

1
2
3
4 **Environmental performances of diluents and hydrogen production**
5
6 **pathways from microalgae in cold climates: open raceway ponds**
7
8 **and photobioreactors coupled with thermochemical conversion**
9
10

11 Stan Pankratz, Mayank Kumar, Adetoyese Olajire Oyedun, Eskinder Gemechu,
12
13

14 Amit Kumar*

15
16
17 Department of Mechanical Engineering, 10-263 Donadeo Innovation Centre for Engineering,
18
19 University of Alberta, Edmonton, Alberta T6G 1H9, Canada.
20
21
22
23

24 **Abstract**

25
26
27 Microalgae are considered renewable energy candidates and are characterized by high yields,
28
29 integration with waste streams, and ability to grow on poor or marginal lands and therefore not
30
31 compete with food production. This paper evaluates the environmental sustainability of pathways
32
33 producing diluents and hydrogen through microalgae in cold climatic conditions such as those in
34
35 Western Canada. Two alternative cultivation systems (open pond raceway and photobioreactor,
36
37 microalgal cultivation systems) and four different thermochemical production platforms
38
39 (hydrothermal liquefaction and pyrolysis for diluent production and supercritical water
40
41 gasification and thermal gasification for hydrogen production) were considered. On a system level,
42
43
44
45

46
47 * Corresponding author: Tel.: +1-780-492-7797
48 *E-mail:* Amit.Kumar@ualberta.ca (Amit Kumar).
49
50
51
52
53
54
55
56

57
58
59 the industrial-scale processing of 2000 T d⁻¹ dry biomass is modeled for all four conversion
60
61 pathways. A “cradle-to-gate” process-based life cycle assessment (LCA) based on a global
62
63 warming potential (GWP) characterization factor is conducted to quantify the greenhouse gas
64
65 (GHG) emissions associated with the material, mass and energy requirements at each life cycle
66
67 stage along with a net energy ratio (NER) analysis. The system boundary includes microalgae
68
69 cultivation through to downstream processing into hydrogen and diluent. Of the thermochemical
70
71 conversion pathways considered in our study, supercritical water gasification shows the best GHG
72
73 emissions mitigation in the production of hydrogen (92.1-138.3 g CO_{2-eq} MJ⁻¹). With respect to
74
75 diluent production, hydrothermal liquefaction processing has environmental benefits and avoids
76
77 energy use and consequently GHG emissions associated with the feedstock drying required in
78
79 pyrolysis (10.2-45.65 g CO_{2-eq} MJ⁻¹). This research is unique due to its focus on cold climates like
80
81 northern Canada.
82
83
84

85 **Keywords:** Diluent; hydrogen; life cycle assessment; microalgae; biomass conversion; Canada
86
87

88 89 **1 Introduction**

90
91
92 Western Canada’s oil sands have been a subject of considerable interest because of declining
93
94 conventional oil reserves and rapidly growing energy market demand. Alberta’s oil sands have
95
96 been evaluated to hold 170.2 billion barrels of oil reserves, next in capacity to reserves found in
97
98 Saudi Arabia and Venezuela [1]. The oil sands extraction and petroleum production are expected
99
100 to increase to around 3.8 million barrels per day by 2022 [9]. Undoubtedly, fossil fuel combustion
101
102 has been directly linked to climate change [2]. Global warming due to rising greenhouse gas
103
104 (GHG) emissions from anthropogenic activities is an ever-growing concern both regionally and
105
106 globally [3-5]. Given that the oil and gas sector contributes significantly to Canada’s GHG
107
108
109
110
111
112

113
114
115 emissions, there are concerted efforts to reduce the carbon footprint of the sector. Improving the
116
117 energy efficiency of oil sands operations, minimizing flaring, venting and fugitive emissions,
118
119 implementing carbon capture and storage systems, and using alternative renewable energy sources
120
121 such as microalgae are a way forward [6].
122

123
124
125 The ability of microalgae to take up CO₂ using photosynthetic energy offers significant
126
127 potential in terms of developing an economic and sustainable renewable energy resource [7].
128
129 Microalgae have the acknowledged advantages of not competing with arable land for food
130
131 production, high yield potential, and the ability to develop high value co-products such as
132
133 nutraceuticals, lipids, proteins, carbohydrates, pigments, and vitamins [8]. Moreover, microalgae
134
135 can use municipal, agricultural, and industrial wastes as a source of key metabolic growth
136
137 nutrients.
138

139
140 Microalgae can be used as a renewable energy source and a chemical in oil sands' operations.
141
142 Under reservoir conditions, oil-bearing bitumen is highly viscous by nature and requires energy-
143
144 intensive recovery and extraction techniques. Large volumes of short-chain, petroleum-based light
145
146 hydrocarbons are used as a diluent to reduce the density and viscosity of the bitumen to make it
147
148 flowable through pipelines to upgrading and refinery facilities [9]. In oil sands industries, diluent
149
150 refers to naphthenic and paraffinic hydrocarbons used to reduce the viscosity and density of heavy
151
152 hydrocarbon molecules in bitumen [10]. Diluent, a diluting agent, is a chemical substance used to
153
154 aid viscous fluidity of heavy molecules through pipelines [11]. Mostly, diluents are known as
155
156 natural gas condensates, which are comprised of compounds with lighter fractions [12]. Given the
157
158 requirement for large amounts of diluent in transporting heavy oils, there is an interest in evaluating
159
160 thermochemical process conversion technologies that have the potential to transform algal biomass
161
162 to diluent [13-16]. The production of a liquid product, bio-diluent, through pyrolysis has been
163
164
165
166
167
168

169
170
171 investigated [15]. Extracting oil using bitumen via the Fischer-Tropsch method has been studied
172
173 [16]. Kumar et al. studied diluent production through thermochemical pathways for oil sands
174
175 applications [13]. Moreover, several thermochemical process conversion technologies that may
176
177 transform algae biomass to both diluent and hydrogen are being investigated. The key
178
179 thermochemical approaches, hydrothermal liquefaction (HTL) and pyrolysis, allow biomass
180
181 conversion to bio-crude in order to produce diluent [13, 17]. Both technologies have been proven
182
183 to be feasible for algal conversion and offer the advantage of converting both lipid and non-lipid
184
185 fractions of biomass into bio-oil [18]. The HTL pathway avoids the energy-intensive drying step
186
187 required for alternative processing [13], while pyrolysis requires a dry feedstock [19]. Though
188
189 pyrolysis has gained significant attention for processing woody biomass [19-22], some studies
190
191 have also focused on microalgae as a feedstock [23-25].
192
193

194
195 In Western Canada, hydrogen derived from a renewable source like algae could be used as an
196
197 alternative to fossil fuel-based hydrogen to upgrade bitumen into synthetic crude oil (SCO).
198
199 Hydrogen, a key component in many chemical reactions, is widely used throughout the petroleum
200
201 industry [26]. In 2005, some 3 million tonnes of hydrogen were produced and used to upgrade 527
202
203 thousand barrels of bitumen/day [27]. There is a projected increase in bitumen upgrading to over
204
205 2 million barrels/day by 2020, bringing with it an extraordinary increased demand for hydrogen
206
207 [27]. Currently, almost all hydrogen is produced from natural gas. Hydrogen could be produced
208
209 from algae biomass via thermochemical processing including supercritical water gasification
210
211 (SCWG) and thermal gasification (TG) [28, 29]. SCWG allows wet biomass to be converted to a
212
213 hydrogen-rich gas. It does not entail energy-intensive drying and is known to provide high gas
214
215 yields with low char/tar formation [30]. Moreover, the fuel produced is devoid of nitrogen,
216
217 permitting the use of the protein-rich microalgae [31]. Algal thermal gasification is regarded as a
218
219
220
221
222
223
224

225
226
227 promising pathway to produce clean hydrogen fuel and generate electricity [32-35] using several
228
229 gasification agents like steam, air, and CO₂ [32].
230
231

232 Commercial microalgal-based thermochemical energy conversion platforms encompass
233 the steps from feedstock production to end products. Open pond raceway (OPR) cultivation
234 systems are conventionally seen as the most economical way to autotrophically produce
235 microalgae feedstock in hot climates [36-40]. Other approaches to producing algae include
236 photobioreactor (PBR) systems, in which algae are cultivated under controlled
237 phototrophic/autotrophic conditions, and employing flat plates, plastic or glass tubular systems
238 [41], and biofilms [42]. In addition, fermenters take advantage of algae's unique ability to grow in
239 heterotrophic conditions in the absence of light and use carbon sources other than sunlight for the
240 energy used in growth [43]. Other algae cultivation systems use both autotrophic and heterotrophic
241 conditions (mixotrophic) to achieve their growth objectives [44].
242
243
244
245
246
247
248
249
250
251
252
253

254 Life cycle assessment (LCA) is a useful tool to evaluate the environmental impacts
255 associated with a product, process, or service [45, 46]. Several LCA studies have quantified the
256 environmental impacts of algae on energy systems and reported a wide range of outcomes [47-50].
257 The associated energy process conversion pathways implemented in these studies are varied, as
258 are their results due to differences in production technologies and assumptions. Significant
259 research efforts have thus far focused on conventional lipid-based extraction systems [51-58]; a
260 few studies consider thermochemical systems [18, 59-61]. Where thermochemical HTL processing
261 of algae has been researched and reported on quite extensively in published literature, pyrolysis,
262 another thermochemical technology, has received less attention [60]. Moreover, the segregation of
263 upstream and downstream methods in such studies limits the use of the results for commercial
264 applications. Hence, it is imperative to analyze thermochemical conversion methods in such a way
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280

281
282
283 that energy requirements and GHG emissions can be compared holistically over the life cycle.
284
285 Furthermore, the environmental impacts of various thermochemical pathways using microalgae as
286 a feedstock need to be evaluated and compared. Within this context, the paper aims to evaluate the
287 environmental sustainability of pathways producing diluents and hydrogen by applying an LCA
288 method to evaluate the associated global warming potential (GWP) together with a net energy ratio
289 (NER) analysis, by considering two microalgae cultivation systems and four thermochemical
290 process pathways.
291
292
293
294
295
296
297

