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Life-Cycle Assessment of Potential Algal Biodiesel Production in the United Kingdom: A Comparison of Raceways and Air-Lift Tubular Bioreactors

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Life-cycle assessment has been used to investigate the global warming potential (GWP) and fossil-energy requirement of a hypothetical operation in which biodiesel is produced from the freshwater alga *Chlorella vulgaris*, grown using flue gas from a gas-fired power station as the carbon source. Cultivation using a two-stage method was considered, whereby the cells were initially grown to a high concentration of biomass under nitrogen-sufficient conditions, before the supply of nitrogen was discontinued, whereupon the cells accumulated triacylglycerides. Cultivation in typical raceways and air-lift tubular bioreactors was investigated, as well as different methods of downstream processing. Results from this analysis showed that, if the future target for the productivity of lipids from microalgae, such as *C. vulgaris*, of ~40 tons ha^{-1} $year^{-1}$ could be achieved, cultivation in typical raceways would be significantly more environmentally sustainable than in closed air-lift tubular bioreactors. While biodiesel produced from microalgae cultivated in raceway ponds would have a GWP ~ 80% lower than fossil-derived diesel (on the basis of the net energy content), if air-lift tubular bioreactors were used, the GWP of the biodiesel would be significantly greater than the energetically equivalent amount of fossil-derived diesel. The GWP and fossil-energy requirement in this operation were found to be particularly sensitive to (i) the yield of oil achieved during cultivation, (ii) the velocity of circulation of the algae in the cultivation facility, (iii) whether the culture media could be recycled or not, and (iv) the concentration of carbon dioxide in the flue gas. These results highlight the crucial importance of using life-cycle assessment to guide the future development of biodiesel from microalgae.

1. Introduction

Microalgae are microscopic, photosynthetic organisms that can be used as a source of food, animal feed, lipids, vitamins, pigments, fertilizers, pharmaceuticals, and other specialty chemicals.[1] At present, microalgae are mainly grown commercially for the production of high-value products, e.g., β-carotene from *Dunaliella salina*.[2] However, when grown under certain specific conditions, such as nutrient limitation, some species produce various classes of lipids, which could be used as a feedstock for the production of biodiesel. One anticipated advantage of microalgae is their potential to produce more oil per hectare than most land-based crops. For example, it is estimated that, with further optimization, microalgae could realistically produce ~40 tons ha^{-1} $year^{-1}$ of oil (throughout this paper, metric tons are used) at a large scale,[3] significantly greater than the yields of oil achieved by land-based oil crops (e.g., oilseed rape grown in the U.K. yields ~1.5 tons of oil ha^{-1} $year^{-1}$). Other advantages of microalgae include[3,4] (i) the ability to cultivate them on non-arable land, therefore avoiding competition with food crops, (ii) the possibility of using wastewaters to provide the nutrients required for their growth (e.g., nitrates and phosphates), therefore reducing inputs and aiding in the processing of wastewater in sewage treatment or other industrial processes, and (iii) the ability to modify the biochemical composition of the algal cells (e.g., increasing the algal oil content) by varying the conditions of growth.

Furthermore, waste CO_2 from the flue gas of power stations or other industrial sources could be used as a carbon source to increase the rate of growth of the algae, provided the chosen species could tolerate the content of CO_2, NO_x, SO_x, dust, and trace elements in the gas. Several species of microalgae have been successfully cultivated using flue gas as the carbon source, including *Chlorella* sp.,[5] *Botryococcus braunii*, and *Scenedesmus* sp.[6]

Currently, most commercial-scale cultivation of microalgae, grown for high-value products or animal feed, is undertaken in raceways. A paddle wheel circulates the biomass, and CO_2 is added by sparging the gas into the bottom of a sump placed at the start of each raceway. The disadvantages of

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raceways include the potential for high losses by evaporation and, therefore, substantial requirements for fresh, makeup water; productivity can be also affected by contamination with adventitious microorganisms.[7] The alternative is to grow algae in photo-bioreactors, which are closed systems that permit, in principle, the growth of monoalgal cultures. The productivity of cellular biomass in photo-bioreactors is generally higher than in raceways; however, they are more expensive to build and operate.[7] Tubular photo-bioreactors have been researched extensively; they generally consist of a reservoir and an array of plastic or glass tubes (the solar collector). The culture flows from the reservoir through the solar collector and back to the reservoir. Within the reservoir, carbon dioxide is added; air is also sparged, so that dissolved oxygen tensions inhibitory to algal growth are not reached.

To maximize the production of oil by microalgae, it has been proposed that a two-stage method of cultivation could be employed in either raceways or photo-bioreactors. Microalgae would be initially grown to a high concentration of biomass under nutrient-sufficient conditions. The supply of nitrogen to the biomass would then be discontinued, resulting in the accumulation of fuel molecules, such as triacylglycerides (TAGs).[3,8] When the desired intracellular content of fuel molecules is achieved, the cells would be dewatered and the oil would be extracted and then converted to biodiesel. The remaining cellular residue, consisting predominantly of proteins and carbohydrates, could be used as an animal feed or for energy generation (e.g., by anaerobic digestion) or converted to bioethanol by hydrolysis and fermentation.

Biofuels such as biodiesel from microalgae have the potential to provide a carbon-neutral alternative to fossil-derived diesel, because growth of the feedstock uses photosynthesis to fix atmospheric CO_2, which is then released upon combustion. The combustion of biodiesel has also been reported to reduce the emission of unburned hydrocarbons, polycyclic aromatic hydrocarbons, particulates, and carbon monoxide, in comparison to fossil-derived fuels.[9] However, the cultivation of biomass and its conversion to a liquid fuel requires input, e.g., electrical power and fertilizer, each of which has an associated environmental burden. It is therefore important to quantify the possible greenhouse gas savings associated with using such biofuels. Life-cycle assessment (LCA) can be used to establish and quantify the total environmental effects of a process or service, from the production of raw materials to the disposal of waste and products at the "end of life". Environmental impacts, such as global warming potential (GWP), acidification potential, and potential for the eutrophication of water can be quantified by relating the emissions released by the process to a reference chemical; e.g., GWP is quantified in terms of the equivalent mass of carbon dioxide emitted. Much research using LCA has been undertaken to assess the environmental performance of first-generation biofuels.[10−16] These are generally made from feedstocks that could also be used for food (e.g., biodiesel from oilseed rape and bioethanol from corn) and are already being produced in considerable quantity. The GWP of these first-generation biofuels has been shown to vary substantially with the particular feedstock,[12] the agricultural procedures employed,[14] and the country in which the biofuel is produced.[12,16] For example, bioethanol produced from sugar cane in Brazil has been reported to have a GWP $\sim$ 70% lower than gasoline, while that made from wheat in Ukraine has a GWP $\sim$ 20% greater than gasoline.[12] Another important factor influencing the environmental performance of first-generation biofuels is whether the cultivation of the energy crop causes either a "direct" or "indirect" change of land use. If uncultivated land requires ploughing to make way for the energy crop (known as a "direct" change of land use), substantial quantities of carbon are released from the soil in the form of carbon dioxide, generally resulting in the biofuel having a higher GWP than fossil-derived diesel.[13,16] If arable land, previously used to produce agricultural commodities, is used to grow energy crops, this can cause a change in land use elsewhere ("indirect" change of land use), which can also significantly reduce the environmental performance of first-generation biofuels.[17,18] Overall, these studies have shown that first-generation biofuels are often unsustainable. Therefore, research into next-generation biofuels, such as biodiesel from algae, is of considerable importance because they are proposed to have the potential to solve many of the issues associated with first-generation biofuels.

Lardon et al.[19] performed a LCA on the production of biodiesel from the freshwater alga *Chlorella vulgaris*, when cultivated in raceways under either nutrient-sufficient or nitrogen-deprived conditions. They found that when *C. vulgaris* is grown in nitrogen-deprived conditions and the TAG is extracted directly from the wet biomass without the need for drying, the biodiesel would have a GWP lower than fossil-derived diesel but higher than biodiesel produced from oilseed rape or palm oil. Clarens et al.[20] investigated the life-cycle impacts of the cultivation of microalgae under nutrient-sufficient conditions, found that the environmental impact was largely driven by the need to supply CO_2 and fertilizers. They concluded that using flue gas as a carbon source and wastewater for nutrients would significantly reduce the overall burden. Kadam[21] investigated the environmental implications of co-firing microalgae, grown using 50% of the flue gas from a 50 MW power station as the carbon source, reporting an overall life-cycle saving of CO_2 released of 36.7% based on the displacement of coal from the power station. No complete

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LCA studies on biodiesel produced from microalgae grown in photo-bioreactors have been published. Lehr and Posten[22] estimated the energy demand of flat-plate, air-lift reactors to be up to a third of the possible chemical energy harvested. However, Rodolfi et al.[3] were unable to achieve a net energy ratio significantly higher than unity for a bag system. It is clear that more complete LCAs of biodiesel production from microalgae are required. In this paper, we address this gap in knowledge by conducting a comparison between hypothetical operations in either raceways or tubular photo-bioreactors. Sensitivity analysis allowed the importance of individual features of the process to be established.

2. Materials and Methods

2.1. Overall Approach. At present, microalgae are not grown on a commercial scale for the production of biodiesel, so that hypothetical scenarios were analyzed. There are many species of microalgae that could be used to produce TAG, as well as different methods of cultivation and downstream processing techniques; therefore, we designed likely processes based on the following assumptions: (i) *C. vulgaris* was chosen as the representative species, because it has high rates of growth and can produce large quantities of lipids when grown under nitrogen limitation.[8] (ii) A two-stage method of cultivation was considered, where the microalgae are initially grown to a high concentration of biomass under nutrient-sufficient conditions, before the supply of nitrogen is discontinued, resulting in the cells accumulating TAGs.[3,8] (iii) Cultivation in typical raceways and air-lift tubular bioreactors was investigated, because these are currently considered to be the most practicable methods for large-scale cultivation.[7] (iv) After oil extraction, anaerobic digestion would be used to generate methane from the residual biomass, from which electricity could be generated and used on-site. (v) Any additional electricity required by the process would be supplied from the national energy network.

2.2. Stages of the LCA. LCA was undertaken via the sequential stages of (i) goal and scope definition, (ii) inventory analysis, (iii) impact assessment, and (iv) interpretation and reporting,[23,24] described below. The analysis used Gabi 4 software to quantify environmental impacts.

2.2.1. Goal and Scope Definition. The basis for comparison or the functional unit was defined as 1 ton of biodiesel, which has been blended to a given fractional volume with conventional, fossil-derived diesel, delivered to a filling station in the U.K. and combusted in a typical, compact-sized car engine. The process chain, summarizing the main activities and mass flows, is shown in Figure 1.

The "control volume" in this study encompassed all of the stages directly used to produce the biodiesel (i.e., the foreground system, including the cultivation of microalgae, oil extraction, and esterification) and also the background system, comprising the homogeneous markets providing the materials and energy used by the foreground system.

2.2.2. Inventory Analysis. Quantitative mass and energy balances were performed over each control volume, an activity requiring substantial data collection. Assumptions regarding typical rates of growth, productivities of lipids, and the nutrient requirements of microalgae were based on results from both commercial- scale[2] and pilot- scale[3] algal cultivation, as well as from our experience of growing *C. vulgaris* in laboratory experiments.[8] Results from the literature were also used to determine the electrical power and construction materials required by different cultivation techniques. Currently, no algal oil-extraction plant is in commercial operation; therefore, a conceptual process was designed by making assumptions regarding a likely processing method, and using results from the literature. It was assumed that the algal oil would be converted to biodiesel in a large-scale biodiesel production plant in the U.K. based on the large-scale plant described in a previous work,[14] with a capacity to produce 250 000 tons of biodiesel/year. The distances over which the raw materials and products would be transported were also assumed to be similar to those used in a previous work.[14] It was therefore possible to generate an inventory table, showing the resource usage and all of the emissions associated with the production of 1 ton of biodiesel.

