algal cake and allocation strategies due to the large quantity of algal cake production (detailed results can be found in the supplementary material). For biodiesel production, using algal cake as feed (scenarios 1, 2 and 3) show higher environmental benefits than closed-loop nutrient and energy recycling scenarios (scenario 4 and 5). There are large uncertainties related to the algal cake treatment, such as the price, the nutrient content, the feasibility to use as animal feed, and perhaps additional processing.

Comparing the recycling strategies of co-products in a closed-loop and selling co-product in an open-loop system, a closed-loop system design avoids the allocation process and results in fewer uncertainties of environmental impacts, while the drawback is the loss of potential economic value (as well as the environmental best-use) from co-products. In general, the HTL pathway results in more consistent environmental performance results and is subject to fewer effects from co-product treatment strategies. This is because HTL yields a very small quantity of co-product (biochar) that can be used outside the production system, reusing most non-fuel products within the system. While the LE pathway exhibits higher uncertainty, it may also hold promise for higher profits from selling the high value algal cake as animal feed, as illustrated in Figure 3 under the bars for Economic Allocation.

4. Uncertainties and Discussion

4.1. Uncertainty of Nutrient Recycling Capacity on HTL Pathway

Microalgae cultivation with recycling of the aqueous phase and gases from HTL may introduce heavy metals and inorganic contaminants into the growth media. However, there are no consistent estimates of nutrient content in the aqueous phase, nor are there studies that have definitively proven the feasibility of recycling the aqueous product to the ORP without affecting algae growth performance due to different experimental conditions and limited data (Biller et al., 2012; Jena et al., 2011; Liu et al., 2013; López Barreiro et al., 2014; Peter J Valdez, Nelson, Wang, Lin, & Savage, 2012). To better estimate the effects of nutrient recycling rates used in the ORP, three recycling rates for N and P from the HTL aqueous phase are tested: the low rate assumes 15% of total input N and 20% of total P can be reused for cultivation; the default rate assumes 50% of total N and 80% of total P can be reused; and the high recycling rate assumes 95% of total N and 95% of total P can be reused for cultivation. Effects on the HTL production system (before co-product treatments) are shown in figure 4.

Without allocation of co-products, HTL system GHG emissions range from 44.2 g CO_{2e} to 67.2 g CO_{2e} to produce 1 MJ renewable diesel from the low rate case to high rate case; while the total energy input ranges from 1.10 MJ/MJ to 0.85 MJ/MJ.

The impact of heavy metals and inorganic contaminants on algae growth and the fate of heavy metals need to be better understood in order to evaluate the potential or limits on recycling HTL products.

4.2. Uncertainty of Algal Cake Price on LE Pathway

Sensitivity analysis of life cycle displacement credits of algal cake at different prices is conducted to understand the potential effect. At lower prices, algal cake offsets more GHG emissions and energy inputs, meaning the credit attributed to the algal biodiesel production system is higher (figure 5). At a lower price, algal cake displaces larger quantities of dry DGS in the feed ration, which has a higher market price and involves higher environmental impacts to produce (as shown in supplementary material). This sensitive response of environmental impacts to prices is critical to the life cycle performance of biodiesel produced from LE pathway. However, estimating the market price of algal cake as feed is challenging to this research, because algal cake is not yet a commercial product in the feed market. Moreover, algal cake may concentrate chemical elements which can be toxic to animal and human health, depending on algae species, cultivation or conversion processes. Thus, the feasibility of using algal cake used for feed still requires further research.

5. Conclusion

This study conducted an LCA model to examine life cycle GHG emissions and energy use of biofuel production from microalgae via two pathways, a HTL renewable diesel and a LE biodiesel. Before co-product allocation, the GHG emissions from renewable diesel (HTL) and biodiesel (LE) were 55 gCO_2e/MJ and 226 gCO_2e/MJ, respectively. After allocation, the carbon intensity of renewable diesel varied from 36 gCO_2e/MJ to 54 gCO_2e/MJ, while the carbon intensity of biodiesel had a dramatic range from -59 gCO_2e/MJ to 125 gCO_2e/MJ. Not surprisingly, a comparison of these two pathways subject to a variety of scenarios that varied the co-product utilization strategies and allocation methods, suggest that more robust carbon intensity estimates are achievable when co-products have little contribution to the performance of the biofuel, or when they are internally recycled.