298 299 **2 Method** 300

301
302 LCA, according to the ISO-14040/44 principles and framework, and guidelines, is developed
303 to evaluate energy and GHG emissions [45, 46]. LCA involves a method that identifies and
304 quantifies mass and energy balances to evaluate GWP by looking at system inputs and outputs at
305 each process stage to identify the associated environmental impacts, along with a NER analysis.
306
307
308
309
310

311 312 **2.1 Goal and scope definition** 313

314
315 The goal of the current LCA is to evaluate and compare OPR and PBR algae cultivation
316 scenarios producing at industrial scale (2,000 T d⁻¹ dry weight) and four thermochemical
317 conversion pathways leading to the production of diluent and hydrogen. For the diluent production
318 pathway, hydrothermal liquefaction and pyrolysis of the algae were considered. Hydrothermal
319 gasification and thermal gasification of the algae are the pathways leading to the production of
320 hydrogen. Each activity involved in these processes is energy intensive and has associated GHG
321 emissions. The LCA follows an “attributional” approach in which inputs and outputs and the
322 associated environmental impacts are attributed to the functional unit using normative allocation
323
324
325
326
327
328
329
330
331
332
333
334
335
336

337
338
339 rules. The different allocation methods, including by mass, energy content, and market value, are
340 described in the literature [64-66]. The energy-based allocation was chosen based on similar
341 studies [61, 67, 68]. GHG emissions are used as the environmental metrics to compare the
342 alternative pathways. The GHG emission characterization factors are based on the IPCC one
343 hundred-year time horizon global warming potential. The analysis includes energy and material
344 requirements for various sub-processes including cultivation, dewatering, and conversion systems
345 for all pathways studied. The LCA is set geographically in Fort Saskatchewan, Alberta, Canada.
346 The Fort Saskatchewan region is recognized for the energy-intensive industrial petrochemical
347 processing facilities associated with oil-sands activities (see Figure 1).
348
349

350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392

The analysis provides useful insights for decisions that may mitigate environmental burdens associated with oil sands activities and the potential for improving the economics of hydrogen and diluent production in Canada.

INSERT FIGURE 1

Figure 1: Map showing location of Fort Saskatchewan and general oil sands deposits

Figure 2 shows the main systems included in the assessment. The functional unit to which the input and output requirements are scaled up is 1 MJ of energy. The net energy ratio (NER) (part of the LCA) is determined as the ratio of output energy to input fossil-fuel energy. The current study, consistent with other studies of microalgae to biofuels processes, excludes the environmental impacts associated with algae cultivation ponds and photobioreactor system construction[69].

The engineering approach used to model the cultivation and downstream processing of algae biomass is shown in the system process flow diagram (Figure 2). The model computes material

393
394
395 and energy balances for each unit operation. The cultivation section was constructed in a
396
397 spreadsheet-based model with the downstream thermochemical conversion computed more
398
399 rigorously through a process model developed through Aspen Plus software [70]. Cultivation
400
401 yields were predicted based on experimental yield data found in the literature and through
402
403 consultation with industry experts[71], coupled with stoichiometric calculations. 20% of surplus
404
405 nutrients beyond the stoichiometric biomass compositional demands was assumed to ensure
406
407 maximum productivity [72].
408
409

410 **INSERT FIGURE 2**

411
412 **Figure 2:** System boundary of the thermochemical pathways considered for diluent and hydrogen
413
414 production
415

416 417 418 **2.2 Life cycle inventory assessment**

419 420 **2.2.1 Algal cultivation**

421
422
423 The life cycle inventory assessment was developed for all stages, from algae cultivation to
424
425 the thermochemical process that delivers 1 MJ of product. Algae cultivation was modeled for OPR
426
427 and PBR systems. Much of research to date for algae-to-energy systems has been conducted at the
428
429 bench scale [73]. Hence, due to the lack of empirical data quantification of environmental impacts
430
431 of these systems at a commercial scale, the results are viewed with skepticism. Furthermore,
432
433 studies are difficult to compare because of modeling difference between studies [74].
434
435

436
437 Microalgae is cultivated in an aqueous media. Nutrients such as carbon dioxide (CO₂),
438
439 nitrogen (N) and phosphate (P), sourced from local industries, as well as light and temperature are
440
441 required to support algae growth. Diammonium phosphate (DAP), a commercial fertilizer, is
442
443 considered the source for P, while ammonia (NH₃) is the source for nitrogen [72]. The inventory
444
445

449
450
451 calculations include the upstream GHG emissions associated with the production of these
452 fertilizers. GHG emissions from direct land use, water use in algae cultivation, dewatering via
453 settling, ultrafiltration, and centrifugation to a produced biomass with 20% solids are evaluated
454 [72]. GHG emissions from the use of equipment such as air compressors for sparging CO₂ into the
455 media, pumps and paddlewheels for circulation, and LED lighting in the PBR system to promote
456 growth are included. Table 1 provides a summary of parameters and input requirements considered
457 in the inventory assessment [75]. These results as well as those found in Table 2 are based on
458 experimental and literature values that are included in the first author's previously published work,
459 where data was normalized and evaluated with respect to both mass and energy balances [75, 76].
460 The input values for the cultivation stage are favorable given an efficient microalgae species and
461 highly controlled, indoor cultivation environment using LEDs to provide both lighting and heat.
462 Land and water requirements are based on productivity, site climatic conditions, and assumptions
463 related to cultivation operations. Water loss due to blowdown is related to the replacement of media
464 to prevent the buildup of ion concentrations in the media.
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481

482 **Table 1:** Data related to the production of 1 kg of algal biomass
483

484
485 **INSERT TABLE 1**
486

487
488 The OPR system was modeled based on values found in Olivares et al. [77] and
489 extrapolated from site-specific satellite climatic data using the predictive analytical model
490 developed by the authors [75]. The algae cultivation model developed to simulate the production
491 of dry biomass at 2,000 T d⁻¹ incorporates design features found in the literature that use site-
492 specific satellite meteorological data [75]. The satellite meteorological data set includes daily mean
493 ambient temperature and solar irradiance values for specific latitude and longitude addresses. The
494
495
496
497
498
499
500
501
502
503
504

505
506
507 data was used to calculate daily algae production volumes for the OPR system located at Fort
508 Saskatchewan. 80% of the OPR algae was harvested when cell densities rose to 0.5 gL^{-1} , at which
509 time pond algae density returned to 0.2 gL^{-1} [72].
510
511

512
513
514 The PBR system's input and output requirements are determined based on a unique
515 columnar photobioreactor design that provides a fully controlled algae growth environment [71].
516 CO_2 is sparged into the PBR, which allows light photons to penetrate deeper into the media and
517 the continuous mixing of media for nutrient exchange. Lighting is provided by flashing-tuned
518 LEDs that provide photons at wavelengths that optimize growth and minimize the amount of
519 energy that is required [78-80]. Under these optimized conditions, cultivation yields of $5 \text{ g L}^{-1}\text{d}^{-1}$
520 were considered based on the developed model [72], [76]. The values are consistent with those in
521 existing literature [81], [82].
522
523
524
525
526
527
528
529
530

531
532 Since PBR systems are enclosed, a negligible amount of water is lost through evaporation.
533 Apart from water loss from evaporation, blowdown, and harvesting, water and the remaining
534 nutrients are recycled into the cultivation system. CO_2 , N, and P were modeled to be provided at
535 20% above actual cultivation requirements [72]. Harvesting the PBR biomass is semi-continuous;
536 10% is removed for processing every 2.4 hours, thereby maintaining cell density at approximately
537 5 gL^{-1} [83].
538
539
540
541
542
543
544
545

546 Energy required for dewatering the algae feedstock after cultivation in both OPR and PBR
547 systems is assumed to be the same since the biomass is allowed to settle to similar densities prior
548 to additional dewatering activities; this assumption is based on literature values provided by Davis
549 et al. [84]. The algae biomass undergoes settling followed by hollow fiber membrane ultrafiltration
550
551
552
553
554
555
556
557
558
559
560

561
562
563 and is then centrifuged to concentrate the biomass to 200 gL⁻¹ [83] in preparation for downstream
564
565 thermochemical conversion, described in the second part of this study.
566
567

568 As seen in Table 2, key energy requirements from the technosphere (man-made biotic
569 resources [85]) are from system operations, i.e., the paddlewheel, sparging, dewatering pumps,
570 and LED lighting. In this study, the 2016 Alberta electricity generation mix emission intensity
571 factor of 0.83 kg CO₂e kWh⁻¹ was considered [86]. The large areas of land affected to cultivate
572 algae for 2000 Td⁻¹ dry biomass using OPR systems are included in the study. Transportation is
573 not part of the study's scope since the selected location for algae cultivation adjoins the refineries
574 that both produce commercial nutrients and use the biomass output of production. The focus in
575 this study is not on a specific species of algae to be cultivated, given that a number of strains,
576 among thousands [87], have been identified for their high growth yield and lipid content [88].
577
578
579
580
581
582
583
584
585
586
587

588 **Table 2.** OPR and PBR system assemblies with input/output operations
589

590
591 **INSERT TABLE 2**
592

593 The OPR system modeled to produce this biomass in Alberta would encompass an area of
594 some 82,000 ha (8.8 townships), whereas the modeled PBRs used to produce the same biomass
595 would require approximately 50 ha. Similarly, the OPR-modeled system would require 4.3 million
596 m³ of water, whereas the PBR system would only require 23.2 thousand m³. In both cases, given
597 that every T of biomass requires 1.8 T of CO₂ to produce, the production of 660,000 T biomass
598 annually would result in sequestering nearly 1.2 MT of CO₂ [89, 90]. While published algae
599 biomass yields vary tremendously, consistent with what published literature and industry believe
600 to be achievable productivities for both OPR and PBR systems [72, 76], the model uses the
601 following values: 0.1 gL⁻¹d⁻¹ for the OPR systems and 5 gL⁻¹d⁻¹ for the PBR systems. The
602 referenced PBR's high productivities are attributed to a proprietary isolated algae species and
603
604
605
606
607
608
609
610
611
612
613