2.2.3. Impact Assessment and Interpretation. Using the LCA software, the inventory table was formulated into a set of environmental themes based on the Environmental Development of Industrial Products (EDIP) 2003 methodology, using estimates of how much each input and emission contributed to certain environmental impacts. EDIP 2003 methodology was chosen because it was developed in concert with the International Organization for Standardization (ISO) standards ISO 14040:2006[23] and ISO 14044:2006[24] and is considered to be one

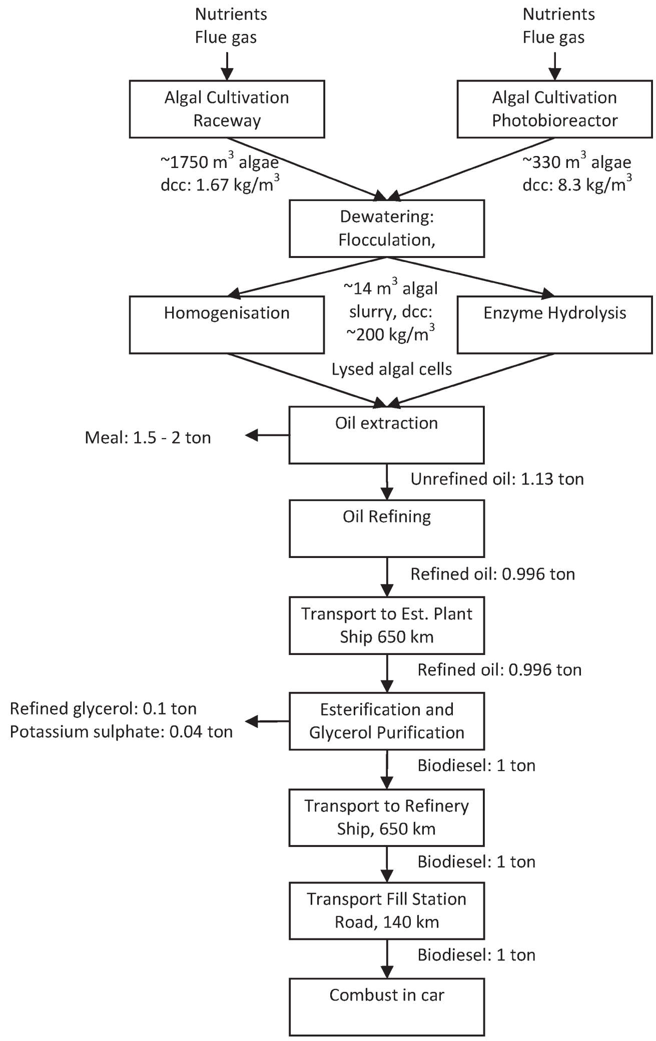

Figure 1. Process chain for the production of biodiesel from microalgae showing the principal mass flows and stages involved in the production of 1 functional unit: 1 ton of biodiesel that has been blended to a given fractional volume with conventional, fossil-derived diesel, delivered to a filling station in the U.K. and combusted in a typical, compact-sized car engine. dcc = dry cell concentration.

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of the most complete and consistent methodologies available.[25] This paper reports on GWP (kg of CO_2 equiv/ton of biodiesel) over a time horizon of 100 years, fossil-energy requirement (GJ/ton of biodiesel), and water usage (m^3/ton of biodiesel).

2.3. Reference System. It is important to use reference systems (LCAs of likely alternative scenarios) for any part of the process chain having an alternative use and a different environmental burden if it were not used in the process under assessment. In the production of biodiesel, a key issue is the alternative use of the land upon which the bioenergy crops are grown. It was assumed that the raceways and photo-bioreactors would be located on degraded or derelict land in the U.K. and that no GWP burden is associated with the change of land use. In the U.K., it was estimated that 8×10^4 ha of derelict or contaminated land existed in 2005;[26] if all of this land were used to grow algae and a productivity of 40 tons ha^{-1} $year^{-1}$ of TAG could be achieved, ~3.2 million tons of biodiesel could be produced per year, representing ~12% of the diesel road fuel consumed in the U.K. during 2008,[27] on an energy basis. However, if flue gas from power stations were to be used as the carbon source, the ponds or reactors would have to be located near the power stations, thereby restricting the availability of suitable land.[28] It is therefore unclear how the cultivation of microalgae at a large scale would affect land use in detail; hence, further research is necessary in this area.

2.4. Methods of Allocation. The production of biodiesel generates the byproducts of algal residue, glycerol, and potassium phosphate. The purpose of allocation is to determine, rationally, how a particular environmental burden, should be shared among the biodiesel and byproduct. A preferred method of allocation is direct substitution,[29] e.g., heat from the combustion of a byproduct could, in principle, replace heat that would otherwise have been supplied from the background system, using coal or gas. However, to use direct substitution, the requirement for the product being replaced must already be satisfied by other processes. Thus, this approach cannot be taken when the product being replaced is always regarded as a byproduct or waste. If direct substitution cannot be used, simpler allocation methods can be applied, including allocation by economic value, calorific value, or mass. In these cases, it is preferable to allocate burdens on the basis of economic value because economic relationships reflect socio-economic demands.[30] The allocation procedures adopted in this study are described below.

It was assumed that the algal residue would be used to produce methane by anaerobic digestion,[31] which could be combusted onsite to satisfy the heat requirements of the process. Any excess would be sent to a power station fired by natural gas to generate electricity. It was assumed that this electrical power would displace electricity supplied by the national electricity network. Therefore, allocation by substitution was employed. For the base case, the glycerol would be used by the pharmaceutical industry. Glycerol is generally manufactured as a byproduct of soap production, making allocation by substitution difficult; therefore, allocation by market price was used. When considering modifications to the base case, the possibility of sending the glycerol to an industrial furnace for the generation of heat was investigated; in this case, allocation by substitution was used, assuming the thermal energy would displace energy produced from combusting heavy fuel oil. Co-products, such as potassium sulfate, are relatively minor in quantity and value; it was therefore decided to use allocation by market price because they do not warrant a more detailed allocation procedure using the substitution method. For the base case, the overall allocation of environmental burdens to the biodiesel was calculated to be 95.6%, using the market prices of biodiesel, glycerol, and potassium sulfate.

2.5. Construction and Maintenance of Process Plants. The quantities of materials required to manufacture the process equipment, e.g., raceways, photo-bioreactors, centrifuges, etc., were estimated to determine the environmental burden associated with the construction of the facilities. If not otherwise specified in the process description, the lifetime of each piece of equipment was assumed to be 20 years. Both raceways and photo-bioreactors require cleaning and therefore must be shut down periodically. Cleaning-in-place operations are generally employed to clean and sanitize photo-bioreactors; for example, sodium hydroxide solution (~1 wt %) may be circulated through the system for 15−20 min.[32] In this study, it was assumed that the environmental impact of the maintenance of the culture facilities would be negligible in comparison to the running costs.

2.6. Emissions from the Combustion of Biodiesel. The emissions associated with the combustion of biodiesel must be considered when determining its overall environmental impacts. Because GWP is considered in this paper, the amounts of nitrous oxide, methane, and fossil-derived CO_2 emitted during the combustion of biodiesel in a typical engine were estimated. For these calculations, the lower calorific value of biodiesel was assumed to be 37.2 MJ/kg.

Because biodiesel is produced from the esterification of triglycerides with methanol, a small proportion of CO_2 released during combustion is from the methanol, which is usually derived from fossil fuels. In this work, it was assumed that each biodiesel molecule contains 19 carbon atoms, with 1 carbon atom originating from fossil methanol, resulting in fossil-derived CO_2 emissions of $\sim 4 \times 10^{-3}$ kg/MJ. Emissions of nitrous oxide and methane released by the combustion of biodiesel were adapted from results given in the 2008 CONCAWE and EUCAR report,[11] where emissions were calculated on the basis of combustion in a typical European compact-size, five-seater car engine, using a direct-injection, compression-ignition (DICI) engine. These emissions were considered to be the same for both biodiesel and fossil-derived diesel.[11]

2.7. Comparisons to Fossil-Derived Diesel. The results from this work have been compared to the environmental impacts of fossil-derived diesel, using results from the literature. Comparisons are calculated on the basis of equivalent net energy content of biodiesel and fossil diesel, assuming the lower calorific value of biodiesel noted above, while that of diesel is 43.1 MJ/kg. The fossil-energy requirement of diesel was taken to be 1.16 GJ/GJ (50 GJ/ton of diesel), and its GWP was taken as 86 kg of CO_2 equiv/GJ (3707 kg of CO_2 equiv/ton of diesel).[12] Here, the fossil-energy requirement of a fuel is calculated from the addition of the fossil-derived process energy and the lower calorific value of the fuel (if fossil-derived), divided by the lower calorific value of the fuel. In the case of a biofuel, this simplifies to the fossil-derived process energy divided by the lower calorific value of the fuel.

2.8. Details of the Process Chains. Two base cases were defined: (i) the production of biodiesel from microalgae cultivated in raceways and (ii) the production of biodiesel from microalgae cultivated in air-lift tubular bioreactors. The assumptions

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made for these base cases are detailed below. Modifications to these base cases were also considered and are detailed later, in section 2.8.3.

2.8.1. Cultivation of Microalgae: Base Case. Flue gas with a content of CO_2 of 12.5 vol % (the maximum value for a natural gas-fired power station[33]) would be used as the carbon source. If this flue gas were not used for the cultivation of microalgae, it would otherwise have been released to the atmosphere. The production of microalgae with high contents of TAG would be achieved using the two-stage approach discussed above, whereby a culture would first be grown under nutrient-sufficient conditions in a raceway or bioreactor to achieve a highly dense culture (stage 1), before being transferred to another raceway or reactor, where the nitrogen source (in this case nitrate) is no longer supplied (stage 2). The culture would then be left until the TAG content increased to the required concentration, before being harvested and sent to a flocculation step. The culture would also be diluted by a factor of 2 when entering the second raceway or bioreactor, to increase the availability of light for each cell. The raceways and bioreactors used for both stages would operate continuously, while the photosynthetic activity of the cells is highest (assumed to be 8 h per day) and held as batch systems for the remaining time.

Results published in the literature were considered when determining likely final concentrations and productivities of biomass and lipids. Andersen[2] reported that the concentration of algal biomass cultivated in photo-bioreactors under nutrient-sufficient conditions typically reaches 5−10 kg (dry biomass)/m^3, while Stephenson et al.[8] achieved a maximum cell concentration equivalent to 5−6 kg/m^3 when growing *C. vulgaris* in shake flasks at a depth of 43 mm, similar to the diameter of the tubes in a tubular bioreactor. Andersen[2] also reported that well-mixed raceways typically yield algal biomass at concentrations of up to 1 kg (dry biomass)/m^3. The final concentrations of biomass achieved in stage 1 were therefore taken to be 5 kg/m^3 for cultivation in air-lift tubular bioreactors and 1 kg/m^3 for cultivation in raceways. Likely biomass growth rates during stage 1 were assumed to be 1 kg m^{-3} day^{-1} for cultivation in air-lift tubular bioreactors and 0.1 kg m^{-3} day^{-1} for raceways, similar to those reported by Chisti et al.[7] Once the cells enter stage 2, an increase in the cell concentration during the first 5 days of nitrogen deprivation, as reported by Stephenson et al.,[8] was accounted for by assuming that the dry cell concentration (excluding the TAG) would double in the first 5 days of stage 2. Stephenson et al.[8] reported a final concentration of TAG in *C. vulgaris*, grown using this two-stage approach, of 35−45 wt % of the dry cell mass. Therefore, for cultivation in both air-lift tubular bioreactors and raceways, the final concentration of TAG within the cells was taken to be 40 wt % of the dry cell mass. The overall productivity of TAG was assumed to be ~40 tons ha^{-1} $year^{-1}$ (excluding the area between the tubes for tubular bioreactors), the value Rodolfi et al.[3] concluded to be a realistic future target. The productivities by volume of biomass and lipid are significantly greater in conventional air-lift tubular bioreactors than raceways; however, owing to the greater depth of culture in raceways, the overall productivity of TAG by area was assumed to be similar for both cases. The sensitivity of the LCA to the productivity of TAG was also considered (section 3.3.1). To determine the nutrient requirements during nitrogen-sufficient growth (stage 1), the composition of the algal biomass was taken to be[7] $CH_{1.83}O_{0.48}N_{0.11}P_{0.01}$. It was assumed that nitrogen would be provided in the form of ammonium nitrate (containing 34.5 wt % nitrogen), while the fertilizer, triple super phosphate (containing 18 wt % phosphorus), would be used to provide the phosphorus.