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Figure Captions

Figure 1 Figure 1 System Description of Algal Biofuel Production through LE and HTL Pathway

Figure 2 Effects of operation conditions on renewable diesel yield, GWP100 and primary energy consumption

Figure 3 GHG emissions (A) and Total Primary Energy (B) for Biodiesel and Renewable Diesel Production with Co-product Treatment. For reference, GHGs from petroleum diesel is approximately 95 g CO_2e/MJ

Figure 4 Effects of Nutrient Recycling Capacity on GHGs and Energy per MJ Renewable Diesel Production (Before co-product treatments)

Figure 5 Sensitivity Analysis of Avoided CO_2e Emissions and Total Energy by 1 kg Algal Cake at Different Prices

Table 1 Growth model assumptions and input summary for cultivation, harvesting and dewatering (all parameters are dry weight based)

Modified Growth Model			
Parameter settings	Unit	Input	Data Source
Growth rate	g/m^2/day	25.00	(Yuan et al., 2014)
Lipid content	wt%	25.00	(Yuan et al., 2014)
Protein	wt%	32.15	(Yuan et al., 2014)
Carbohydrate	wt%	34.85	(Yuan et al., 2014)
Ash	wt%	8.00	(Yuan et al., 2014)
C	g/kg biomass	500.00	(Yuan et al., 2014)
N	g/kg biomass	52.50	(Yuan et al., 2014)
P	g/kg biomass	12.92	(Yuan et al., 2014)
CO_2 requirement	kg/kg biomass	1.83	(Yuan et al., 2014)
CO_2 use efficiency		0.87	(Yuan et al., 2014)
Ammonium nitrate (NH_4NO_3) requirement	kg/kg biomass	0.15	modeled
Triple superphosphate ($Ca(H_2PO_4)_2$) requirement	kg/kg biomass	0.10	modeled
Energy for CO_2 injection	MJ/kg biomass	0.18	(Yuan et al., 2014)
Energy for paddlewheel	MJ/kg biomass	0.68	(Yuan et al., 2014)
Energy for water pumping	MJ/kg biomass	0.78	(Yuan et al., 2014)
Energy for water pumping within the system	MJ/kg biomass	0.76	(Yuan et al., 2014)
Mixing energy for flocculation	MJ/kg biomass	0.0032	(Yuan et al., 2014)
Energy for DAF	MJ/kg biomass	0.1203	(Yuan et al., 2014)
Biomass recovery from harvesting		90%	(Yuan et al., 2014)
Biomass recovery from dewatering		96%	(Yuan et al., 2014)
Electricity for centrifugation	MJ/kg biomass	0.576	(Yuan et al., 2014)
Polymer Use for DAF	g/kg biomass	20	(Yuan et al., 2014)
Water content after dewatering	L/kg biomass	5.56	(Yuan et al., 2014)
Water Evaporation rate	L/m^2/day	5.97	(Yuan et al., 2014)
Evaporation Loss	L/kg biomass	238.66	(Yuan et al., 2014)
Pond Area	ha	400.00	(Yuan et al., 2014)
Annual Biomass Yield	tonne/ha/yr	75.00	(Yuan et al., 2014)

Table 2 Inputs and Outputs Summary of HTL Pathway at 350°C for 15 minutes (dry weight based)