617
618
619 highly controlled environmental parameters associated with the PBR design [83]. The mass and
620
621 energy balances of downstream processing for LCA calculations were estimated through the
622
623 development of the process model in Aspen Plus. This model is described in earlier publications
624
625 by the authors [13, 91]. The life cycle assessment was conducted based on a global warming
626
627 potential (GWP) characterization factor following steps outlined in 2006 IPCC Guidelines for
628
629 National Greenhouse Gas Inventories. The inventory values are translated to GHG emissions per
630
631 functional unit using the IPCC one-hundred-year time horizon emissions factor [46]. The outcomes
632
633 of the study are subject to a certain amount of uncertainty associated with the chosen theoretical
634
635 conditions, system boundary selection, data used, and modelling approach. A sensitivity analysis
636
637 was performed to estimate the effects of key input parameters on the outcome of the study for
638
639 better interpretation of the results.
640
641

642 643 2.2.2 *Process conversion* 644 645

646
647 The following thermochemical conversions pathways were considered for the algal biomass
648
649 feedstock: HTL, fast pyrolysis, supercritical water gasification, and thermal gasification. These
650
651 systems were modeled through Aspen Plus software. Figure 2 shows the basic unit operations
652
653 involved in each pathway followed by a brief discussion of each process. In this analysis, the
654
655 cultivation and conversion facilities are considered to be located near each other and thus the
656
657 effects of transportation are negligible. For conversion, the algae production facility is considered
658
659 to be 2000 dry tonnes/day based on the scale designed for large-scale biomass-based systems [14,
660
661 92].
662
663

664
665 **INSERT FIGURE 3**
666
667
668
669

673
674
675 **Figure 3:** Schematic of the thermochemical conversion pathway for diluent and hydrogen
676
677 production from biomass
678
679
680
681
682

683 **2.2.2.1 Fast pyrolysis**

684
685 Fast pyrolysis refers to the thermochemical conversion of biomass to bio-oil at high
686 temperatures in the absence of oxygen. The thermal decomposition process dries the biomass to
687 a moisture content of less than 10% to reduce water content in bio-oil produced [93]. Since the
688 algal biomass from the cultivation facility is 20 wt% dry biomass, it requires additional drying to
689 bring it down to 5-10 wt% [94] before it can be fed into the fast pyrolysis reactor. Other parameters
690 of importance in fast pyrolysis include temperature, pressure, particle size, and residence time.
691 After the drying process, the algal biomass is passed through a fluidized bed pyrolysis reactor at
692 520 °C at a particles size less than 2 mm [95]. Following this step, solid residues are removed by
693 cyclones, resulting in a bio-oil [91, 96, 97]. Products from the pyrolysis process were found to
694 have mass yields of 55.9%, 23%, and 21.1% for the bio-oil, gases and solid char, respectively. In
695 general, the oil product yield from fast pyrolysis is from 55 to 65 wt% [98, 99]. Bio-oil from the
696 fast pyrolysis is hydrotreated to produce diluent [100]. Table 3 shows the total energy requirement
697 per kg of diluent produced through fast pyrolysis. The primary energy source for drying microalgae
698 is natural gas, which acts as a critical energy burden during algal biomass pyrolysis, as also
699 reported previously [101]. Other energy inputs to the pyrolysis process are in the form of
700 electricity, used to run pumps and compressors [102].
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722

723 **Table 3:** Energy requirements for the pyrolysis of algae
724
725
726
727
728

729
730
731 **INSERT TABLE 3**
732

733 **2.2.2.2 Hydrothermal liquefaction**
734

735 HTL is a known thermochemical conversion process that converts biomass into bio-crude
736 using water as reactive medium[13]. The process disintegrates macromolecules into smaller
737 fractions and hydrotreats them to lower the amount of deoxygenated compounds. It produces
738 diluent at medium temperature and high reaction pressure and high water concentration, with bio-
739 crude being its intermediate product [13]. During the HTL process, biomass is pumped at 18 MPa
740 and the resulting stream is passed through heat exchangers, which increases its temperature to
741 350 °C. At this state, water is at slightly below the supercritical point, which allows for the
742 dissolution of biomass in the solution [103]. The incoming effluent goes through the HTL reactor,
743 wherein biomass molecules are converted into bio-crude. Products from the HTL process include
744 bio-crude, an aqueous phase, gases, and solids with yields by mass of 40.3%, 53.8%, 4.9%, and
745 1%, respectively; these are within the ranges reported by others [104-106]. The bio-crude
746 undergoes hydrotreating where it is deoxygenated to produce diluent [100]. For HTL, no additional
747 drying requirement exists and feedstock is available at 20% dry content at the inlet of the HTL
748 reactor. The inputs to the liquefaction process are natural gas to heat the reactor units and electricity
749 to run pumps and provide cooling, as reported in literature [18, 67, 102]. Table 4 shows the energy
750 requirements for diluent production through algal HTL process.
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769

770 **Table 4:** Energy requirements for the hydrothermal liquefaction of algae
771
772
773
774

775 **INSERT TABLE 4**
776
777
778
779
780
781
782
783
784

785
786
787 **2.2.2.3 *Supercritical water gasification***
788

789 Supercritical water gasification is the thermochemical conversion pathway that allows the
790 supercritical conditions of water to act as a reactant. This occurs with the initiation of bond
791 cleavage between biomass macromolecules through hydrolysis [107]. The reaction occurs at a
792 range of temperatures (300-600 °C) and high pressures (12-34 MPa) with biomass's initial
793 concentration in the range of 10-30 wt% [108]. The product obtained is syngas, which undergoes
794 purification into H₂ using Selexol and is then enriched into H₂ [91]. Table 5 shows the energy
795 requirement for different operations for the supercritical water gasification of algae.
796
797
798
799
800
801
802
803
804

805 **Table 5:** Energy requirements for the supercritical gasification of algae
806

807
808 **INSERT TABLE 5**
809

810
811
812 **2.2.2.4 *Thermal gasification***
813

814 The thermal gasification process converts biomass feedstock into gaseous products at high
815 temperature (up to 850 °C) and atmospheric pressure. Biomass usually enters the process at a 5-
816 10% moisture content. The algal biomass from the cultivation needs to be dried to reduce its
817 moisture content. Syngas is the output from thermal gasification and it should pass through H₂
818 treatment unit for purification [91]. Table 6 summarizes the energy requirement for different
819 operations for thermal water gasification of algae.
820
821
822
823
824
825
826
827

828 **Table 6:** Energy requirements for the thermal gasification of algae
829
830

831 **INSERT TABLE 6**
832

833
834 **3 Results and discussion**
835
836
837

841
842
843 This section presents and discusses the main findings of the study. First, the GHG emission
844 results for algal cultivation were identified by comparing unit operation environmental impact
845 results from OPR and PBR cultivation and dewatering processes. Then unit-process thermo-
846 chemical conversion results were compared. The aggregate results from these comparative
847 calculations are presented below.
848
849
850
851
852
853

854 **3.1 Algal cultivation**

855
856
857
858 The environmental impacts associated with algae cultivation in both OPR and PBR systems
859 are discussed in this section. Figure 4 provides a breakdown of the emissions associated with unit
860 operations for both OPR and PBR algae production systems. An OPR appears to have a relatively
861 better GHG emissions performance than a PBR. In both scenarios, electricity accounts for the
862 majority of the energy requirements associated with the algae cultivation processes, 70-76%,
863 followed by the fertilizer (23-30%). The contribution from North Saskatchewan River water use
864 is minimal, less than 1% in both cases. Given that 1.8 T of CO₂ is captured in the production of
865 algae biomass, the calculated net results for OPRs and PBRs are 1.0 and 0.9 T of CO₂ removed
866 from the atmosphere, respectively. Although the electricity use differs significantly between the
867 OPR and PBR systems, the outcomes are relatively close. In the case of OPR systems, the
868 paddlewheel and pumping systems used to move water through the vast pond systems come
869 relatively close to the relatively minor use of pumps in the PBR systems, but a greater amount of
870 energy is required to drive the artificial lighting systems. The results are higher than those reported
871 by Verma et al., 0.42 and 0.39 T of CO_{2eq} removed from the atmosphere for every T biomass
872 produced in a study using *Nannochloropsi sp* and *A. platensis* algae species [7].
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890

891 **INSERT FIGURE 4**

897
898
899 **Figure 4:** Algae biomass production – CO₂_{eq} emissions unit operation
900
901

902 Because of the commercial scale of the renewable energy operations modeled, it is useful to
903 compare CO₂ sequestration through algae cultivation with carbon sequestration in existing forests
904 in the region that could be considered for the production of renewable energy. Spruce and aspen
905 trees can be harvested every 80 years and they yield 180 m³ha⁻¹ or 2.25 m³yr⁻¹; 1 m³ of wood has
906 approximately 200 kg C [109]. This can be calculated as 0.165 kg CO₂ sequestered m⁻²yr⁻¹. From
907 Table 1, for our modeled OPR algae cultivation system, 0.804 kg CO₂ m⁻²yr⁻¹ is sequestered; this
908 is an approximate 5-fold increase in CO₂ sequestration. The PBR system can sequester 2083 kg
909 CO₂ m⁻²yr⁻¹ or an approximate 12,600-fold increase in CO₂ sequestration.
910
911
912
913
914
915
916
917
918
919