2.8.1.1. Raceways. The raceways would be built above ground, using concrete blocks as the material of construction, because this is considered to be the most effective material in terms of both cost of construction and operation if freshwater algae are to be cultivated. In each raceway, a paddle wheel would be used to provide the mixing, while a countercurrent carbonation sump of 3 m depth would be used for 8 h each day to transfer an assumed 70% of the carbon dioxide in the flue gas to the culture. The parameters assumed in the design of the raceways are shown in Table 1, while details of the calculations used to determine the material and energy requirements of this cultivation step are provided in Appendix 1.

Table 1. Assumed Design Parameters for Raceways

	units	raceway stage 1	raceway stage 2
depth	m	0.3	0.3
length	m	150	190
width	m	10	20
hydraulic mean depth	m	0.28	0.28
pond area	ha	0.33	0.88
pond volume	m^3	994	2651
mean liquid velocity	m/s	0.3	0.3
Reynolds number		85000	87000
residence time	day	10	13
dilution time[a]	h/day	8	8
flue gas (STP)[b]	m^3/day	1445	1926
outlet flow rate[b]	m^3/day	100	200
outlet biomass density	kg/m^3	1	1.7

[a] Hours per day when microalgae are continuously removed and fresh medium is supplied. During the remaining time, it was assumed that the raceways would be held as batch systems. [b] During dilution time only.

Table 2. Assumed Design Parameters for the Air-Lift Tubular Photo-bioreactors

	units	reactor stage 1	reactor stage 2
tube internal diameter	m	0.053	0.1
tube external diameter	m	0.06	0.11
tube length	m	95	193
nominal land area	m^2	13	22
reactor volume	m^3	0.23	1.6
mean liquid velocity	m/s	0.5	0.5
Reynolds number		26000	50000
residence time	day	5	17
gas for pump (STP)	m^3/day	68	271
useful power provided by gas	W	18.2	64.7
overall efficiency of air-lift device[a]	%	43	39
dilution time[b]	h/day	8	8
flue gas (STP)[c]	m^3/day	2.5	1.3
riser height	m	4.4	4.8
outlet flow rate[c]	m^3/day	0.046	0.092
outlet biomass density	kg/m^3	5	8.3

[a] Proportion of electrical power provided to the compressor, which is used to provide useful energy to the liquid. [b] Hours per day when microalgae is continuously removed and fresh medium is supplied. During the remaining time, it was assumed that the reactors would be held as batch systems. [c] During dilution time only.

2.8.1.2. Air-Lift Tubular Bioreactors. The design was based on that proposed by Molina et al.,[34] who integrated principles of fluid mechanics, gas−liquid transfer, and irradiance-controlled algal growth to optimize the productivity of biomass in an air-lift tubular reactor. They also proved the design by the continuous outdoor culture of the marine diatom *Phaeodactylum tricornutum*.[34] The culture would be circulated through the tubes (the "solar receiver") using an air-lift pump, before returning to the air-lift system where oxygen, accumulated from photosynthesis, would be stripped in the riser using the air (also used to pump the liquid) and flue gas. The solar receivers of conventional tubular bioreactors are typically less than 0.1 m in

(33) Khartchenko, N. *Advanced Energy Systems*; Taylor and Francis: London, U.K., 1997.

(34) Molina, E.; Fernandez, J.; Acien, F. G.; Chisti, Y. *J. Biotechnol.* **2001**, *92*, 113–131.

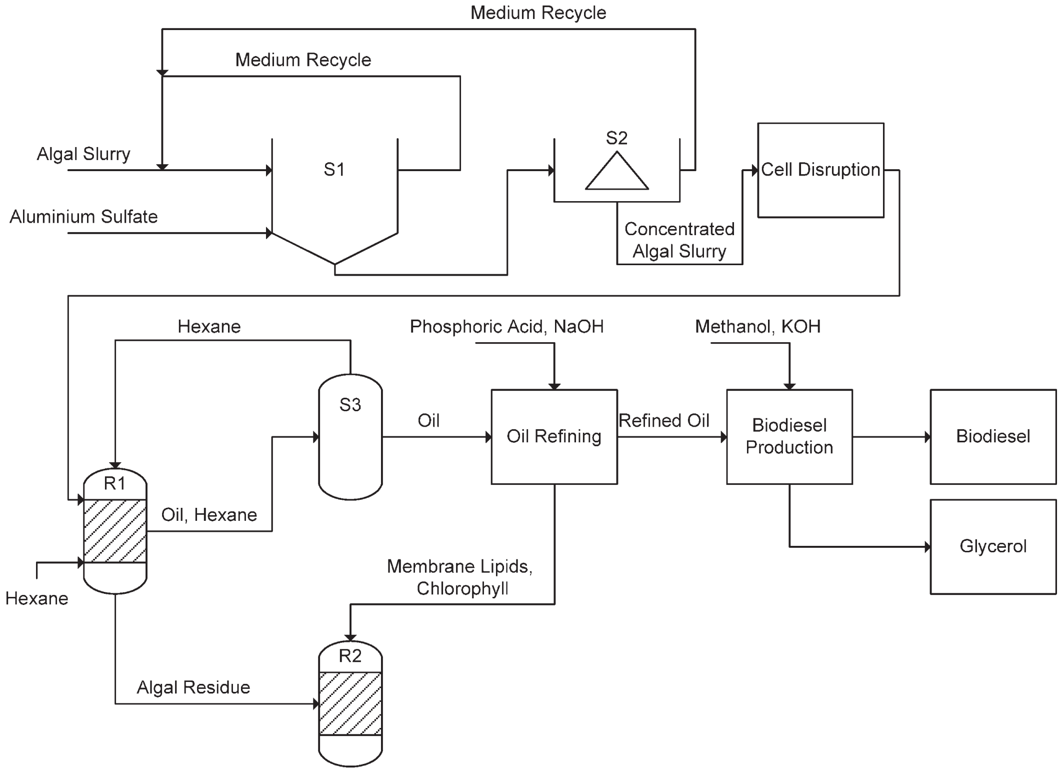

Figure 2. Process flow diagram showing the stages involved in the downstream processing of algal slurry to biodiesel. S1, flocculation for dewatering; S2, centrifugation for dewatering; S3, stripper to recover hexane; R1, solvent extraction (either five mixer-settlers or three extraction decanters); R2, anaerobic digester.

diameter because the penetration of light is limited in the dense culture broths required to ensure a high productivity of biomass in the reactor;[7] therefore, the reactors used in stage 1 of cultivation were assumed to have a diameter of 0.053 m, and those used in stage 2 would have a diameter of 0.1 m. A gas–liquid separator at the top of the air-lift column would be provided to ensure that few bubbles are recirculated to the solar receiver. The reactors would be manufactured from polymethyl methacrylate (Perspex). The main parameters assumed in the design of the air-lift tubular bioreactors can be seen in Table 2, while details of the calculations used to determine the material and energy requirements of this cultivation step are provided in Appendix 2.

2.8.2. Downstream Processing. A process flow diagram, depicting the main stages involved in the production of biodiesel from *C. vulgaris*, is shown in Figure 2, while a detailed description of each stage can be found in Appendix 3. The base case represents one modeled scenario; however, some variations in the flowsheet were considered, as described in section 2.8.3.

2.8.2.1. Dewatering. The algal slurry would first be sent to a flocculation step[35] (S1 in Figure 2), to reduce the water content by a factor of 25. Aluminum sulfate would be used as the flocculant, because it has been shown to be effective for *Chlorella* and *Scenedesmus*.[36] The spent medium would be pumped back to the cultivation facilities, while the algal slurry would be pumped to the next stage in the process. Algae harvested from raceways would be less concentrated than algae harvested from photo-bioreactors; therefore, after the flocculation step, algae from the raceways would be dewatered further using decanter centrifuges (S2).

2.8.2.2. Cell Disruption. Homogenization would be used to break open the cells to make the TAG accessible to solvent extraction.

2.8.2.3. Oil Extraction. The algal lipids would be extracted from the lysed cells using hexane, a nonpolar solvent effective in the extraction of TAGs from oil seeds. The mixture of solvent and algal biomass would first be agitated (R1 in Figure 2) to ensure adequate contact between the solvent and water-suspension phases to leach and dissolve the TAG in the solvent, and the phases would be separated. TAG is immiscible with water; however, a countercurrent system with more than one equilibrium stage is likely to be required because a proportion of the TAG would be retained in the biomass after each equilibrium stage. Preliminary experiments using a mixture of chloroform and methanol as the solvent phase have shown that approximately five stages are required to achieve 99% recovery;[37] however, further experiments using hexane as the solvent are required for more accurate results. A countercurrent cascade of five mixer-settlers would be used, as well as a volumetric flow ratio of solvent to algal slurry of 0.5, resulting in 99 wt % of the TAG and chlorophyll and 90 wt % of the phospholipids and glycolipids in the disrupted cells being extracted.

2.8.2.4. Solvent Recovery and Refining the Oil. The solvent stream, containing the dissolved lipid, would be sent to a stripper column (S3) for separation. Such a column was modeled using HYSYS, applying the Peng–Robinson equation of state for vapor–liquid equilibria, as recommended for such calculations.[38] The bottoms, consisting of the oils, would be refined to remove the chlorophyll and membrane lipids; the oil-refining step would remove 98 wt % of the membrane lipids and chlorophyll, 50 wt % of the hexane, and 1 wt % of the TAG, and these co-products would be sent to the anaerobic digester

(35) Weissman, J. C.; Goebel, R. P. *Design and Analysis of Microalgal Open Pond Systems for the Purpose of Producing Fuels*; U.S. Department of Energy Solar Energy Research Institute: Golden, CO, 1987; Report XK-3-03153-1.

(36) Molina, E.; Belarbi, E. H.; Acien Fernandez, F. G.; Robles Medina, A. R.; Chisti, Y. *Biotechnol. Adv.* **2003**, *20*, 491–515.

(37) Griffiths, M. Private communication. Chemical Engineering Department, University of Cape Town, Rondebosch, South Africa, 2009.

(38) Aspen Technology. *Aspen HYSYS: Simulation Basis*; Aspen Technology, Inc.: Burlington, MA, 2006.

(R2). The process used to refine the oil was assumed to be the same as that used for the production of first-generation biodiesel from oil-seed rape at a large scale in the U.K.[14] Owing to different quantities of membrane lipids and chlorophyll being present in algal lipids and rapeseed oil, further research into refining algal lipids is merited.