Parameter	Unit	Value	Data source
HTL Electricity	MJ/kg biomass	0.001	modeled
HTL Natural Gas (NG)	MJ/kg biomass	0.003	modeled
Biocrude Oil	Kg/kg biomass	0.420	modeled
Gas Phase	Kg/kg biomass	0.014	modeled
Aqueous Phase	Kg/kg biomass	0.485	modeled
Solid Phase	Kg/kg biomass	0.081	modeled
Pumping Electricity	MJ/kg biomass	0.001	(Yuan et al., 2014)
Oil Upgrading Electricity	MJ/kg biomass	0.05	(Palou-Rivera & Wang, 2010)
Oil Upgrading NG	MJ/kg biomass	0.80	(Palou-Rivera & Wang, 2010)
Oil Upgrading H_2	MJ/kg biomass	0.20	(Palou-Rivera & Wang, 2010)
Oil Upgrading Gasoline	MJ/kg biomass	0.002	(Palou-Rivera & Wang, 2010)
Oil Upgrading Water	Gallon/kg biomass	0.16	(Palou-Rivera & Wang, 2010)
Renewable Diesel	MJ/kg biomass	15.05	modeled
N recycled from Aqueous phase	g/kg biomass	26.25	modeled
P recycled from Aqueous phase	g/kg biomass	10.33	modeled
Ammonium nitrate input after recycling	kg/kg biomass	0.08	modeled
Triple superphosphate input after recycling	kg/kg biomass	0.02	modeled

Table 3 Scenario Description of Co-product Treatment for HTL Pathway and LE Pathway

Pathway	Products	**Scenario 1**	**Scenario 2**	**Scenario 3**	**Scenario 4**	**Scenario 5**	**Scenario 6**
HTL	Bio-char	Economic Allocation	Energy Allocation	Mass Allocation	Soil Amendment Displacement	Combusted in CHP* to produce Heat and Electricity	Combusted in Boiler to produce Heat
	Aqueous Phase	Recycled	Recycled	Recycled	Recycled	Recycled	Recycled
	CO_2	Reused for Cultivation	Reused for Cultivation	Reused for Cultivation	Reused for Cultivation	Reused for Cultivation	Reused for Cultivation
LE	Glycerol	Economic Allocation Glycerol Price	Displace Glycerol 1:1 mass	Displace Glycerol 1:1 mass	Displace Glycerol 1:1 mass	Displace Glycerol 1:1 mass	--
	Algal Cake	Economic Allocation Cattle Feed Price	Displace CA Dairy Cattle Feed PCDairy Model	Displace Fishmeal Protein Based	Recycle Nutrients and Energy in AD	Recycle Nutrients and Energy in HTL	--

*CHP=Combined heat and power system

Table 4 California Dairy Feed Rations with Algal Cake Addition ($175/ton, Dry Matter Based)

	No Algal Cake	With Algal Cake
Algal cake (kg/day)	0.00	1.36
Corn silage (kg/day)	3.89	4.44
Wet GDS (kg/day)	3.79	3.81
Barley (kg/day)	5.50	5.88
Alfalfa hay (kg/day)	4.68	4.14
Almond hulls& shell (kg/day)	3.03	3.04
Dry DGS (kg/day)	2.72	0.23
Beet pulp (kg/day)	0.00	0.80
Dicalcium phosphate (kg/day)	0.07	0.00
Limestone (kg/day)	0.05	0.11

Table 5 Life Cycle GHGs and Energy by Process per MJ Renewable Diesel Production[*] without co-product allocation

	Cultivation & Harvesting	HTL processing	Upgrading	Sum
Primary Energy (MJ/MJ)	8.51E-01	4.66E-04	1.05E-01	9.57E-01
Fossil Energy (MJ/MJ)	6.64E-01	4.12E-04	1.02E-01	7.66E-01
GWP_{100} (kg CO_2e/MJ)	5.71E-02	2.28E-05	4.3E-03	5.59E-02
GWP_{20} (kg CO_2e/MJ)	6.27E-02	2.69E-05	5.40E-03	6.18E-02

[*]HTL was modeled at 350°C for 15 minutes.