920 **3.2 Process conversion**
921

922 The GHG emissions for diluent production from algae biomass feedstock through HTL and
923 pyrolysis, as well as for hydrogen produced from SCWG and TG, are discussed in this section.
924 The GHG emissions in the HTL pathway contribute 29.6 g CO₂-eq MJ⁻¹, as shown in Figure 5. 60%
925 of GHG emissions in HTL are from the hydrothermal liquefaction unit, and the rest are from the
926 hydrotreating section of the HTL plant. This is mainly due to the high energy demand in the high
927 temperature and pressure reactor of the HTL plant. Diluent production from HTL has advantages
928 in that it can handle high moisture containing microalgae, thereby avoiding the energy use and
929 corresponding emissions of microalgal drying. The GHG emissions from fossil fuel-based
930 products are more than 67% (90.8 g CO₂-eq MJ⁻¹) higher than from HTL [110].
931
932
933
934
935
936
937
938
939
940
941
942

943 The algal-based pyrolysis pathway results in 81.1 gCO₂-eqMJ⁻¹ of diluent. In pyrolysis,
944 microalgae conversion incorporates two main processes, both of which are energy intensive:
945 microalgae drying and pyrolysis; both require heat for the reactor using natural gas. Together these
946
947
948
949

953
954
955 processes have a direct influence on environmental impacts and make up 64.7% of the GHG
956
957 emissions. The hydrotreating plant contributes 35.3%, which is more than HTL because of the
958
959 requirement for a two-step hydrotreating process in pyrolysis. If char, which is produced during
960
961 the pyrolysis process, is used instead of natural gas for heat supply from pyrolysis, the GHG
962
963 emissions are reduced to 51.3 gCO_{2-eq}MJ⁻¹ of diluent. HTL offers better environmental
964
965 performance than pyrolysis, mainly due to the requirement for dry biomass and excessive energy
966
967 demand in the pyrolysis reactor.
968
969
970

971 **INSERT FIGURE 5**

972
973
974 **Figure 5:** Breakdown of GHG emissions from HTL and pyrolysis in diluent production
975
976

977 For hydrogen production, the SCWG pathway has lower GHG emissions than TG, as Figure
978
979 6 shows. Hydrogen production in the SCWG pathway emits GHGs of 28.5 g CO_{2-eq} MJ⁻¹ of
980
981 hydrogen. SCWG uses high moisture containing biomass such as microalgae, thereby reducing the
982
983 energy and corresponding emissions from microalgal drying. Microalgae conversion using the TG
984
985 pathway has higher GHG emissions (173.8 gCO_{2-eq}MJ⁻¹) than the SCWG pathway as it involves
986
987 the energy intensive drying process. The use of hydrogen for drying in thermal gasification reduces
988
989 the GHG emissions to 133.2 gCO_{2-eq} MJ⁻¹.
990
991
992

993 **INSERT FIGURE 6**

994
995 **Figure 6:** Breakdown of GHG emissions for SCWG and TG for hydrogen production
996
997

998 **3.3 Global warming potential**

1000
1001 The state-of-the-art development of thermochemical technologies for microalgae to desired
1002
1003 products has prompted an evaluation of the technologies with respect to global warming potentials.
1004
1005
1006
1007
1008

1009
1010
1011 LCA allows us to compare various sub-processes in an entire process to understand and quantify
1012
1013 GHG emissions. The combined results for algal thermochemical conversion systems including
1014
1015 growth, cultivation, and conversion systems for diluent and hydrogen production are summarized
1016
1017 in Table 7. In general, the global warming potential values reported for algal-based fuel systems
1018
1019 range widely, from -75 to 534 g CO_{2-eq} MJ⁻¹ [18, 69]. In this study, a negative 5.9-11.5 g CO_{2-eq}
1020
1021 MJ⁻¹ of GHG emissions was estimated in the HTL process. HTL conversion of algae biomass to
1022
1023 diluent represents slightly less than half (43% PBR and 47% OPR) of the combined emissions.
1024
1025 Juneja et al. conducted a life cycle analysis of renewable diesel production from microalgae grown
1026
1027 on wastewater and estimated GHG emissions of -110 g CO_{2-eq} MJ⁻¹ of renewable diesel [104].
1028
1029 Bennion et al. conducted a life cycle analysis reporting GHG emissions for the conversion of
1030
1031 microalgae to renewable diesel via the HTL pathway of -11.4 g CO_{2-eq} MJ⁻¹ [102]. At a productivity
1032
1033 of 25 g (afdw) m⁻²d⁻¹ with a bio-crude yield of 38 % (afdw), a GWP of -44 g CO_{2-eq} MJ⁻¹ was
1034
1035 reported by Frank et al. [61], signifying a net negative GWP resulting from the carbon credit due
1036
1037 to CO₂ uptake during algal growth.
1038
1039

1040
1041
1042 Very few studies have evaluated microalgae as a biomass for pyrolysis. In our study, 10.2-
1043
1044 45.65 g CO_{2-eq} MJ⁻¹ of GHG emissions was estimated for the pyrolysis process. Pyrolysis accounts
1045
1046 for 68% (PBR) and 71% (OPR) of the combined emissions for conversion to diluent. With respect
1047
1048 to GWP, producing diluent through HTL offers significant benefits compared to pyrolysis as it
1049
1050 avoids the energy penalty and GHG emissions associated with drying. The requirement of dry
1051
1052 biomass together with energy demands in the pyrolysis reactor make it challenging to obtain an
1053
1054 environmentally favorable algal-based product. In addition, microalgae drying and reactor heating
1055
1056 have a direct influence on the environmental impact in pyrolysis. Bennion et al. studied the energy
1057
1058 requirements for the pyrolysis of microalgae and found GHG emissions from 166-210 g CO_{2-eq}
1059
1060

MJ⁻¹ [102]. Grierson et al. performed an environmental assessment of microalgal pyrolysis systems and reported GHG emissions of 290.24 g CO_{2-eq} MJ⁻¹ [60]. It is believed that the key factor influencing the outcome of life cycle analysis is the energy recovery in the form of a desired product [82]. Hence, any amelioration in process technologies ranging from algal productivity to conversion methods will reduce environmental impacts.

In this study, a negative 7.0-12.56 g CO_{2-eq} MJ⁻¹ of GHG emissions was estimated in the supercritical water gasification process leading to the production of hydrogen. The SCWG process represents 43% (PBR) and 47% (OPR) of the combined emissions, similar to the HTL pathway leading to diluent. Galera et al. conducted an LCA of hydrogen and electricity production via supercritical water reforming of glycerol and attributed 19.14 g CO_{2-eq} MJ⁻¹ (2.68 gCO_{2-eq} H₂ g⁻¹) production to sub-processes involving supercritical water reforming, including water-gas shift and pressure swing absorption (PSA) systems [111]. Gasafi et al. studied the environmental impacts of SCWG using sewage sludge at approximately 5 gCO_{2-eq} MJ⁻¹ (0.7 gCO_{2-eq} H₂ g⁻¹) [112].

There are few published LCA studies that have evaluated the environmental impacts associated with the thermal gasification (TG) of algae for the production of hydrogen. In the current study, GHG emissions in the algal thermal gasification pathway to produce hydrogen had a predicted range from 92.1-138.3 gCO_{2-eq} MJ⁻¹. TG conversion to hydrogen production make up 82% (PBR) and 84% (OPR) of the combined emissions. These high GHG emissions in the thermal gasification pathway are due to the drying step involved with high moisture containing algae.

Table 7. LCA of thermochemical technologies for diluent and hydrogen production (gCO_{2-eq} MJ⁻¹)

INSERT TABLE 7

3.4 *Net energy ratio*

Along with calculating GHG emissions in this study, we evaluated the thermochemical pathways for diluent and hydrogen production on the basis of net energy ratio (NER). The NER is a ratio of the net energy output to the total net energy input from a non-renewable energy source into the system. The NER is the relationship between energy produced and energy consumed. The NER is an indicator of energy effectiveness in a system. Hence, an NER greater than one is desirable.

In this study, an NER of 1.26 was obtained for large-scale hydrothermal liquefaction to produce diluent. This value is in accordance with others reported previously, which range from 1-1.23 [61, 102, 113-115]. The differences in NERs from HTL conversion pathways are due to differences in product yields, recovery, and heating values. The NER for pyrolysis was 0.59; this is in accordance with the values reported in the literature [102]. The more favorable HTL NER results are attributed to HTL not requiring the energy intensive drying step necessary for the pyrolysis pathway. This finding is supported by other studies [103], [116]. Further improvements in process efficiency would help increase diluent yield, thereby improving the NER of the HTL pathway.

For hydrogen production, an NER of 1.15 was obtained for the supercritical water gasification pathway. The NER for these processes depends on microalgae yield and energy input requirements, as they relate to cultivation and processing, respectively [117].