2.8.2.5. Production of Biodiesel. The refined oil would be transported by ship (3000 ton capacity), a distance of 650 km,[14] to a biodiesel production plant, where it would be transesterified to produce biodiesel and glycerol. The biodiesel product would be transported another 650 km by ship[14] (3000 ton capacity) to a refinery, where it would be blended with fossil-derived diesel to a given fractional volumetric ratio, before being transported a further 140 km by road to filling stations. These distances are based on those employed for the large-scale production of biodiesel from first-generation feedstocks in the U.K.[14] As with other plant-derived oils used for the production of biodiesel, the fatty acids present in TAG produced from the nitrogen starvation of *C. vulgaris* are predominantly palmitic, oleic, linoleic, and linolenic acids;[8] therefore, it was assumed that the process used to convert TAG to biodiesel would be the same as that used for the production of first-generation biodiesel from oil-seed rape at a large scale in the U.K.[14]

2.8.2.6. Anaerobic Digestion. The aqueous stream from the oil extraction stage (R1), which would contain the residual biomass, and the waste stream from the oil-refining step would be sent to an anaerobic digester (R2) to generate methane. If the algal species has a cell wall, they are protected to some extent against enzymes produced during anaerobic digestion, reducing their biodegradability.[31] To account for this, it was assumed that only the homogenized cells would be digested. A proportion of the methane (~16% in the base case) would be sent to a boiler to provide the process heat, with a fuel-to-steam efficiency of 75%,[39] while the remainder would be piped back to the gas-fired power station using compressors, where the pressure loss in the distribution system would be similar to that in the flue gas system (0.07 bar).[35] The power station fired by natural gas was assumed to have an electrical efficiency of 60% based on the GE 50 Hz combined-cycle platform, turbine model S109H.[40]

2.8.3. Modifications of the Base Cases. To determine the parameters to which the LCA is most sensitive, several modifications of the base cases were considered. These were (1) productivities of TAG by area of cultivation facility, (2) the velocity with which the culture is pumped through the bioreactor, (3) the design of the carbonation sump used in raceways, (4) the effect of passing the spent medium to wastewater treatment rather than recycling it, (5) disrupting the cells by enzymatic hydrolysis rather than homogenization, (6) using three extraction decanters to extract the lipids from the microalgae rather than five mixer-settlers, (7) recycling nutrients from anaerobic digestion to cell cultivation, (8) sending the glycerol co-product to an industrial furnace, and (9) changing the mode of transport and distances involved in distributing the biodiesel product.

3. Results and Discussion

3.1. Base Cases: Raceways versus Air-Lift Tubular Bioreactors. The fossil-energy requirement and GWP associated with the production of biodiesel from *C. vulgaris*, cultivated in raceways and air-lift tubular bioreactors and processed via the base method, are shown in panels a and b of Figure 3, respectively. The burdens associated with the heat and electricity requirements of each processing step are shown,

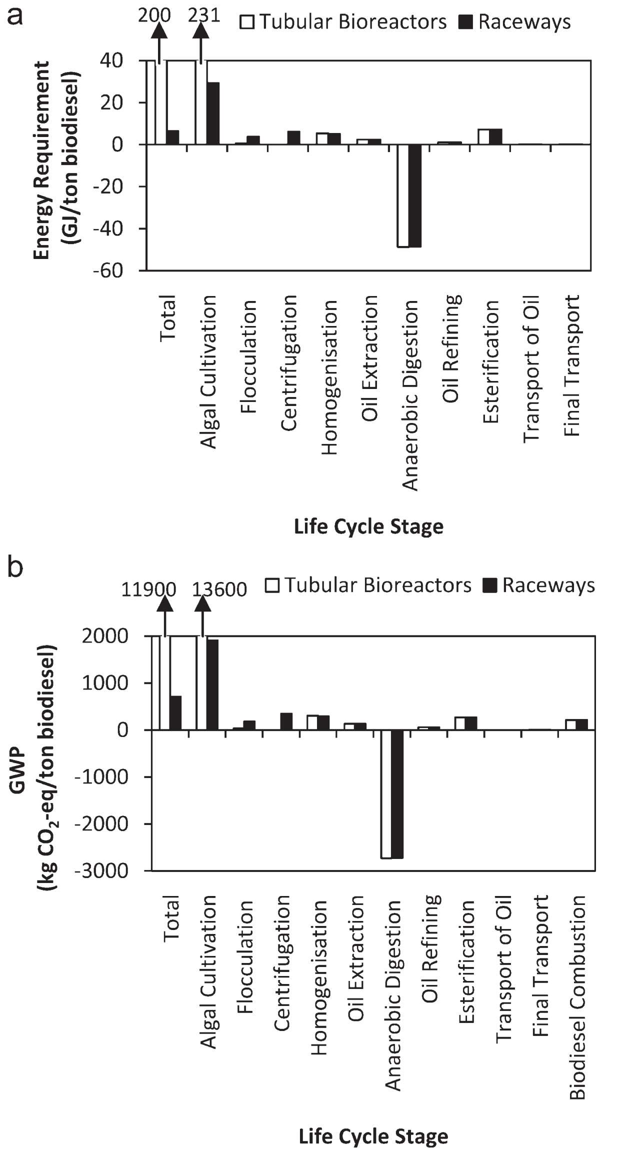

Figure 3. LCA results for the base case production of biodiesel from *C. vulgaris* cultivated either in raceways or air-lift tubular bioreactors: (a) fossil-energy requirement and (b) GWP.

as well as the burden offset by the production of heat and electricity from the methane generated by anaerobic digestion of the residual algal biomass. These results show that the cultivation of the microalgae in the particular design of the air-lift tubular photo-bioreactor chosen[34] consumes significantly more energy than cultivation in raceways; hence, the GWP is also greater. Indeed, whereas the fossil-energy requirement and GWP of biodiesel produced from *C. vulgaris* grown in raceways are ~85 and 78% lower than fossil-derived diesel, respectively, on an energy basis if air-lift tubular bioreactors are used, these values are 362 and 273% greater.

These results indicate that biodiesel from *C. vulgaris* cultivated in raceways would have a lower fossil-energy requirement and GWP than many first-generation biofuels. For example, biodiesel from oil-seed rape, sunflower, or soy beans grown on idle arable land in South Africa has been reported to save 50−60% fossil-energy requirement and 20−25% GWP when compared to fossil-derived diesel,[16] while biodiesel produced from palm oil grown on peatland

(39) Natural Resources Canada. *Boilers and Heaters: Improving Energy Efficiency*; Natural Resources Canada: Ottawa, Canada, 2001; http://www.energysolutionscenter.org/boilerburner/Eff_Improve/Index/Index_Boiler_Eff_Start.asp.

(40) GE Energy. *Heavy Duty Gas Turbine Products*; GE Energy, Atlanta, GA, 2009; GEA-12985H (06/09).

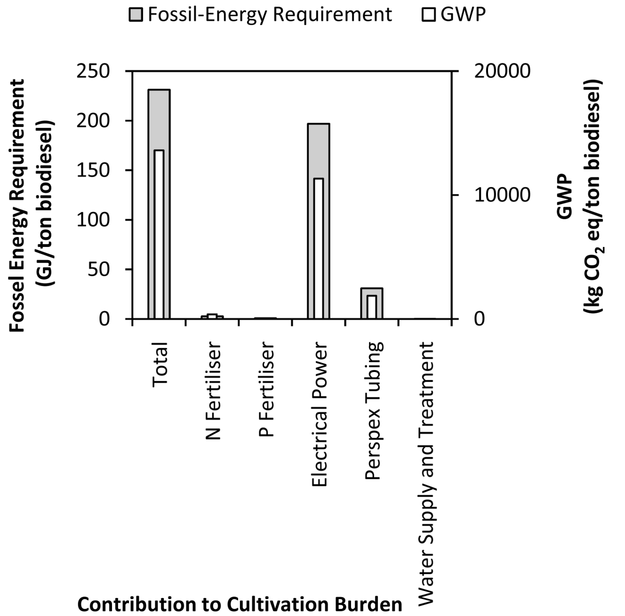

Figure 4. LCA results for the base case cultivation of *C. vulgaris* in air-lift tubular bioreactors for use as a biodiesel feedstock.

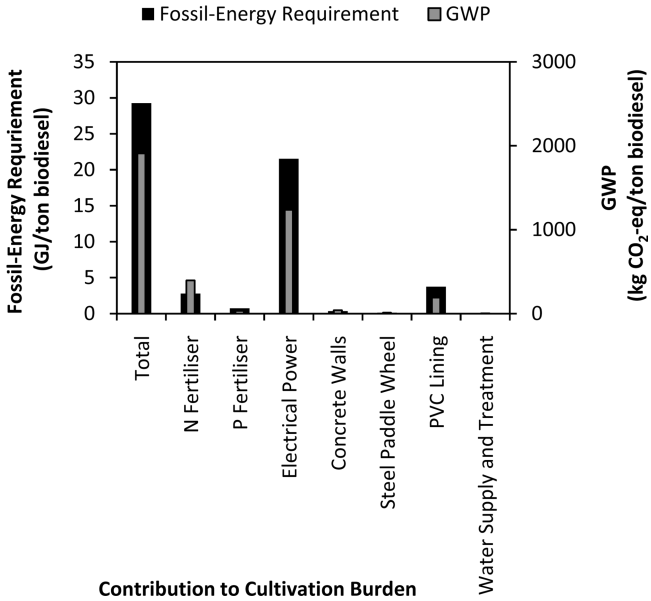

Figure 5. LCA results for the base case cultivation of *C. vulgaris* in raceways for use as a biodiesel feedstock.

forest in Malaysia has been reported to have a GWP ~ 350% greater than fossil-derived diesel.[13] Furthermore, the results of this study show similar GWP benefits to those of other second-generation biofuels. For example, Levelton[41] and Spatari et al.[42] demonstrated that bioethanol from corn stover and switch grass in Canada would have a GWP 75–96% lower than fossil-derived gasoline.

The requirements for process water were found to be 3.8 and 13.7 m^3/ton of biodiesel, when cultivating the microalgae in raceways and photo-bioreactors, respectively. The raceways were found to require less water than air-lift tubular bioreactors because the annual rainfall in the U.K.[43] was considered to be greater than evaporation. In localities where evaporation is greater than rainfall, raceways would require more water than tubular bioreactors. For example, if raceways were built in the Mediterranean, the average annual evaporation would be greater than rainfall by ~300 mm,[19] resulting in the total requirement of process water increasing significantly to 101 m^3/ton of biodiesel. However, tubular bioreactors are likely to require cooling during hot periods. If this were performed, e.g., by spraying water on the surface of the tubes, evaporation losses are likely to be ~1–2 kg/day per m^2 of tube area;[1] therefore, an additional 362 m^3 of water per ton of biodiesel would be required.

It can be seen from panels a and b of Figure 3 that the cultivation of the biomass contributes the most to the fossil-energy requirement and GWP of the production of biodiesel using either method of cultivation. The burdens associated with the cultivation of *C. vulgaris* in air-lift tubular bioreactors are shown in more detail in Figure 4. It can be seen that the electrical power requirement and the manufacture of the solar collector tubing are the only inputs significantly affecting these environmental burdens; the electrical power requirement was found to contribute 85 and 83% to the total fossil-energy requirement and GWP of the cultivation step, respectively, while the manufacture of the solar tubing would contribute 13 and 14%. This direct power requirement was calculated to be 68 GJ/ton of biodiesel (excluding the indirect energy required to produce the electricity), significantly greater than the electricity generated by combusting the excess methane produced by anaerobic digestion of the residual biomass (~15.8 GJ/ton of biodiesel). Although the burdens associated with the manufacture of the solar collector tubing are much less than those resulting from the power requirement for pumping the culture, they are still significant. The GWP associated with the manufacture of the solar collector alone is roughly equal to the GWP of the entire cultivation stage of the raceway system.