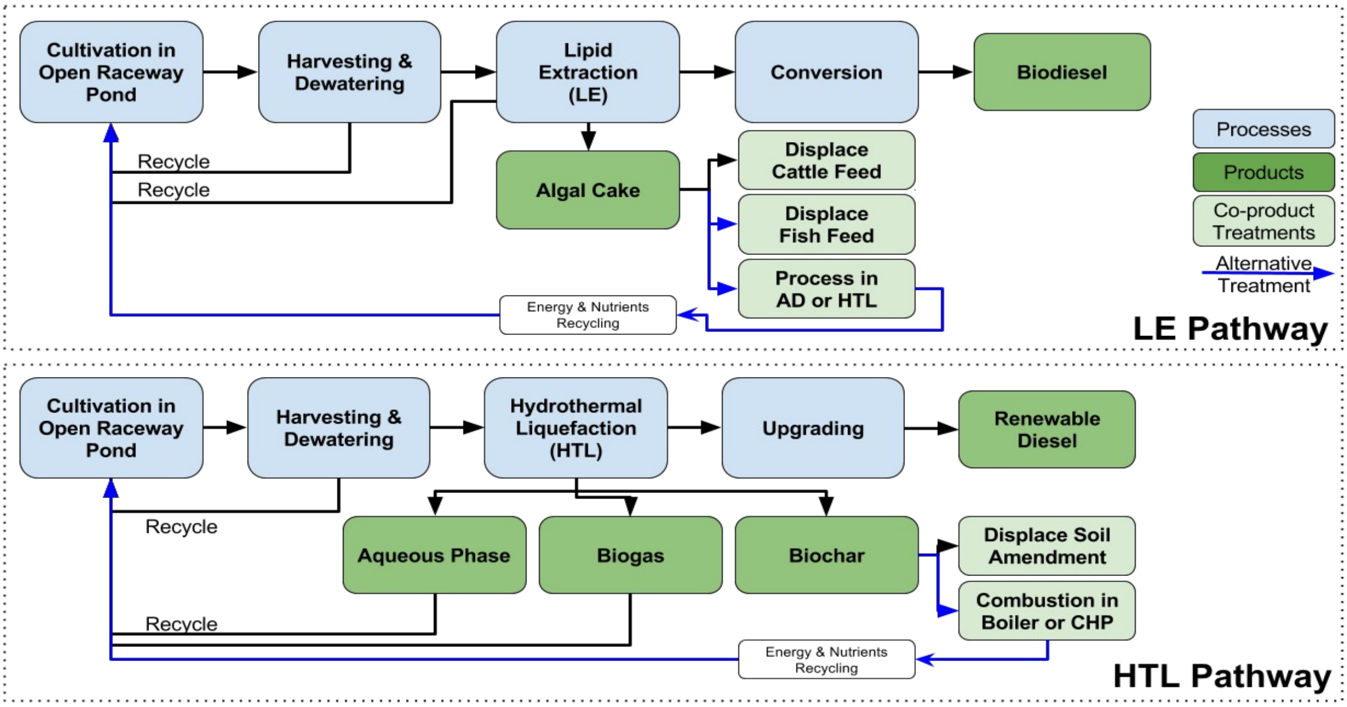


Figure 1 System Description of Algal Biofuel Production through LE and HTL Pathway