4 **Sensitivity analysis**

1177
1178
1179 Sensitivity analysis provides an appraisal of how changes to major input factors affect or
1180 influence results of a process. In this study, input factors of production were increased and
1181 decreased by 10% to understand the sensitivity of these changes in influencing life cycle GHG
1182 emissions. The choice to use a 10% variance was sufficient to clarify environmental impact
1183 differences between OPR and PBR technologies. (See Appendix Tables A1, A2)
1184
1185
1186
1187
1188
1189

1190
1191 Figure 7 provides the key GHG emissions associated with OPR systems. Apart from the
1192 fertilizer nutrient inputs, these factors all consume electricity. The greatest sensitivity, at 0.023 kg
1193 CO_{2-eq} kg⁻¹ biomass produced, is attributed to the electricity required to process (dewatering via
1194 centrifugation) a shift of 10% in the volume of media. This is followed by the associated pumping
1195 requirement (0.022 kg CO_{2-eq} kg⁻¹ biomass produced), the additional (reduction) media to be
1196 processed, which in a similar manner impacts the power used for the filtration of the media (0.0095
1197 kg CO_{2-eq} kg⁻¹ biomass produced), and the paddlewheels (0.002 kg CO_{2-eq} kg⁻¹ biomass produced)
1198 required to keep the media in motion. A 10% shift in the amount of NH₃ and DAP commercial
1199 fertilizer used in cultivation results in environmental impact changes of 0.019 kg CO_{2-eq} kg⁻¹
1200 biomass produced and 0.005 kg CO_{2-eq} kg⁻¹ biomass produced, respectively. Environmental
1201 impacts related to water use, lighting, chiller, and sparging have minimal impacts (cumulatively
1202 <0.001 kg CO_{2-eq} kg⁻¹ biomass produced).
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216

1217 **INSERT FIGURE 7**

1218
1219
1220 **Figure 7:** Key factor environmental impact sensitivity for OPR algae cultivation systems by kg
1221 CO_{2-eq} kg⁻¹ biomass produced
1222
1223
1224

1225
1226 Figure 8 shows the key environmental impacts associated with PBR systems. In this
1227 scenario, although environmental factors are primarily related to electrical energy use, the most
1228
1229
1230
1231
1232

1233
1234
1235 significant sensitivity is from the PBR lighting systems at close to 0.053 kg CO_{2-eq} kg⁻¹ biomass
1236
1237 produced for a 10% shift in the amount of energy required for this factor. Altering the amount of
1238
1239 fertilizer used by 10% would shift the environmental impact by the same amount as in the OPR
1240
1241 system, 0.019 kg CO_{2-eq} kg⁻¹ biomass produced for NH₃ and 0.005 kg CO_{2-eq} kg⁻¹ biomass produced
1242
1243 for DAP. Sparging impacts would increase (0.013 kg CO_{2-eq} kg⁻¹ biomass produced) because of
1244
1245 the higher pressures and volumes of air / CO₂ required for the respective technology's application.
1246
1247 However, since much lower quantities of media are processed with PBRs, impacts would be lower
1248
1249 than those experienced by OPR systems, 0.004 and 0.002 kg CO_{2-eq} kg⁻¹ biomass produced for
1250
1251 centrifugation and membrane filtration, respectively. Environmental impacts related to 10% shifts
1252
1253 in chilling, water use, and pumping are below 0.001 kg CO_{2-eq} kg⁻¹ biomass produced
1254
1255 cumulatively, and there is no requirement for the use of a paddlewheel.
1256
1257
1258

1259 **INSERT FIGURE 8**

1260
1261
1262 **Figure 8:** Key factor environmental impact sensitivity for PBR algae cultivation systems by kg
1263
1264 CO_{2-eq} kg⁻¹ biomass produced
1265
1266

1267 We note that where changes in key cultivation factors have measurable environmental
1268
1269 impacts, the factors with greatest sensitivity to change differ depending on the system (OPR or
1270
1271 PBR). In OPRs, centrifugation and pumping are the primary factors. In PBRs, the lighting system
1272
1273 will have slightly greater environmental impacts than the centrifugation and pumping associated
1274
1275 with the OPRs have.
1276
1277
1278

1279 **5 Improvement measures and comparison with other known systems**

1280
1281
1282
1283
1284
1285
1286
1287
1288

1289
1290
1291 Improved energy integration through optimized energy use for diluent and hydrogen
1292 production, the use of renewable electricity, and adopting efficient algal cultivation systems would
1293 considerably improve environmental performance metrics. Developing advanced catalysts in
1294 terms of selectivity and the ability to withstand high temperatures would improve the energetics
1295 and reduce the environmental impacts of the system [111]. For gasification systems, the gasifier
1296 could be optimized to produce more hydrogen and less methane. Power recovery methods from
1297 turbines and the use of heat exchangers to transfer waste heat from one operation to another would
1298 also save energy, thereby reducing environmental impacts. Using autothermal processes and
1299 combusting a portion of the produced gas for the heat required in the reactor would reduce heat
1300 losses during heat transfer, a method used in supercritical water oxidation [112]. More refined
1301 sensitivity analysis would help us understand process sensitivity to variations in operating
1302 parameters and identify opportunities for additional energy savings.
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317

1318 **6 Conclusion**

1319
1320

1321 In keeping with the objectives of our research project, we conducted a comparative LCA on
1322 Canadian microalgae feedstock cultivated in both open raceway pond and photobioreactor systems
1323 and subsequently processed via thermochemical conversion to end products (diluent and
1324 hydrogen) based on a commercial algae biomass scale of 2,000 T d⁻¹. Of the thermochemical
1325 conversion pathways considered in our study, the best performance in terms of GHG emissions
1326 for hydrogen production is via SCWG (92.1-138.3 g CO_{2-eq} MJ⁻¹) and an NER of 1.15, followed
1327 by TG. Similarly, for diluent production through HTL and pyrolysis, only HTL processing shows
1328 an environmental benefit (10.2-45.65 g CO_{2-eq} MJ⁻¹) and an NER of 1.26. This is because it can
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344

1345
1346
1347 use wet biomass feedstock, thereby avoiding energy use and the GHG emissions associated with
1348
1349 feedstock drying.
1350

1351
1352 These results will be useful for making better informed investment decisions related to these
1353
1354 processes.
1355

1356 1357 **7 Acknowledgements**

1358
1359
1360 The authors are grateful for the financial support from the Natural Sciences and Engineering
1361
1362 Research Council of Canada (NSERC), Alberta Innovates (AI), Emissions Reduction Alberta
1363
1364 (ERA), and Symbiotic EnviroTek Limited to carry out this research. Astrid Blodgett is thanked for
1365
1366 editing this paper.
1367
1368

1369 1370 **Declaration of authors' contributions**

1371
1372 Each author contributed as follows:
1373

1374
1375
1376 Stan Pankratz: conception and design of the study, acquisition, analysis and interpretation of
1377
1378 the algae biomass production data, drafting the article, final approval of the version to be
1379
1380 submitted.
1381

1382
1383 Mayank Kumar: conception and design of the downstream processing of algae biomass study,
1384
1385 acquisition, analysis and interpretation of the data, drafting the article, final approval of the
1386
1387 version to be submitted.
1388

1389
1390 Adetoyese Olajire Oyedun: administrative and technical support, critical revision of the design
1391
1392 of the study and the final article, final approval of the version submitted.
1393
1394

1401
1402
1403 Eskinder Gemechu: administrative and LCA technical support, critical revision of the design
1404 of the study and the final article, final approval of the version submitted.
1405
1406

1407
1408 Amit Kumar: conception and design of the study, technical and logistic support, critical
1409 revision of the article, final approval of the version submitted.
1410
1411

1412
1413 Stan Pankratz and Mayank Kumar take responsibility for the integrity of the work as a whole,
1414 from inception to finished article.
1415
1416
1417

1418 **Statement of Informed Consent**

1419

1420
1421 No conflicts, informed consent, human or animal rights applicable
1422
1423

1424 **References**

1425

- 1426
1427 [1] Facts and Stats - Energy in Alberta. <[https://open.alberta.ca/dataset/b3fd8657-f6ee-4883-afbc-1339e7b7f476/resource/856e78a2-4f4f-4557-9ef1-676648eb9c3d/download/2015-facts-
1428 stats-energy-alberta-quick-facts-2015-02.pdf](https://open.alberta.ca/dataset/b3fd8657-f6ee-4883-afbc-1339e7b7f476/resource/856e78a2-4f4f-4557-9ef1-676648eb9c3d/download/2015-facts-stats-energy-alberta-quick-facts-2015-02.pdf)>, 2013 (accessed May 14, 2019.).
1429
1430 [2] G. Spampinato, D.E. Massimo, C.M. Musarella, P. De Paola, A. Malerba, M. Musolino, Carbon
1431 sequestration by cork oak forests and raw material to built up post carbon city, Smart Innovation,
1432 Systems and Technologies, 2019, pp. 663-671.
1433
1434 [3] L. Bernstein, A. Lee, S. Crookshank, Carbon dioxide capture and storage: A status report,
1435 Climate Policy 6(2) (2006) 241-246.
1436
1437 [4] r.t. Watson, M.C. Zinyowera, R.H. Moss, Technologies, Policies and Measures for Mitigating
1438 Climate Change, Intergovernmental Panel on Climate Change, 1996.
1439
1440 [5] Anthropogenic and natural radiative forcing, Climate Change 2013 the Physical Science Basis:
1441 Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on
1442 Climate Change 2013, pp. 659-740.
1443
1444 [6] G.B. Parker, R.T. Dahowski, The elephant in the room: Dealing with carbon emissions from
1445 synthetic transportation fuels production?, Strategic Planning for Energy and the Environment
1446 28(1) (2008) 12-33.
1447
1448 [7] R. Verma, R. Kumar, L. Mehan, A. Srivastava, Modified conventional bioreactor for microalgae
1449 cultivation, Journal of Bioscience and Bioengineering 125(2) (2018) 224-230.
1450
1451 [8] S. Pankratz, A.O. Oyedun, X. Zhang, A. Kumar, Algae production platforms for Canada's
1452 northern climate, Renewable and Sustainable Energy Reviews 80 (2017) 109-120.
1453
1454 [9] N. Choquette-Levy, H.L. MacLean, J.A. Bergerson, Should Alberta upgrade oil sands bitumen?
1455 An integrated life cycle framework to evaluate energy systems investment tradeoffs, Energy
1456 policy 61 (2013) 78-87.