The burdens associated with the cultivation of biomass in raceways (Figure 5) show that the electricity required to power the paddle wheel contributes the most to the fossil-energy requirement and GWP of the cultivation process, representing 74 and 65% of the total burdens, respectively. The use of fertilizers would represent 12 and 22% of the fossil-energy requirement and GWP, respectively. Because the microalgae are grown under nitrogen deficiency during stage 2 of the cultivation, the use of fertilizer was found to be less influential on the overall burden than Clarens et al.[20] reported for nutrient-sufficient growth. The burden from the manufacture of the polyvinyl chloride (PVC) lining was found to represent 13 and 10% of the fossil-energy requirement and GWP, respectively, and was shown to be the only material of construction making a significant contribution to these environmental burdens. This is because the manufacture of PVC has a significantly higher fossil-energy requirement than both lightweight concrete blocks and carbon steel per unit mass used. Also, it was assumed that the PVC lining has a lower life expectancy than the concrete walls and paddle wheel (5 years versus 20 years). When producing biodiesel from *C. vulgaris* cultivated in raceways, the base

(41) Levelton. *Assessment of Net Emissions of Greenhouse Gases from Ethanol-Blended Gasolines in Canada: Lignocellulosic Feedstocks*; Levelton Engineering Ltd. and (S&T)2 Consultants: Ottawa, Canada, 2000; Report R-2000-2.

(42) Spatari, S.; Zhang, Y.; Maclean, H. L. *Environ. Sci. Technol.* **2005**, *36*, 9750–9758.

(43) Meteorological Office. *U.K. Climate and Weather Statistics—Climate Averages 1971–2000*; Met Office: Devon, U.K., 2009; http://www.metoffice.gov.uk/climate/uk/averages/19712000.

case results show that the methane generated by anaerobic digestion of the residual algal biomass offsets both the heat and electrical power requirement of the process plant (3.9 and 12.0 GJ/ton of biodiesel, respectively), making the process energetically self-sufficient while also producing 3.8 GJ/ton of biodiesel of excess electrical power.

These results show that biodiesel produced from microalgae cultivated in air-lift tubular bioreactors is less sustainable than that produced in raceways, because the energy requirement for circulation of the culture in an air-lift tubular bioreactor is significantly more than in a raceway. This can be seen by examining the power losses from friction when cultures are circulated in the tubular bioreactors and raceways. Equation 1 gives the ratio of power required to circulate a given volume of liquid in a tubular bioreactor (P_t) to the power required to circulate the same volume in a raceway (P_r), considering only frictional losses and ignoring hold-up in air-lift pumps.

$$\frac{P_t}{P_r} = \left(\frac{v_t}{v_r}\right)^3 \left(\frac{4f_t}{f_r}\right)\left(\frac{R_h}{d_t}\right) \tag{1}$$

Here, v_t and v_r are the mean velocities of flow in the tubular bioreactor and raceway, respectively, while f is the friction factor, R_h is the hydraulic mean depth of the raceway (0.28 m), and d_t is the internal diameter of the tubular bioreactor (0.053 for stage 1 of cultivation and 0.1 m for stage 2 of cultivation). For turbulent flow in the tubular bioreactors, envisaged as a length of smooth pipe, the friction factor was taken to be proportional to $Re^{-0.25}$. Here, f_t equals 0.0062 and 0.0053 for tubular reactors of diameter 0.053 and 0.1 m, respectively. Manning's eq 2 describes the friction factor in open channels of raceways

$$f_r = \frac{2gn^2}{R_h{}^{1/3}} \tag{2}$$

where n is Manning's friction coefficient (units of s/m$^{1/3}$) and g is acceleration due to gravity. Here, n was taken to be 0.012, an estimated value for flow over smooth plastic on granular earth;[2] therefore, f_r was calculated to be 0.0043. Using eq 1, the power required to circulate a volume of culture in the tubular bioreactors of diameter 0.053 m would be 140 times more than that required for a raceway, while circulation in those of diameter 0.1 m would require 64 times more power. The concentration of biomass in tubular bioreactors is considered to be ~5 times greater than in raceways; therefore, these power ratios reduce to 28 and 13, when considering the power required to circulate a given mass of algae. However, it is still evident that, for the designs considered here, frictional losses are significantly greater in the tubular bioreactors than raceways.

3.2. Comparison of other LCAs for Raceways. The results of calculations to find the principal energy and material inputs to the process are shown in Table 3, where they are compared to estimates made by Lardon et al.,[19] who performed an energy analysis on a similar process, producing biodiesel from *C. vulgaris* cultivated in a raceway and deprived of nitrogen during their growth. It can be seen that the requirements of the cultivation and esterification stages reported by Lardon et al.[19] are similar to those determined in this paper, apart from the quantity of nitrate supplied during cultivation. This is because Lardon et al.[19] used a single-stage algal cultivation under nitrogen-deprived conditions, which would require less nitrogen than the two-stage approach, where microalgae are first grown under nitrogen-sufficient conditions to a high concentration of cells, before the nitrate supply is ceased. However, the former approach is likely to achieve lower productivities of lipid than the two-stage method, owing to lower rates of algal growth under nitrogen-deprived conditions.[3,8]

Table 3. Principal Energy and Material Requirements for the Production of Biodiesel from Microalgae Grown in Raceways Using Nitrogen-Deprivation Methods

	units	this study	Lardon et al.[19]
cultivation			
electricity	GJ/ton of biodiesel	7.2	5.7
carbon dioxide	kg/ton of biodiesel	6700	7500
nitrogen	kg of N/ton of biodiesel	59	6
flocculation			
electricity	GJ/ton of biodiesel	0.50	
flocculant	kg/ton of biodiesel	260	
centrifugation			
electricity	GJ/ton of biodiesel	2.0	
homogenization			
electricity	GJ/ton of biodiesel	1.7	
oil extraction			
electricity	GJ/ton of biodiesel	0.2	3.9
heat	GJ/ton of biodiesel	1.7	10.2
hexane	kg/ton of biodiesel	3	25
oil refining			
electricity	GJ/ton of biodiesel	0.1	
heat	GJ/ton of biodiesel	0.6	
esterification			
electricity	GJ/ton of biodiesel	0.2	
heat	GJ/ton of biodiesel	1.6	0.9
methanol	kg/ton of biodiesel	110	114
anaerobic digestion			
electricity	GJ/ton of biodiesel	0.1	
energy from methane			
electricity	GJ/ton of biodiesel	15.8	
heat	GJ/ton of biodiesel	3.9	

It can also be seen in Table 3 that the method of oil extraction adopted in this paper, where the initial extraction occurs at ambient temperature and heat is only required to separate the TAG from the hexane once it has been extracted from the cells, uses less energy than estimated by Lardon et al.[19] They assumed that the heat and hexane requirements of the process are proportional to the total volume of processed material, and therefore, both the aqueous and solvent phases are heated during the process.

3.3. Modifications of the Base Case. As stated earlier, biodiesel is not currently produced from microalgae on a commercial scale; therefore, the results presented above are based on a set of assumptions describing the stages of a hypothetical biodiesel production process. Consequently, it is important to determine the sensitivity of the results to the key assumptions. The LCA results for modifications of the base cases are displayed in Tables 4 and 5 for algae cultivated in raceways and air-lift tubular bioreactors, respectively. It can be seen that the results are highly sensitive to several of the parameters investigated here, highlighting the importance of pilot-scale trials to investigate the underlying assumptions.

3.3.1. Productivities of TAG by Area. The productivities of biomass and TAG used in our model are approximate and based on laboratory- or small-scale operations. We therefore investigated the sensitivity of the fossil-energy requirement and GWP of biodiesel to these values (Tables 4 and 5).

Table 4. Fossil-Energy Requirement and GWP of Biodiesel from *C. vulgaris* Cultivated in Raceways, Considering Modifications to the Base Case[a]

scenario	fossil-energy requirement: GJ/ton of biodiesel	fossil-energy requirement: savings (%)[b]	GWP: kg of CO_2 equiv/ton of biodiesel	GWP: savings (%)[b]
Base Case				
raceway base	6.5	85	713	78
Modifications to the Base Case				
productivity by area (base = 40 tons ha^{-1} year^{-1})				
80 tons ha^{-1} year^{-1}	−0.1	100	331	90
20 tons ha^{-1} year^{-1}	19.9	54	1482	54
10 tons ha^{-1} year^{-1}	46.7	−8	3023	6
velocity of culture (base = 0.3 m/s)				
0.15 m/s	−1.5	103	255	92
0.45 m/s	28.3	35	1963	39
depth of sump (base = 3 m)				
1.5 m	2.9	93	193	94
6 m	16.0	63	1259	61
concentration of CO_2 in flue gas (base = 12.5 vol %)				
9 vol %	11.0	74	974	70
5 vol %	23.7	45	1702	47
water use (base = recycle spent medium to cultivation step)				
spent medium to WWT[c]	13.3	69	1961	39
flush pond every 2 months	8.6	80	1090	66
cell disruption (base = homogenization)				
enzyme treatment	24.1	44	1782	44
oil extraction (base: five mixer-settlers)				
three extraction decanters	8.1	81	807	75
recycling nutrients (base = no recycling)				
recycle 80%	6.1	86	508	84
use of glycerol (base = pharmaceutical industry)				
industrial furnace	5.6	87	644	80
transport of biodiesel (base = ship, 650 km)				
ship, 325 km	6.5	85	711	78
34 ton truck, 325 km	6.7	85	724	77

[a] The values for the base case are shown at the top of the table, and the values calculated by changing each of the parameters in turn (keeping all other values the same as the base case) are given below. [b] Savings when compared to fossil-derived diesel on a net energy basis. [c] WWT = wastewater treatment.

As expected, if the productivity of lipid is increased, these burdens decrease and vice versa. These results show that, if the productivity of TAG by area were to double, biodiesel produced from microalgae grown in raceways would have a GWP ~ 90% lower than fossil-derived diesel, although for algae grown in air-lift tubular bioreactors, it would still be 67% greater than fossil-derived diesel. This lends support to the finding in section 3.1 that it is more environmentally beneficial to grow microalgae in raceways than in air-lift tubular bioreactors.

Productivities of biomass and lipids are very much dependent upon the temperature of the culture; cultivation during the winter in the U.K. could therefore result in low productivities unless the culture is heated. In turn, as well as resulting in low productivities per unit area of TAG, the biodiesel produced may save little or no fossil-energy and GWP when compared to fossil-derived diesel, even when grown in raceways. Solar heating or use of low-grade heat from power stations or other industrial operations, may provide a means of overcoming this issue.

3.3.2. Velocity with which the Culture is Pumped in the Cultivation Facilities. Assuming that the productivity of TAG is constant, it can be seen that the LCA is highly sensitive to this velocity, and if it could be reduced without affecting the productivity of TAG, significantly greater savings of fossil-energy requirement and GWP could be achieved. The velocity of circulation of cultures in raceways or air-lift tubular bioreactors was chosen to ensure that adequate mixing is achieved; however, these results indicate that it is important to ensure that this velocity is optimized.

Experiments have been performed to investigate the feasibility of growing microalgae in air-lift tubular photobioreactors while circulating the culture at lower velocities than those assumed in the base case of this paper. Molina et al.[34] investigated growing *P. tricornutum* in an air-lift tubular reactor using circulation speeds of 0.5, 0.35, and 0.17 m/s. It was reported that the culture quickly died when liquid speeds of 0.17 m/s were employed, apparently owing to photo-oxidation effects resulting from the longer circulation time; at 0.17 m/s, shorter lengths of tube of ~30 m would have to be used, according to eq A5. However, the two higher speeds achieved similar biomass productivities. If the speed of the culture assumed in this paper was reduced to from 0.5 to 0.35 m/s, the direct power requirement for pumping would fall to 40 GJ/ton biodiesel, resulting in the overall fossil-energy requirement and GWP reducing to 121 GJ/ton of biodiesel and 7410 kg of CO_2 equiv/ton of biodiesel; however, these values are still 181 and 132% greater than fossil-derived diesel, respectively.

3.3.3. Design of the Carbonation System in Raceways. The calculations used to arrive at a rough design of the carbonation sump to be used in raceways are fairly crude; pilot-scale trials would be needed to determine more accurate values of the sparger depth required and the mass transfer achieved.