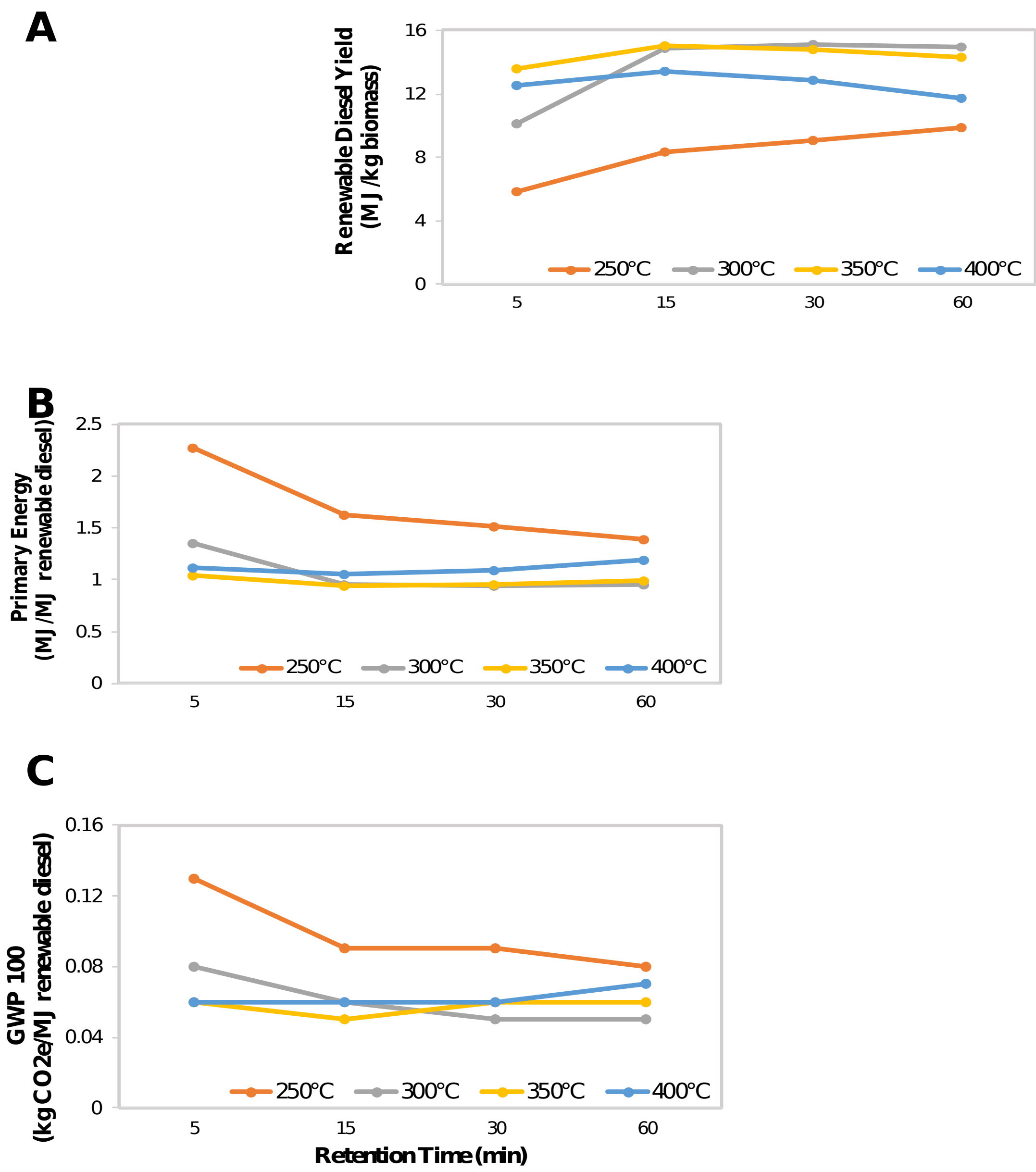
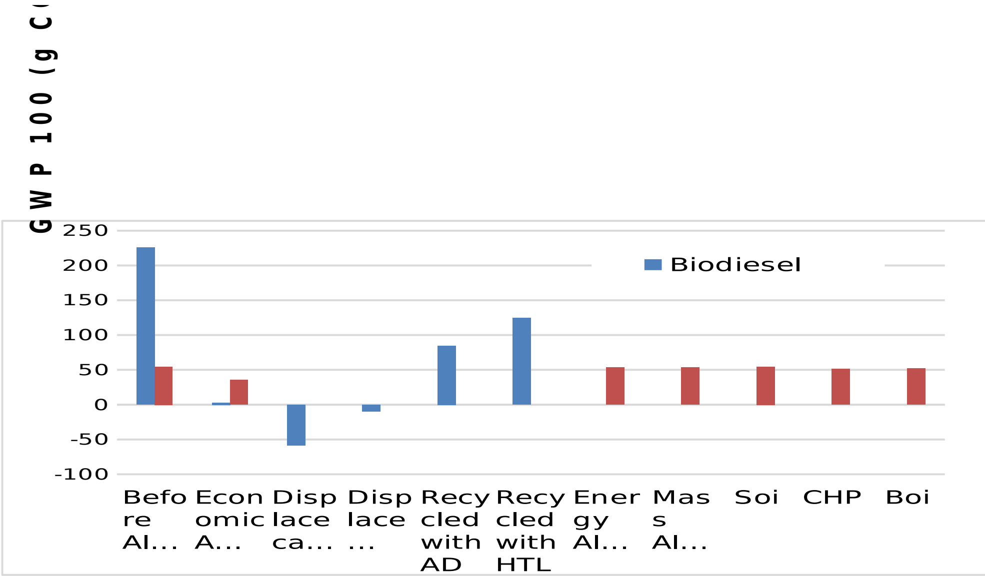