- 1457
1458
1459
1460 [10] F. Rao, Q. Liu, Froth treatment in Athabasca oil sands bitumen recovery process: A review, *Energy & Fuels* 27(12) (2013) 7199-7207.
- 1461
1462 [11] A. Miadonye, N. Doyle, A. Britten, N. Latour, V. Puttagunta, Modelling viscosity and mass
1463 fraction of bitumen-diluent mixtures, *Journal of Canadian Petroleum Technology* 40(07) (2001).
- 1464 [12] R.N. Tipman, Y.-C. Long, Solvent process for bitumen separation from oil sands froth, Google
1465 Patents, 1999.
- 1466 [13] M. Kumar, A.O. Oyedun, A. Kumar, Hydrothermal liquefaction of biomass for the production
1467 of diluents for bitumen transport, *Biofuels, Bioproducts and Biorefining* 11(5) (2017) 811-829.
- 1468 [14] E. Nogueira Junior, M. Kumar, S. Pankratz, A.O. Oyedun, A. Kumar, Development of life cycle
1469 water footprints for the production of fuels and chemicals from algae biomass, *Water Research*
1470 140 (2018) 311-322.
- 1471 [15] A.J. Pollard, D.S. Banasiak, C.J. Ellens, J.N. Brown, Methods, apparatus, and systems for
1472 incorporating bio-derived materials into oil sands processing, Google Patents, 2015.
- 1473 [16] D. Tessel, Systems and methods for using gas to liquids (gtl) technology, Google Patents,
1474 2015.
- 1475 [17] C. ELLENS, J. Brown, A. POLLARD, D. BANASIAK, Methods, apparatus, and systems for
1476 incorporating bio-derived materials into oil sands processing, Google Patents, 2012.
- 1477 [18] X. Liu, B. Saydah, P. Eranki, L.M. Colosi, B.G. Mitchell, J. Rhodes, A.F. Clarens, Pilot-scale data
1478 provide enhanced estimates of the life cycle energy and emissions profile of algae biofuels
1479 produced via hydrothermal liquefaction, *Bioresource technology* 148 (2013) 163-171.
- 1480 [19] D. Mohan, C.U. Pittman, P.H. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review,
1481 *Energy & fuels* 20(3) (2006) 848-889.
- 1482 [20] M. Corbetta, A. Frassoldati, H. Bennadji, K. Smith, M.J. Serapiglia, G. Gauthier, T. Melkior, E.
1483 Ranzi, E.M. Fisher, Pyrolysis of centimeter-scale woody biomass particles: Kinetic modeling and
1484 experimental validation, *Energy & Fuels* 28(6) (2014) 3884-3898.
- 1485 [21] S. Septien, S. Valin, C. Dupont, M. Peyrot, S. Salvador, Effect of particle size and temperature
1486 on woody biomass fast pyrolysis at high temperature (1000-1400 C), *Fuel* 97 (2012) 202-210.
- 1487 [22] J. Wannapeera, B. Fungtammasan, N. Worasuwanarak, Effects of temperature and holding
1488 time during torrefaction on the pyrolysis behaviors of woody biomass, *Journal of Analytical and*
1489 *Applied Pyrolysis* 92(1) (2011) 99-105.
- 1490 [23] X. Miao, Q. Wu, C. Yang, Fast pyrolysis of microalgae to produce renewable fuels, *Journal of*
1491 *analytical and applied pyrolysis* 71(2) (2004) 855-863.
- 1492 [24] L. Gao, J. Sun, W. Xu, G. Xiao, Catalytic pyrolysis of natural algae over Mg-Al layered double
1493 oxides/ZSM-5 (MgAl-LDO/ZSM-5) for producing bio-oil with low nitrogen content, *Bioresource*
1494 *technology* 225 (2017) 293-298.
- 1495 [25] A. Aboulkas, H. Hammani, M. El Achaby, E. Bilal, A. Barakat, Valorization of algal waste via
1496 pyrolysis in a fixed-bed reactor: Production and characterization of bio-oil and bio-char,
1497 *Bioresource technology* 243 (2017) 400-408.
- 1498 [26] R. Ramachandran, R.K. Menon, An overview of industrial uses of hydrogen, *International*
1499 *Journal of Hydrogen Energy* 23(7) (1998) 593-598.
- 1500 [27] S. Sarkar, A. Kumar, Biohydrogen production from forest and agricultural residues for
1501 upgrading of bitumen from oil sands, *Energy* 35(2) (2010) 582-591.
- 1502 [28] M. Kumar, A.O. Oyedun, A. Kumar, A review on the current status of various hydrothermal
1503 technologies on biomass feedstock, *Renewable and Sustainable Energy Reviews* (2017).
- 1504
1505
1506
1507
1508
1509
1510
1511
1512

- 1513
1514
1515
1516 [29] J.A. Onwudili, A.R. Lea-Langton, A.B. Ross, P.T. Williams, Catalytic hydrothermal gasification
1517 of algae for hydrogen production: composition of reaction products and potential for nutrient
1518 recycling, *Bioresource technology* 127 (2013) 72-80.
- 1519 [30] Q. Guan, C. Wei, P.E. Savage, Hydrothermal gasification of *Nannochloropsis* sp. with Ru/C,
1520 *Energy & Fuels* 26(7) (2012) 4575-4582.
- 1521 [31] J.A. Onwudili, A.R. Lea-Langton, A.B. Ross, P.T. Williams, Catalytic hydrothermal gasification
1522 of algae for hydrogen production: Composition of reaction products and potential for nutrient
1523 recycling, *Bioresource Technology* 127(Supplement C) (2013) 72-80.
- 1524 [32] G. Duman, M.A. Uddin, J. Yanik, Hydrogen production from algal biomass via steam
1525 gasification, *Bioresource Technology* 166(Supplement C) (2014) 24-30.
- 1526 [33] M. Kaewpanha, G. Guan, X. Hao, Z. Wang, Y. Kasai, K. Kusakabe, A. Abudula, Steam co-
1527 gasification of brown seaweed and land-based biomass, *Fuel Processing Technology*
1528 120(Supplement C) (2014) 106-112.
- 1529 [34] L. Sanchez-Silva, D. López-González, A.M. Garcia-Minguillan, J.L. Valverde, Pyrolysis,
1530 combustion and gasification characteristics of *Nannochloropsis gaditana* microalgae, *Bioresource*
1531 *Technology* 130(Supplement C) (2013) 321-331.
- 1532 [35] M.R. Díaz-Rey, M. Cortés-Reyes, C. Herrera, M.A. Larrubia, N. Amadeo, M. Laborde, L.J.
1533 Alemany, Hydrogen-rich gas production from algae-biomass by low temperature catalytic
1534 gasification, *Catalysis Today* 257(Part 2) (2015) 177-184.
- 1535 [36] R.M. Handler, C.E. Canter, T.N. Kalnes, F.S. Lupton, O. Kholiqov, D.R. Shonnard, P. Blowers,
1536 Evaluation of environmental impacts from microalgae cultivation in open-air raceway ponds:
1537 Analysis of the prior literature and investigation of wide variance in predicted impacts, *Algal*
1538 *Research* 1(1) (2012) 83-92.
- 1539 [37] M.H. Huesemann, J. Van Wagenen, T. Miller, A. Chavis, S. Hobbs, B. Crowe, A screening
1540 model to predict microalgae biomass growth in photobioreactors and raceway ponds,
1541 *Biotechnology and Bioengineering* 110(6) (2013) 1583-1594.
- 1542 [38] K. Kumar, S.K. Mishra, A. Shrivastav, M.S. Park, J.W. Yang, Recent trends in the mass
1543 cultivation of algae in raceway ponds, *Renewable and Sustainable Energy Reviews* 51 (2015) 875-
1544 885.
- 1545 [39] A. Demirbas, M.F. Demirbas, *Algae Energy: Algae as a New Source of Biodiesel*, *Green Energy*
1546 *and Technology*, 2010, p. 139.
- 1547 [40] E.C. Odjadjare, T. Mutanda, A.O. Olaniran, Potential biotechnological application of
1548 microalgae: a critical review, *Critical Reviews in Biotechnology* 37(1) (2017) 37-52.
- 1549 [41] G.B. Leite, A.E.M. Abdelaziz, P.C. Hallenbeck, Algal biofuels: Challenges and opportunities,
1550 *Bioresource Technology* 145 (2013) 134-141.
- 1551 [42] C.E. Sharp, S. Urschel, X. Dong, A.L. Brady, G.F. Slater, M. Strous, Robust, high-productivity
1552 phototrophic carbon capture at high pH and alkalinity using natural microbial communities,
1553 *Biotechnology for Biofuels* 10(1) (2017).
- 1554 [43] V. Klassen, O. Blifernez-Klassen, Y. Hoekzema, J.H. Mussnug, O. Kruse, A novel one-stage
1555 cultivation/fermentation strategy for improved biogas production with microalgal biomass,
1556 *Journal of Biotechnology* 215 (2015) 44-51.
- 1557 [44] M.C. Matsudo, T.F. Sousa, L.S. Pérez-Mora, R.P. Bezerra, S. Sato, J.C.M. Carvalho, Ethanol as
1558 complementary carbon source in *Scenedesmus obliquus* cultivation, *Journal of Chemical*
1559 *Technology and Biotechnology* 92(4) (2017) 781-786.
- 1560
1561
1562
1563
1564
1565
1566
1567
1568