Table 5. Fossil-Energy Requirement and GWP of Biodiesel from *C. vulgaris* Cultivated in Air-Lift Tubular Bioreactors, Considering Modifications to the Base Case[a]

scenario	fossil-energy requirement: GJ/ton of biodiesel	fossil-energy requirement: savings[b]	GWP: kg of CO_2 equiv/ton of biodiesel	GWP: savings[b]
Base Case				
tubular bioreactor base	199.5	−362	11919	−273
Modifications to the Base Case				
productivity of TAG by area (base = 40 tons ha^{-1} $year^{-1}$)				
80 tons ha^{-1} $year^{-1}$	85.9	−99	5344	−67
20 tons ha^{-1} $year^{-1}$	427.7	−889	25070	−684
10 tons ha^{-1} $year^{-1}$	879.1	−1937	51258	−1502
velocity of culture (base = 0.5 m/s)				
0.25 m/s	89.1	−106	5571	−74
0.75 m/s	444.2	−929	25987	−712
water use (base = recycle spent medium to cultivation step)				
spent medium to WWT[c]	200.8	−365	12149	−280
cell disruption (base = homogenization)				
enzyme treatment	247.2	−473	14731	−360
oil extraction (base = five mixer-settlers)				
three extraction decanters	201.3	−366	12020	−296
recycling nutrients (base = no recycling)				
recycle 80%	196.8	−356	11593	−262
use of glycerol (base = pharmaceutical industry)				
industrial furnace	207.3	−380	12358	−286
transport of biodiesel (base = ship, 650 km)				
ship, 325 km	199.5	−362	11917	−272
34 ton truck, 325 km	199.7	−363	11930	−273

[a] The values for the base case are shown at the top of the table, and the values calculated by changing each of the parameters in turn (keeping all other values the same as the base case) are given below. [b] Savings when compared to fossil-derived diesel on a net energy basis. [c] WWT = wastewater treatment.

The depth of the sparger was therefore varied to investigate its effect on the fossil-energy requirement and GWP of the biodiesel produced by the process: clearly, a greater depth would require the flue gas to be compressed to a higher pressure but should give a greater transfer of CO_2. The effect on the burdens is investigated in Table 4, in which the depth of submergence of the sparger required to transfer 70% of CO_2 in the flue gas to the culture is changed. It can be seen that the savings achieved are sensitive to this depth; therefore, it is important to design a carbonation system that can achieve adequate mass transfer using low sump depths.

The quantity of gas to be compressed before entering the carbonation sump is dependent upon the proportion of carbon dioxide in the flue gas. In the base case, the concentration of carbon dioxide was assumed to be 12.5 vol %; however, in some cases, it may be as low as 5 vol %.[33] The effects of the increased volume of gas requiring compression when using lower concentrations of carbon dioxide in the flue gas on the fossil-energy requirement and GWP of biodiesel are also shown in Table 4. Here, it was assumed in all cases that 70% of the CO_2 in the flue gas is transferred to the culture. It can be seen that these burdens are highly dependent upon the concentration of CO_2 in the flue gas; if lower concentrations are used, the fossil-energy requirement and GWP of biodiesel are significantly higher. If more dilute gas were used, the volumetric flow rate of gas would increase and, therefore, so would the volumetric liquid-side gas−liquid mass-transfer coefficient (k_La); however, the concentration driving force would reduce. As a result, the mass transfer of CO_2 to the liquid would be affected and the depth of the sparger might, therefore, need to be changed to provide adequate gas exchange, affecting the fossil-energy requirement and GWP of the biodiesel, as discussed above.

3.3.4. Sending the Spent Medium to Wastewater Treatment. It is likely to be undesirable to reuse the spent medium for algal cultivation, owing to contamination or the accumulation of products inhibiting growth; therefore, sending it for wastewater treatment was also considered. If the spent medium could not be recycled, raceways would require significantly more water than tubular bioreactors because the harvested algal culture would be more dilute, with raceways requiring 1750 m^3/ton of biodiesel, compared to 335 m^3/ton of biodiesel for tubular bioreactors. The total energy requirement and GWP of the biodiesel would increase significantly if the algae were cultivated in raceways, as shown in Table 4. An alternative method of controlling contaminants and inhibitory compounds in raceways would be to flush it regularly with freshwater (approximately every 2 months).[19] In this case, the total water requirement was calculated to be 530 m^3/ton of biodiesel and the fossil-energy and GWP savings would be 80 and 66%, respectively. For air-lift tubular bioreactors, the additional GWP and fossil-energy requirement arising from the higher requirement for water if the spent medium cannot be recycled is insignificant compared to the burden associated with the cultivation stage. Hence, there is little change in the fossil-energy requirement and GWP from the base case.

3.3.5. Method of Cell Disruption. If enzyme treatment were used to gain access to the contents of the cells rather than homogenization, both the fossil-energy and GWP savings of combusting the biodiesel rather than fossil-derived diesel would fall considerably when using microalgae cultivated in raceways or air-lift tubular photo-bioreactors. Figure 6 shows how the GWP associated with each stage of the process would be different for each method of cell disruption if the microalgae were cultivated in raceways. It can be seen that

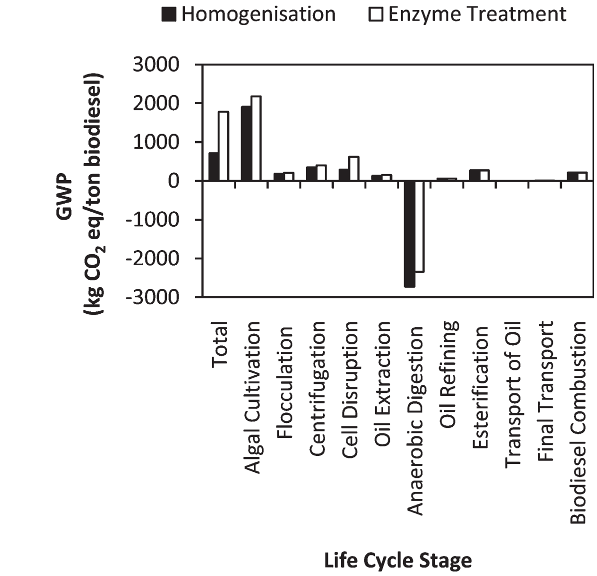

Figure 6. GWP of biodiesel produced from *C. vulgaris* cultivated in raceways, using either homogenization or enzyme treatment to disrupt the cell walls.

the burden associated with algal cultivation, flocculation, and centrifugation would increase if enzyme treatment were employed. This is because it was assumed that only 80 wt % of the cells would be disrupted by treatment with enzymes, while 96 wt % would be disrupted using the homogenization process; therefore, less TAG would be produced when treating the same volume of algal slurry. This also reduces the amount of methane produced by anaerobic digestion, because it was assumed that less of the algal residue would be digestible; as a result, less electricity is generated and only 0.05 GJ (as opposed to 3.8 GJ) of electrical power is exported to the national energy network, per ton of biodiesel produced. Moreover, the GWP associated with enzyme treatment of the algal slurry would be approximately twice as large as homogenization, with heat and enzyme requirements each representing 43% of this burden. Experimental work is needed to investigate these assumptions.

3.3.6. Method of Oil Extraction. It can be seen from Tables 4 and 5 that the method used to extract the oil from the cells was not found to have a great impact on the fossil-energy requirement or GWP of biodiesel produced from microalgae.

3.3.7. Recycling of Nutrients. In contrast, the burden associated with biodiesel from algae cultivated in raceways could be reduced significantly by recycling the nitrogen and phosphorus present in the residual algal biomass (Tables 4 and 5). This is because anaerobic digestion mineralizes algal waste, producing ammonium and phosphate ions, which may then be reused.[31] Because TAG contains no nitrogen or phosphorus and the rest of the contents of the cells are sent to anaerobic digestion (apart from any losses of membrane lipids and chlorophyll in the refining step), it should be possible to recover a high proportion of the nitrogen and phosphorus added during the cultivation step. This is a similar finding to that of Clarens et al.,[20] who reported that using wastewater rather than inorganic fertilizer would significantly reduce the environmental burden associated with the cultivation of microalgae. However, for the case of air-lift tubular bioreactors, this would have a negligible effect on the overall fossil-energy requirement and GWP of the biodiesel, because the burden associated with the power required to pump the culture around the system far outweighs all other burdens.

3.3.8. Use of Glycerol. Because the production of biodiesel has increased globally, the market for glycerol of pharmaceutical grade has become saturated; therefore, an alternative option of its use as a fuel for industrial furnaces has been considered here. It was assumed that the glycerol would be transported by road a distance of 300 km to an industrial furnace with an efficiency (defined as the proportion of the lower calorific value, which is converted to useful heat) of 60%.[44] Allocation by substitution is employed rather than by market value, as described in section 2.4. It can be seen from Tables 4 and 5 that the use of the glycerol has little impact on the overall fossil-energy requirement and GWP of the biodiesel.

3.3.9. Distribution of Biodiesel. Similarly, the final transport of the biodiesel has little impact on its environmental performance. The fossil-energy requirement and GWP of the biofuel reduce slightly if the distance it is transported by ship is halved and increase slightly if it is transported by road rather than by ship.

4. Conclusions

Our LCA has shown that, if the future target[3] for the productivity of lipids from microalgae, such as *C. vulgaris*, of ~40 tons ha^{-1} $year^{-1}$ could be achieved, cultivation in raceways of depth ~0.3 m would be significantly more environmentally sustainable than fossil-derived diesel and many first-generation biofuels. In the base case, using raceways would be energetically self-sufficient, with the heat and power requirement of the process being provided by combusting the methane generated from the anaerobic digestion of the residual algal biomass. In contrast, if air-lift tubular bioreactors with solar receivers of diameter 0.053−0.1 m were used, the power required to pump the culture around the system and the manufacture of the solar collector tubes would significantly increase these burdens and the biodiesel would have a fossil-energy requirement of 200 GJ/ton of biodiesel, 362% higher than fossil-derived diesel, and a GWP of 11.9×10^3 kg of CO_2 equiv/ton of biodiesel, 273% higher than fossil-derived diesel.

The electricity required during cultivation was found to contribute the most to the overall requirement for fossil energy and GWP of the biodiesel produced from *C. vulgaris* cultivated in either raceways or air-lift tubular bioreactors. In contrast, the fossil-energy requirements and GWP of each of the algal processing steps were found to be significantly lower than for the cultivation, and the burdens associated with the transport of the oil feedstock and biodiesel product were negligible. As a result, if the velocity with which culture is circulated in reactors could be reduced without detrimentally affecting the productivities of biomass and oil, the environmental performance of biodiesel produced from algae cultivated in either raceways or air-lift tubular bioreactors could be significantly improved. However, owing to high frictional losses in the solar receivers of the tubular bioreactors, even if the velocity employed to circulate the culture were reduced from 0.5 m/s assumed in the base case to 0.25 m/s, the

(44) Trinks, W.; Mawhinney, M. H.; Shannon, R. A.; Reed, R. J.; Garvey, J. R. *Industrial Furnaces*, 6th ed.; John Wiley and Sons, Ltd.: New York, 2004.

fossil-energy requirement and GWP would still be significantly greater than fossil-derived diesel, on a net energy basis. Alternatively, frictional losses in tubular bioreactors could be reduced by increasing the diameter of the solar receiver (see eq 1). However, at larger diameters, light penetration would be diminished and, therefore, biomass productivity would also be likely to decrease. If biodiesel produced from microalgae grown in tubular bioreactors is to have a lower fossil-energy requirement and GWP than fossil-derived diesel, the burdens associated with the cultivation step must be reduced from 231 GJ/ton of biodiesel and 13 600 kg of CO_2 equiv/ton of biodiesel for the total fossil-energy requirement and GWP, respectively, to lower than 75 GJ/ton of biodiesel and 4880 kg of CO_2 equiv/ton of biodiesel. Research into alternative methods of mixing microalgae cultivated in photo-bioreactors is evidently required if such systems are to be used in the future. One possible solution is the oscillatory flow reactor,[45] where efficient vortex mixing is achieved when an oscillatory fluid motion interacts with orifice plate baffles in a tube. Preliminary experiments have shown that high rates of algal growth and concentrations of biomass can be achieved at lower net Reynolds numbers than those typically employed for the operation of tubular bioreactors.[46] Other designs, for example, flat-plate reactors, may also offer similar benefits.