Figure 2 Effects of operation conditions on renewable diesel yield, GWP100 and primary energy consumption

A



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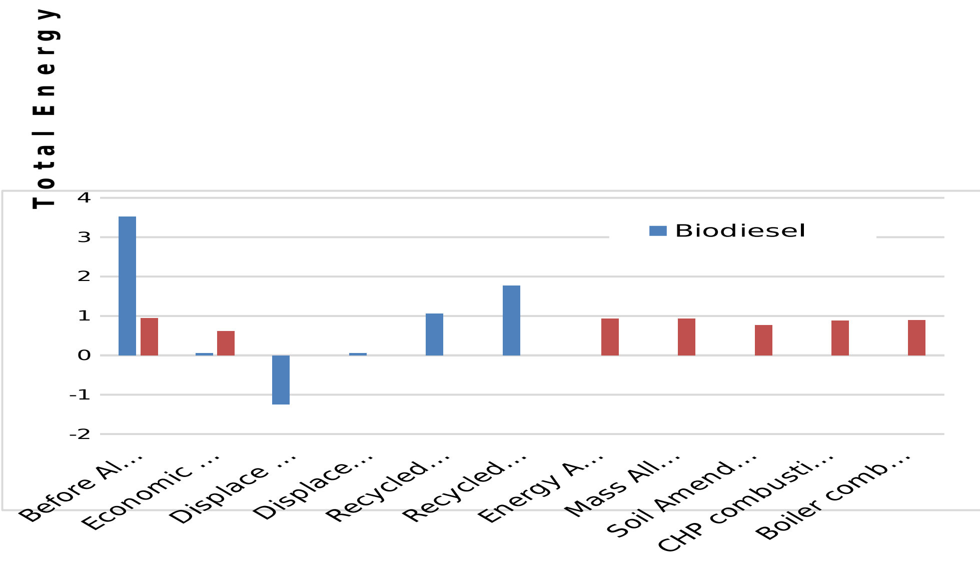

Figure 3 GHG emissions (A) and Total Primary Energy (B) for Biodiesel and Renewable Diesel Production with Co-product Treatment. For reference, GHGs from petroleum diesel is approximately 95 g CO_2e/MJ.