- 1569
1570
1571 [45] I. ISO, 14040: Environmental management–life cycle assessment–principles and framework,
1572 London: British Standards Institution (2006).
1573 [46] I. Norm, 14044: 2006, Life cycle assessment: Requirement and guidelines, Environmental
1574 management (ISO) 2006b (2006).
1575 [47] A. Clarens, L. Colosi, Life Cycle Assessment of Algae-to-Energy Systems, in: J.W. Lee (Ed.),
1576 Advanced Biofuels and Bioproducts, Springer New York 2013, pp. 759-778.
1577 [48] A.F. Clarens, E.P. Resurreccion, M.A. White, L.M. Colosi, Response to comment on
1578 "environmental life cycle comparison of algae to other bioenergy feedstocks", Environmental
1579 Science and Technology 44(9) (2010) 3643.
1580 [49] O. Jorquera, A. Kiperstok, E.A. Sales, M. Embiruçu, M.L. Ghirardi, Comparative energy life-
1581 cycle analyses of microalgal biomass production in open ponds and photobioreactors,
1582 Bioresource Technology 101(4) (2010) 1406-1413.
1583 [50] K. Sander, G.S. Murthy, Life cycle analysis of algae biodiesel, International Journal of Life
1584 Cycle Assessment 15(7) (2010) 704-714.
1585 [51] L. Batan, J. Quinn, B. Willson, T. Bradley, Net energy and greenhouse gas emission evaluation
1586 of biodiesel derived from microalgae, Environmental science & technology 44(20) (2010) 7975-
1587 7980.
1588 [52] L.B. Brentner, M.J. Eckelman, J.B. Zimmerman, Combinatorial life cycle assessment to inform
1589 process design of industrial production of algal biodiesel, Environmental science & technology
1590 45(16) (2011) 7060-7067.
1591 [53] P.K. Campbell, T. Beer, D. Batten, Life cycle assessment of biodiesel production from
1592 microalgae in ponds, Bioresource technology 102(1) (2011) 50-56.
1593 [54] H. Passell, H. Dhaliwal, M. Reno, B. Wu, A.B. Amotz, E. Ivry, M. Gay, T. Czartoski, L. Laurin, N.
1594 Ayer, Algae biodiesel life cycle assessment using current commercial data, Journal of
1595 environmental management 129 (2013) 103-111.
1596 [55] T. Shirvani, X. Yan, O.R. Inderwildi, P.P. Edwards, D.A. King, Life cycle energy and greenhouse
1597 gas analysis for algae-derived biodiesel, Energy & Environmental Science 4(10) (2011) 3773-3778.
1598 [56] V. Vasudevan, R.W. Stratton, M.N. Pearlson, G.R. Jersey, A.G. Beyene, J.C. Weissman, M.
1599 Rubino, J.I. Hileman, Environmental performance of algal biofuel technology options,
1600 Environmental science & technology 46(4) (2012) 2451-2459.
1601 [57] P. Azadi, G. Brownbridge, S. Mosbach, A. Smallbone, A. Bhave, O. Inderwildi, M. Kraft, The
1602 carbon footprint and non-renewable energy demand of algae-derived biodiesel, Applied Energy
1603 113 (2014) 1632-1644.
1604 [58] R. Baliga, S.E. Powers, Sustainable algae biodiesel production in cold climates, International
1605 Journal of Chemical Engineering 2010 (2010).
1606 [59] K. de Boer, N.R. Moheimani, M.A. Borowitzka, P.A. Bahri, Extraction and conversion
1607 pathways for microalgae to biodiesel: a review focused on energy consumption, Journal of
1608 Applied Phycology 24(6) (2012) 1681-1698.
1609 [60] S. Grierson, V. Strezov, J. Bengtsson, Life cycle assessment of a microalgae biomass
1610 cultivation, bio-oil extraction and pyrolysis processing regime, Algal Research 2(3) (2013) 299-
1611 311.
1612 [61] E.D. Frank, A. Elgowainy, J. Han, Z. Wang, Life cycle comparison of hydrothermal liquefaction
1613 and lipid extraction pathways to renewable diesel from algae, Mitigation and Adaptation
1614 Strategies for Global Change 18(1) (2013) 137-158.
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624

- 1625
1626
1627
1628 [62] I.S.O. (ISO), ISO 14040:2006(en) Environmental management - Life cycle assessment -
1629 Principles and framework, 2016.
1630 [63] M.C.-D. David J. Murphy, Devin Moeller, Comparing Apples to Apples: Why the Net Energy
1631 Analysis Community Needs to Adopt the Life-Cycle Analysis Framework, *energies* 9 (2016) 15.
1632 [64] M. Wang, H. Lee, J. Molburg, Allocation of energy use in petroleum refineries to petroleum
1633 products, *The International Journal of Life Cycle Assessment* 9(1) (2004) 34-44.
1634 [65] H. Khoo, C. Koh, M. Shaik, P. Sharratt, Bioenergy co-products derived from microalgae
1635 biomass via thermochemical conversion–life cycle energy balances and CO2 emissions,
1636 *Bioresource technology* 143 (2013) 298-307.
1637 [66] D.L. Sills, V. Paramita, M.J. Franke, M.C. Johnson, T.M. Akabas, C.H. Greene, J.W. Tester,
1638 Quantitative uncertainty analysis of life cycle assessment for algal biofuel production,
1639 *Environmental science & technology* 47(2) (2012) 687-694.
1640 [67] E.B. Connelly, L.M. Colosi, A.F. Clarens, J.H. Lambert, Life cycle assessment of biofuels from
1641 algae hydrothermal liquefaction: the upstream and downstream factors affecting regulatory
1642 compliance, *Energy & Fuels* 29(3) (2015) 1653-1661.
1643 [68] I.J. Tews, Y. Zhu, C. Drennan, D.C. Elliott, L.J. Snowden-Swan, K. Onarheim, Y. Solantausta, D.
1644 Beckman, Biomass Direct Liquefaction Options. TechnoEconomic and Life Cycle Assessment,
1645 Pacific Northwest National Lab.(PNNL), Richland, WA (United States), 2014.
1646 [69] J.C. Quinn, R. Davis, The potentials and challenges of algae based biofuels: A review of the
1647 techno-economic, life cycle, and resource assessment modeling, *Bioresource Technology* 184
1648 (2015) 444-452.
1649 [70] AspenTech, Aspen Plus V8.8 [Online]. Available at:
1650 <<http://www.aspentech.com/products/Aspen-Plus/V88/>>, (accessed May 3, 2018.).
1651 [71] B. Mroz, Hy-Tek Bio. LLC. <<http://www.hytekbio.com/home.html>>, 2016 (accessed February
1652 20, 2017.).
1653 [72] R. Davis, J. Markham, C. Kinchin, N. Grundl, E.C.D. Tan, D. Humbird, Process design and
1654 economics for the production of algal biomass: algal biomass production in open pond systems
1655 and processing through dewatering for downstream conversion, in: [NREL] National Renewable
1656 Energy Lab. Golden CO (United States) (Ed.) USDOE Office of Energy Efficiency and Renewable
1657 Energy (EERE), Bioenergy Technologies Office (EE-3B), United States, 2016, pp. 1-128.
1658 [73] X. Miao, Q. Wu, Biodiesel production from heterotrophic microalgal oil, *Bioresource*
1659 *Technology* 97(6) (2006) 841-846.
1660 [74] A. Clarens, L. Colosi, Life cycle assessment of algae-to-energy systems, *Advanced Biofuels*
1661 *and Bioproducts* 2012, pp. 759-778.
1662 [75] S. Pankratz, A.O. Oyedun, A. Kumar, Novel satellite based analytical model to predict
1663 microalgae yields in open pond raceway systems and applied to Canadian sites, *Algae Research*
1664 39(101431) (2019) 1-11.
1665 [76] B. Mroz, Hy-Tek Bio. LLC, in: Personal Communication Feb. 20 (Ed.) 2017.
1666 [77] J.A. Olivares, National Alliance for Advanced Biofuels and Bioproducts (NAABB)- Synopsys,
1667 in: E.E.a.R.E.C.-E. U.S. Department of Energy, Office of Biomass Programs (Bioenergy
1668 Technologies Office, BETO) (Ed.) National Alliance for Advanced Biofuels and Bioproducts
1669 (NAABB), 2014, pp. 1-28.
1670 [78] I. Martín-Girela, M.D. Curt, J. Fernández, Flashing light effects on CO2 absorption by
1671 microalgae grown on a biofilm photobioreactor, *Algal Research* 25 (2017) 421-430.
1672
1673
1674
1675
1676
1677
1678
1679
1680

- 1681
1682
1683
1684 [79] S. Abu-Ghosh, D. Fixler, Z. Dubinsky, D. Iluz, Flashing light in microalgae biotechnology, *Bioresource Technology* 203 (2016) 357-363.
1685
1686 [80] A.A. Lunka, D.J. Bayless, Effects of flashing light-emitting diodes on algal biomass
1687 productivity, *Journal of Applied Phycology* 25(6) (2013) 1679-1685.
1688 [81] A.C. Apel, C.E. Pfaffinger, N. Basedahl, N. Mittwollen, J. Göbel, J. Sauter, T. Brück, D. Weuster-
1689 Botz, Open thin-layer cascade reactors for saline microalgae production evaluated in a physically
1690 simulated Mediterranean summer climate, *Algal Research* 25 (2017) 381-390.
1691 [82] T.M. Mata, A.A. Martins, N.S. Caetano, Microalgae for biodiesel production and other
1692 applications: A review, *Renewable and Sustainable Energy Reviews* 14(1) (2010) 217-232.
1693 [83] S. Pankratz, A.O. Oyedun, A. Kumar, Development of cost models of algae production in cold
1694 climate using different production systems, *Biofuels, Bioproducts and Biorefining* (Early view
1695 publication May 02, 2019) (2019) 15.
1696 [84] R. Davis, C. Kinchin, J. Markham, E. Tan, L. Laurens, D. Sexton, D. Knorr, P. Schoen, J. Lukas,
1697 Process Design and Economics for the Conversion of Algal Biomass to Biofuels: Algal Biomass
1698 Fractionation to Lipid- and Carbohydrate-Derived Fuel Products, 2014, p. Medium: ED; Size: 110
1699 pp.
1700 [85] E. Crenna, S. Sozzo, S. Sala, Natural biotic resources in LCA: Towards an impact assessment
1701 model for sustainable supply chain management, *Journal of Cleaner Production* 172 (2018) 3669-
1702 3684.
1703 [86] M. Davis, M. Ahiduzzaman, A. Kumar, How will Canada's greenhouse gas emissions change
1704 by 2050? A disaggregated analysis of past and future greenhouse gas emissions using bottom-up
1705 energy modelling and Sankey diagrams, *Applied Energy* 220 (2018) 754-786.
1706 [87] A. Kumar, S. Ergas, X. Yuan, A. Sahu, Q. Zhang, J. Dewulf, F.X. Malcata, H. van Langenhove,
1707 Enhanced CO₂ fixation and biofuel production via microalgae: Recent developments and future
1708 directions, *Trends Biotechnol.* 28(7) (2010) 371-380.
1709 [88] Y. Xu, W.J. Boeing, Modeling maximum lipid productivity of microalgae: Review and next
1710 step, *Renewable and Sustainable Energy Reviews* 32 (2014) 29-39.
1711 [89] Y. Chisti, Biodiesel from microalgae, *Biotechnology Advances* 25(3) (2007) 294-306.
1712 [90] M.E. Montingelli, S. Tedesco, A.G. Olabi, Biogas production from algal biomass: A review,
1713 *Renewable and Sustainable Energy Reviews* 43 (2015) 961-972.
1714 [91] M. Kumar, A.O. Oyedun, A. Kumar, A comparative analysis of hydrogen production from the
1715 thermochemical conversion of algal biomass, *International Journal of Hydrogen Energy* 44(21)
1716 (2019) 10384-10397.
1717 [92] G. Berndes, Bioenergy and water—the implications of large-scale bioenergy production for
1718 water use and supply, *Global environmental change* 12(4) (2002) 253-271.
1719 [93] M.M. Wright, D.E. Daugaard, J.A. Satrio, R.C. Brown, Techno-economic analysis of biomass
1720 fast pyrolysis to transportation fuels, *Fuel* 89 (2010) S2-S10.
1721 [94] A. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, *Organic*
1722 *geochemistry* 30(12) (1999) 1479-1493.
1723 [95] S.B. Jones, C. Valkenburt, C.W. Walton, D.C. Elliott, J.E. Holladay, D.J. Stevens, C. Kinchin, S.
1724 Czernik, Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and
1725 hydrocracking: a design case, Pacific Northwest National Lab.(PNNL), Richland, WA (United
1726 States), 2009.
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736