Our work also found that the environmental performance of biodiesel produced from the algae harvested from raceways would be highly sensitive to the power required to compress the flue gas; therefore, it would be favorable to use flue gas with higher concentrations of carbon dioxide, to reduce the volume of gas requiring compression and increase the rate of mass transfer of carbon dioxide to the culture. It is also important to achieve high yields of TAG in the cultivation facility. If the productivity of TAG fell below $\sim$10 tons ha^{-1} $year^{-1}$, then the fossil-energy requirement and GWP of the biodiesel would increase substantially and, in the case of cultivation in raceways, it would have a greater fossil-energy requirement than fossil-derived diesel and a similar GWP. This could limit the growing season in the U.K. unless methods, such as solar heating, or low-grade heat from industry, could be employed, because the productivity of biomass and lipids is greatly dependent upon the temperature of the culture.

For cultivation in raceways, recycling of both spent medium and nutrients is also important if the biodiesel is to be environmentally sustainable. If the spent medium from cultivation in raceways could not be recycled owing to its content of contaminants, the supply and treatment of the water would contribute significantly to the overall fossil-energy requirement and GWP of the process and the fossil-energy and GWP savings of using biodiesel rather than fossil-derived diesel would reduce. The water requirement of the process would also increase substantially. Practically, it is likely to be difficult to recycle the spent medium from raceways because the system is open to the environment and, therefore, faces a high risk of contamination from adventitious organisms, while heavy metals and other inhibitory substances are also likely to accumulate. However, rather than continuous treatment of the spent medium, other strategies might be available. A greater understanding of algal community biology may provide the means to establish cultures that are more resistant to contamination. The pond may be flushed with freshwater regularly, although this method would also increase the environmental burdens of the biodiesel. Alternatively, if a halotolerant species, such as *D. salina*, were cultivated close to the sea, seawater could be used in the process, reducing freshwater requirements.

It is evident from the results of this paper that the cultivation of microalgae in raceways has the potential to produce an environmentally sustainable feedstock for the production of biodiesel. However, the environmental performance of the biofuel is highly dependent upon the method of cultivation; therefore careful design will be essential. Moreover, there is an urgent need for pilot scale trials of algal biodiesel production to allow LCA of actual operations.

Appendix 1. Cultivation of Microalgae in Raceways

It was assumed that the external walls and central divider of the raceways would have a lifetime of 20 years and would be constructed using concrete hollow blocks, with a density of 650 kg/m^3 and dimensions of $0.44 \times 0.22 \times 0.215$ m.[47] A white PVC linear of 0.75×10^{-3} m thickness and lifetime of 5 years would be installed to ensure uniform flow rates of the culture and to avoid the resuspension of sediments causing the water to cloud.[2]

In each raceway, a paddle wheel would be used to provide the mixing, operating with a typical electrical efficiency (proportion of inlet power transferred to the liquid) of 17%,[2] while a countercurrent carbonation sump would be used to supply carbon dioxide to the system. Equation A1 was used to determine the hydraulic power requirement (P_{PW}) of the paddle wheel, where Q_L is the volumetric flow rate, ρ_L is the liquid density, h is the head loss, g is acceleration due to gravity, and η_{PW} is the efficiency of the paddle wheel.

$$P_{PW} = \frac{Q_L \rho_L h g}{\eta_{PW}} \tag{A1}$$

Here, the head loss originates from the friction losses (h_1) as the liquid flows around the raceway and head losses in the carbonation sump (h_2). Manning's eq A2 was used to determine h_1, where j_L is the superficial velocity of the liquid, n is Manning's friction coefficient (units of s/$m^{1/3}$), L_c is the channel length, and R_h is the hydraulic mean depth. Here, n was taken to be 0.012, an estimated value for flow over smooth plastic on granular earth.[2]

$$h_1 = \frac{{j_L}^2 n^2 L_c}{{R_h}^{4/3}} \tag{A2}$$

A countercurrent carbonation sump of 3 m depth would be used for 8 h each day in each raceway, transferring 70% of the carbon dioxide in the flue gas to the culture. In reality, the gas–liquid transfer rate would be highly dependent upon the distribution of bubble sizes in the sparged flue gas; however, results by Weissman and Goebel[35] suggest that the above assumptions provide a conservative estimate when sparging with flue gas with a CO_2 concentration of $\sim$12.5 vol %. The loss of head in the carbonation sump was determined using eq A3, where D_s is the distance between the sparger level and the outflow liquid level and ε_g is the gas hold-up. An

(45) Stonestreet, P.; Harvey, A. P. *Trans. IChemE, Part A* **2002**, *80*, 31–44.
(46) Taylor, B. Private communication. Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, U.K., 2009.
(47) Concrete Block Association (CBA). *Aggregate Concrete Blocks: A Guide to Selection and Specification.* CBA: Leicester, U.K., 2007; Data Sheet 1, www.cba-blocks.org.uk.

additional 1% of the total determined using eq A3 was added to account for minor frictional losses in the sump.[35]

$$h_2 = \frac{D_s \varepsilon_g}{1 - \varepsilon_g} \quad \text{(A3)}$$

Equation A4 was used to determine ε_g, where Q_G is the total flow rate of gas, Q_L is the total flow rate of liquid, C_{PE} is an average pressure correction factor for the compression of a gas at sub-surface depths (considered to be 0.89 for a depth of 3 m), $u_{b,\infty}$ is the average bubble rise velocity relative to the water (assumed to be 0.3 m/s), and A_x is the cross-sectional area of the sump, which can be increased by widening the width of the sump, W_s, beyond the depth of the raceway.[35]

$$\varepsilon_g = \frac{Q_G C_{PE}}{C_{PE} Q_G - Q_L + A_x u_{b,\infty}} \quad \text{(A4)}$$

In this paper, it was assumed that W_s was widened, so that the superficial liquid velocity in the sump would be 0.1 m/s. The volume of flue gas supplied to the raceway was calculated by assuming that 120% of CO_2 required for the average growth rate of biomass would be transferred to the culture medium. A compressor with an isentropic efficiency of 80% would be used to compress the flue gas to the required pressure, considering the 3 m static head at the sump bottom, friction losses in the distribution system of 0.07 bar, and a pressure drop across the sparger of 0.07 bar.[35]

When cultivating microalgae in the open, water losses from evaporation can be substantial, with losses up to 10×10^{-3} m^3 m^{-2} day^{-1} in tropical, dry regions.[1] Because these raceways were assumed to be situated in the U.K., a moderate evaporative loss of 3×10^{-3} m^3 m^{-2} day^{-1} was assumed. Rainfall was also considered, using a figure for the average annual rainfall in the U.K. between the years 1971 and 2000, of 1126 mm/year.[43]

Appendix 2. Cultivation of Microalgae in Air-Lift Tubular Photo-bioreactors

The tubing of the solar receiver would be arranged in two layers, where the distance between adjacent tubes on the horizontal plane would be 0.09 m and the vertical distance between the external walls of the tubes in each layer would be 0.03 m. Such a system has been reported to minimize the area of land required.[34] Molina et al.[34] reported that a liquid velocity of 0.5 m/s provides adequate turbulence for maximum cell growth, without causing damage to the cells; therefore, this velocity was assumed. If lower velocities are employed, the maximum length (L_{max}) of the solar collector tubing would have to be reduced to counter the effect of the build up of oxygen by photosynthesis. The consequent value of the length was determined from

$$L_{max} = \frac{j_L([O_2]_{out} - [O_2]_{in})}{R_{oxy}} \quad \text{(A5)}$$

where j_L is the superficial velocity culture, $[O_2]_{out}$ is the maximum acceptable concentration of dissolved oxygen in the culture, taken to be 300% of air saturation,[34] $[O_2]_{in}$ is the concentration of dissolved oxygen at the inlet of the solar receiver, taken to be 100% of air saturation, and R_{oxy} is the volumetric rate of oxygen generation by photosynthesis in the tube, calculated from the maximum productivity of biomass, assumed to be 1.5 kg m^{-3} day^{-1} in stage 1 and 0.75 kg m^{-3} day^{-1} in stage 2. In the base case, the maximum lengths were calculated to be 100 and 199 m for the reactors used in stages 1 and 2, respectively.

The superficial velocity of the liquid induced by the air-lift pump is dependent upon the geometric configuration of the circulation loop and the difference in gas hold-up in the riser and downcomer zones of the air-lift column, according to the following:[48]

$$j_L = \sqrt{\frac{2g(\varepsilon_r - \varepsilon_{dc})h_r}{\frac{K_T}{(1-\varepsilon_r)^2} + K_B\left(\frac{A_r}{A_d}\right)^2 \frac{1}{(1-\varepsilon_{dc})^2}}} \quad \text{(A6)}$$

where K_T and K_B are frictional loss coefficients of the top and bottom zones of the air-lift loop, respectively (here, the top zone is the riser, and the bottom zone consists of the downcomer and the solar receiver), h_r is the height of the riser, A_r and A_d are the cross-sectional areas of the riser and downcomer, respectively, ε_r is the gas hold-up in the riser, and ε_{dc} is the gas hold-up in the downcomer (assumed to be 0 because no bubbles recirculate). In air-lift devices generally, the energy loss in the top zone is significantly less than the bottom zone; this is particularly true for the loop configuration assumed here because the entire solar collector constitutes the bottom zone; therefore, K_B would be significantly larger than K_T. K_T was therefore neglected, while K_B was calculated from the following empirical formula for turbulent flow in a continuous smooth pipe:[34]

$$K_B = 0.3164\text{Re}^{-0.25}\left(\frac{L_{eq}}{d_t}\right) \quad \text{(A7)}$$

where Re is the Reynolds number, L_{eq} is the equivalent length of the loop (straight length plus an additional length, L_{add}, to allow for pipe bends, etc.), and d_t is the internal diameter of the pipe. Finally, ε_r was calculated, according to the Zuber and Findlay equation[49]

$$\varepsilon_r = \frac{C_\alpha}{C_\beta + \frac{u_{b,\infty}}{j_G + j_L}} \quad \text{(A8)}$$

where j_G and j_L are the superficial velocities of the gas and liquid in the riser, C_α is the ratio of the superficial gas velocity to the total superficial velocity in the riser, C_β is a characteristic parameter (taken to be 1.1), and $u_{b,\infty}$ is the bubble rise velocity, assumed to be 0.3 m/s.[34] Equations A6–A8 were solved simultaneously to determine the height of the riser, h_r, and flow rate of the gas to provide the required culture velocity.

To estimate the capacity of the air-lift column for the removal of oxygen, the overall gas–liquid volumetric mass-transfer coefficient, $k_L a$, was estimated according to[48]

$$\frac{k_L}{d_B} = \frac{k_L a(1-\varepsilon_r)}{6\varepsilon_r} \quad \text{(A9)}$$

where k_L is the true mass-transfer coefficient and d_B is the mean bubble diameter. It has been shown that the ratio k_L/d_B is constant for a given fluid, irrespective of the aeration rate, and that for air–water dispersions and suspensions in which

(48) Chisti, Y. *Air-Lift Bioreactors*; Elsevier: Amsterdam, The Netherlands, 1989.