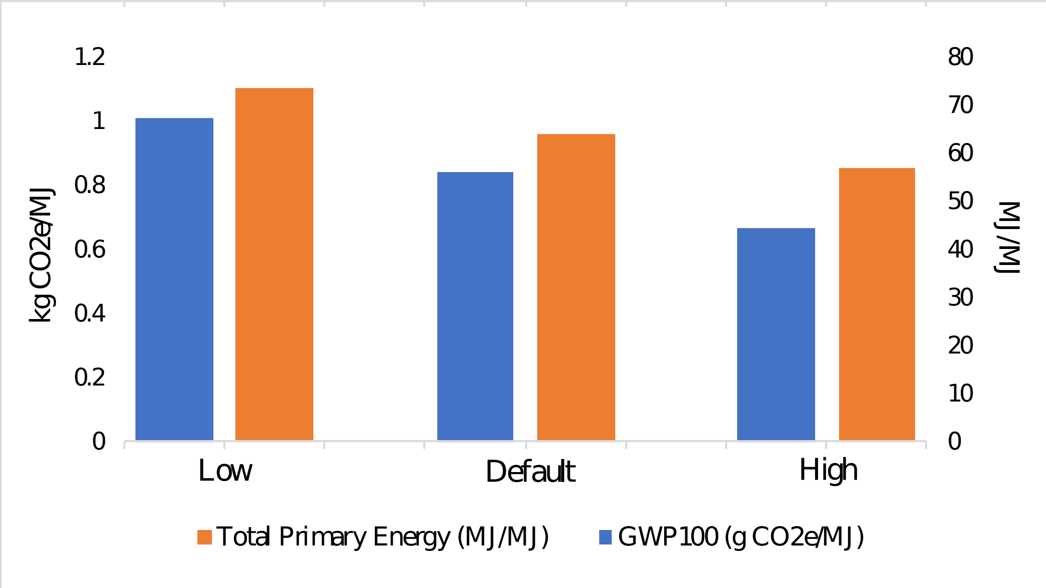

Figure 4 Effects of Nutrient Recycling Capacity on GHGs and Energy per MJ Renewable Diesel Production (Before co-product treatments)

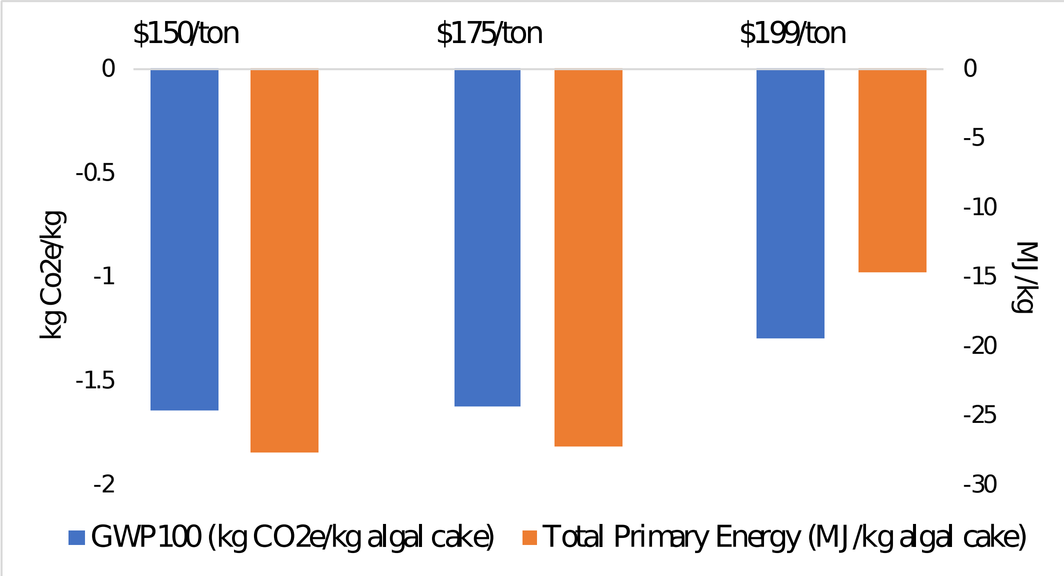

Figure 5 Sensitivity Analysis of Avoided CO_2e Emissions and Total Energy by 1 kg Algal Cake at Different Prices