(49) Zuber, N.; Findlay, J. A. *J. Heat Transfer* **1965**, *18*, 453–468.

the suspending fluid has properties approximating those of water, k_L/d_B can be calculated from[48]

$$\frac{k_L}{d_B} = 5.63 \times 10^{-5}\left(\frac{gD_L\rho_L{}^2\sigma}{\mu_L{}^3}\right)^{0.5} e^{-0.131C_s{}^2} \qquad \text{(A10)}$$

where C_s is the concentration of solids in suspension (dry wt/vol %), D_L is the diffusivity of gas in liquid, and σ is the interfacial tension. Using eqs A9 and A10, the k_La of the air-lift systems were determined to be 0.132 and 0.125 s^{-1} for the reactors used in stages 1 and 2, respectively. These values were calculated to be sufficient to reduce the dissolved oxygen concentration from 300% of air saturation to less than 150% of air saturation at the entrance to the solar receiver, for each design. The maximum tolerable dissolved oxygen level is considered to be ∼400% air saturation,[7] deeming the above performance adequate.

The volumetric flow rate of air required to provide the flow in the reactors would be significantly greater than the quantity of flue gas needed to supply the CO_2 required as a carbon source; therefore, the ratio of air to flue gas added could be varied, depending upon the pH of the culture. It was assumed that a compressor with an isentropic efficiency of 80% would be used to compress the flue gas to the required pressure, considering the static head at the bottom of the riser, friction losses in the distribution system of 0.07 bar, and a pressure drop across the sparger of 0.07 bar.[35]

It was assumed that the algae leaving the cultivation step would have a composition of 40.0 wt % TAG, 5.0 wt % membrane lipids, 0.2 wt % chlorophyll, 49.3 wt % carbohydrates, and 5.5 wt % protein.[8]

Appendix 3. Downstream Processing

In all cases, it was assumed that all pumps would have an overall efficiency (total power transferred to the liquid) of 70% and generate a total dynamic head of 10 m. The water supply and treatment was assumed to be provided by the local water company, and the average values for fossil-energy requirement and GWP for the supply and treatment of water by U.K. water companies during 2006−2007 were used in the LCA.[50]

Flocculation. It was assumed that the aluminium sulphate flocculant would be added to the culture to give a final concentration of 0.15 kg/m^3 in a tank, with a residence time of 1200 s and an agitation power[51] of 100 W/m^3. The slurry would then be sent to an excavated circular settling pond of depth[35] 3 m, assumed to be lined with PVC of 0.75×10^{-3} m thickness; here, the algae would settle to the bottom of the pond at a speed of ∼1.5 m/h, reaching the bottom in ∼2 h.[1] Rotating flight scrapers would transfer the settled algal sludge to a central hopper, requiring electricity at a rate of 0.8 W/m^2 of pond area.[52]

Centrifugation. It was assumed that each centrifuge could treat 2 m^3/h slurry. This step would concentrate the algae to 220 kg/m^3, requiring electricity at a rate of 28.8 MJ/m^3 of algal slurry entering the centrifuge.[36] It was assumed that 5 wt % of the algal cells would be lost in this step.[36]

Cell Disruption. The homogenizer modeled in this paper was based on the GEA Ariete homogenizer, model NS-3037, which treats 2 m^3/h of slurry when operated at a pressure of 600 bar. This homogenizer requires cooling water at a rate of 0.09 m^3/h, is constructed from 2.1 tons of stainless steel, and is powered by a 37 kW motor; therefore, electricity requirements were calculated to be 67 MJ/m^3 of algal slurry treated per pass.[53] Experiments performed by GEA Process Engineering[54] indicate that 79 wt % of *Chlorella* cells are disrupted per pass; therefore, it was assumed that 2 passes would be employed, disrupting a total of 96% of the cells. A recovery of 95 wt % of the dry cell mass was assumed.

The design of the enzymatic hydrolysis step was based on an industrial process used in Denmark to fractionate the oils, proteins, and hulls of rapeseeds.[55] The culture would first be heated to 95 °C and kept at this temperature in an insulated holding tank for 900 s to inactivate any myrosinases and lipases. The temperature of the culture would then be reduced to 50 °C by heat exchange with cooling water; the pH would be adjusted to 4.5 by the addition of ∼2.75 kg of phosphoric acid (75 wt %) per m^3 of liquid; and enzymes would be added. It was assumed that the cellulolytic enzyme manufactured by Novozymes A/S, "Cellic Ctec", would be used to break open the cell walls, at a dosage of 0.02 kg/kg of dry biomass.[56] The enzyme treatment would be undertaken in a continuous stirred reactor, of residence time 4 h, and agitated[51] at 1 kW/m^3, assuming an overall motor efficiency of 90% (energy transferred to the liquid divided by the total electrical energy supplied to the agitator). It was assumed that this process would disrupt 80 wt % of the cells.[55]

Extraction of the Oil from the Cells. A countercurrent cascade of five steel mixer-settlers was investigated, with each mixer having a residence time of 600 s and a vessel height/diameter ratio[57] of 1. Each vessel would contain four vertical baffles, of width $^1/_{12}$ of the diameter of the vessel, while a flat-blade turbine with six blades would be used to provide agitation, with a diameter (D_i) $^1/_3$ of the diameter of the vessel (D_v). In a mixer-settler, the phase with the greatest volumetric flow rate is usually dispersed in the other phase because this creates a larger interfacial area; therefore, the algal slurry would be dispersed in the solvent phase.[58] The power requirement (P_M) of the mixer was determined by solving eqs A11−A14 simultaneously[57]

$$P_M = s^3 P_o D_i{}^5 \rho_M \qquad \text{(A11)}$$

$$s_{min} = \left(1.03 g\varepsilon_d{}^{1.06}\left(\frac{D_v}{D_i}\right)^{2.76}\left(\frac{\mu_M{}^2\sigma}{D_i{}^5\rho_M g^2(\rho_d-\rho_c)^2}\right)^{0.084}\left(\frac{\rho_d-\rho_c}{\rho_M D_i}\right)\right)^{0.5} \qquad \text{(A12)}$$

(50) Water U.K. *Sustainable Water: State of the Water Sector Report*; Water U.K.: London, U.K., 2008.

(51) Coulson, J. M.; Richardson, J. F.; Sinnott, R. K. *Coulson and Richardson's Chemical Engineering*, 3rd ed.; Butterworth-Heinemann: Oxford, U.K., 1999; Vol. 6: Chemical Engineering Design.

(52) Liu, D.; Liptak, B. G. *Environmental Engineering Handbook*, 2nd ed.; Lewis Publishers: New York, 1997.

(53) GEA Process Engineering. *GEA Niro Soavi, Leading Pressure. Ariete N3 3037 Brochure*; GEA Niro Soavi: Parma, Italy, 2009; www.niro-soavi.it.

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(56) Novozymes. *Application Sheet Cellic CTec and HTec. Advanced Enzymes for Hydrolysis of Lignocellulosic Materials*; Novozymes: Bagsvaerd, Denmark, 2009.

(57) Benitez, J. *Principles and Modern Applications of Mass Transfer Operations*, 2nd ed.; John Wiley and Sons, Ltd.: New York, 2009.

(58) Couper, J. R.; Penney, W. R. *Chemical Process Equipment. Selection and Design*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2005.

$$\rho_M = \varepsilon_d \rho_d + \varepsilon_c \rho_c \tag{A13}$$

$$\mu_M = \frac{\mu_c}{\varepsilon_c}\left(1 + \frac{1.5\mu_d \varepsilon_d}{\mu_c + \mu_d}\right) \tag{A14}$$

where s is the impeller rotational speed (Hz), assumed to be $1.1 \times$ the minimum speed of rotation, s_{min}, given by eq A12, P_o is the power number, which, for the impeller described above, is equal to 5.7 if the impeller Reynolds number is greater than 10 000, and σ is the interfacial tension between the two phases. Further, ρ_M is the two-phase mixture density, and μ_M is the two-phase mixture viscosity, calculated from eqs A13 and A14, respectively, where ρ_d and μ_d are the density and viscosity of the dispersed phase, while ρ_c and μ_c are the values for the continuous phase. Finally, ε_d and ε_c are the hold-ups in the dispersed and continuous phases, respectively, where the ratio of $\varepsilon_d/\varepsilon_c$ is assumed to be the same as the volumetric flow ratio between the two phases. Values for σ, ρ_c, and μ_c were taken from the literature, while ρ_d was estimated to be $\sim$1200 kg/m^3, and preliminary experiments by Taylor[46] were used to determine μ_d. In these experiments, the viscosity of a slurry of *Scenedesmus obliques*, with a dry cell mass of 200 kg/m^3, was determined to be 1 Pa s, when agitated at a rotation rate of 5 Hz. Using eqs A11−A14, it was calculated that each mixer would be agitated at a rotation rate of $\sim$5.3 Hz and draw power at $\sim$3.3 kW/m^3 of the mixer volume. The overall motor efficiency of the agitator was assumed to be 90%.

The algal slurry would next enter a settling tank, where the two phases separate. It was assumed that flocculant additional to that added in the previous flocculation step would not be needed. Upon separation, the phases would be pumped in a countercurrent mode to the next mixer-settlers in the cascade. Finally, at one end of the cascade, the solvent would be pumped to the de-solventizing step, while, at the other end, the aqueous suspension would be sent to anaerobic digestion.

(59) GEA Process Engineering. *Westfalia Separator CA 226-29 Countercurrent Extraction Decanter. Data Sheet*; GEA Process Engineering: Columbia, MD, 2009.

The use of extraction decanters was also considered, specifically, countercurrent extraction decanters manufactured by Westfalia (CA 226-29 model), which treat 1.5−2 m^3/h of slurry using 0.75−1 m^3/h of solvent.[59] This extraction decanter is able to achieve up to 1.7 theoretical equilibrium stages per decanter; therefore, it was assumed that three extraction decanters would be required to achieve the same recoveries of TAG as the train of mixer-settlers. The decanter is powered by an 11 kW motor; therefore, electricity requirements were calculated to be 20 MJ/m^3 of algal slurry.

Solvent Recovery. The solvent stream, containing the dissolved lipid, would be sent to a stripper column for separation. The tops would be condensed by heat exchange with the inlet stream to maximize energy efficiency, thereby heating the inlet from 25 to 60 °C. The model showed that, for recoveries $>$99.5% of hexane in the tops and oil in the bottoms, the total heat requirement of the reboiler would be $\sim$1.6 kJ/kg TAG entering the distillation column. In comparison, the heating requirement of a conventional large-scale solvent extraction facility used to extract oil from oil-seed rape is $\sim$2.6 kJ/kg oil.[14]

Anaerobic Digestion. The specific methane yields (as measured at 1 bar and 20 °C) were assumed to be[31] 0.851 m^3 of methane/kg of protein, 0.415 m^3 of methane/kg of carbohydrate, and 1.014 m^3 of methane/kg of lipid. The digester would remove 20 kg of chemical oxygen demand (COD) m^{-3} day^{-1} from the algal slurry[60] from an initial COD content of $\sim$161 kg of O_2/m^3 while being gently agitated with a power requirement[61] of $\sim$10 W/m^3. The following chemicals were taken to be required by the process: urea (2.7×10^{-3} kg/kg of COD removed), phosphoric acid (0.9×10^{-3} kg/kg of COD removed), caustic soda (50 wt % NaOH in water) (60×10^{-3} kg/kg of COD removed), and micronutrients, such as iron, manganese, copper, and nickel (0.15×10^{-3} kg/kg of COD removed).[61] The waste stream leaving the digesters would be pumped to a wastewater treatment plant.

(60) Polprasert, C. *Organic Waste Recycling—Technology and Management*, 3rd ed.; IWA Publishing: London, U.K., 2007.

(61) Aden, A.; Ruth, M.; Ibsen, K.; Jechura, J.; Neeves, K.; Sheehan, J.; Wallace, B.; Montague, L.; Slayton, A.; Lukas, J. *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*, NREL Technical Report; National Renewable Energy Laboratory: Golden, CO, 2002; NREL/TP-510-32438.