- 1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
- [96] R.E. Davis, D.B. Fishman, E.D. Frank, M.C. Johnson, S.B. Jones, C.M. Kinchin, R.L. Skaggs, E.R. Venteris, M.S. Wigmosta, Integrated evaluation of cost, emissions, and resource potential for algal biofuels at the national scale, *Environmental science & technology* 48(10) (2014) 6035-42.
- [97] M. Ringer, V. Putsche, J. Scahill, Large-scale pyrolysis oil production: a technology assessment and economic analysis, National Renewable Energy Laboratory report. <<https://www.nrel.gov/docs/fy07osti/37779.pdf>>, 2006 (accessed May 14, 2019.).
- [98] X. Wang, L. Sheng, X. Yang, Pyrolysis characteristics and pathways of protein, lipid and carbohydrate isolated from microalgae *Nannochloropsis* sp, *Bioresource technology* 229 (2017) 119-125.
- [99] S.B. Jones, P.A. Meyer, L.J. Snowden-Swan, A.B. Padmaperuma, E. Tan, A. Dutta, J. Jacobson, K. Cafferty, Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: fast pyrolysis and hydrotreating bio-oil pathway, Pacific Northwest National Lab.(PNNL), Richland, WA (United States), 2013.
- [100] M. Kumar, A.O. Oyedun, A. Kumar, A Comparative Techno-Economic Analysis of Algal Thermochemical Conversion Technologies for Diluent Production, *Energy Technology* (2019).
- [101] G.G. Zaines, V. Khanna, Microalgal biomass production pathways: evaluation of life cycle environmental impacts, *Biotechnology for biofuels* 6(1) (2013) 88.
- [102] E.P. Bennion, D.M. Ginosar, J. Moses, F. Agblevor, J.C. Quinn, Lifecycle assessment of microalgae to biofuel: Comparison of thermochemical processing pathways, *Applied Energy* 154 (2015) 1062-1071.
- [103] D.R. Vardon, B.K. Sharma, G.V. Blazina, K. Rajagopalan, T.J. Strathmann, Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis, *Bioresource Technology* 109 (2012) 178-187.
- [104] A. Juneja, G.S. Murthy, Evaluating the potential of renewable diesel production from algae cultured on wastewater: techno-economic analysis and life cycle assessment, *AIMS Energy* 5(2) (2017) 239-257.
- [105] T.M. Brown, P. Duan, P.E. Savage, Hydrothermal liquefaction and gasification of *Nannochloropsis* sp, *Energy & Fuels* 24(6) (2010) 3639-3646.
- [106] J.L. Faeth, P.J. Valdez, P.E. Savage, Fast hydrothermal liquefaction of *Nannochloropsis* sp. to produce biocrude, *Energy & Fuels* 27(3) (2013) 1391-1398.
- [107] A. Kruse, Hydrothermal biomass gasification, *The Journal of Supercritical Fluids* 47(3) (2009) 391-399.
- [108] M.H. Waldner, F. Vogel, Renewable production of methane from woody biomass by catalytic hydrothermal gasification, *Industrial & engineering chemistry research* 44(13) (2005) 4543-4551.
- [109] G.C. Van Kooten, G. Hauer, Global climate change: Canadian policy and the role of terrestrial ecosystems, *Canadian Public Policy* 27(3) (2001) 267-278.
- [110] A. Wong, H. Zhang, A. Kumar, Life cycle assessment of renewable diesel production from lignocellulosic biomass, *The International Journal of Life Cycle Assessment* 21(10) (2016) 1404-1424.

- 1793
1794
1795 [111] S. Galera, F.J. Gutiérrez Ortiz, Life cycle assessment of hydrogen and power production by
1796 supercritical water reforming of glycerol, *Energy Conversion and Management* 96 (2015) 637-
1797 645.
1798
1799 [112] E. Gasafi, L. Meyer, L. Schebek, Using Life-Cycle Assessment in Process Design, *Journal of*
1800 *industrial ecology* 7(3-4) (2003) 75-91.
1801 [113] J. Barlow, *Engineering Ssystem Modeling for Sustainability Assessment*, Colorado State
1802 University, Fort Collins, Colorado, 2016.
1803 [114] E.P. Bennion, *Lifecycle Assessment of Microalgae to Biofuel: Thermochemical Processing*
1804 *through Hydrothermal Liquefaction or Pyrolysis*, Utah State University, 2014.
1805 [115] H.M. Summers, R.N. Ledbetter, A.T. McCurdy, M.R. Morgan, L.C. Seefeldt, U. Jena, S. Kent
1806 Hoekman, J.C. Quinn, Techno-economic feasibility and life cycle assessment of dairy effluent to
1807 renewable diesel via hydrothermal liquefaction, *Bioresource Technology* 196 (2015) 431-440.
1808 [116] K.F. Tzanetis, J.A. Posada, A. Ramirez, Analysis of biomass hydrothermal liquefaction and
1809 biocrude-oil upgrading for renewable jet fuel production: The impact of reaction conditions on
1810 production costs and GHG emissions performance, *Renewable Energy* 113 (2017) 1388-1398.
1811 [117] M. Brandenberger, J. Matzenberger, F. Vogel, C. Ludwig, Producing synthetic natural gas
1812 from microalgae via supercritical water gasification: A techno-economic sensitivity analysis,
1813 *biomass and bioenergy* 51 (2013) 26-34.
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848

FIGURES



Figure 1. Map showing location of Fort Saskatchewan and general oil sands deposits

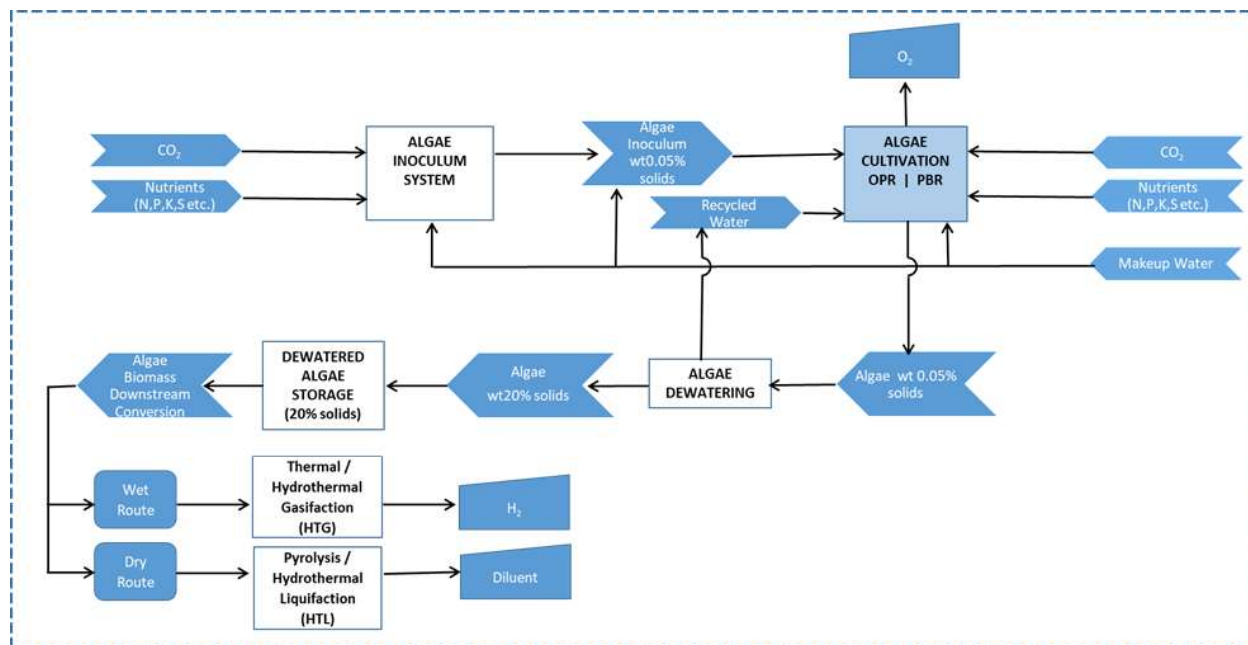


Figure 2: System boundary of the thermochemical pathways considered for diluent (hydrothermal liquefaction [HTL] and pyrolysis) and hydrogen production (hydrothermal gasification [HTG] and thermal gasification [TG]) from microalgae produced via open pond raceway (OPR) and photobioreactor (PBR) systems.

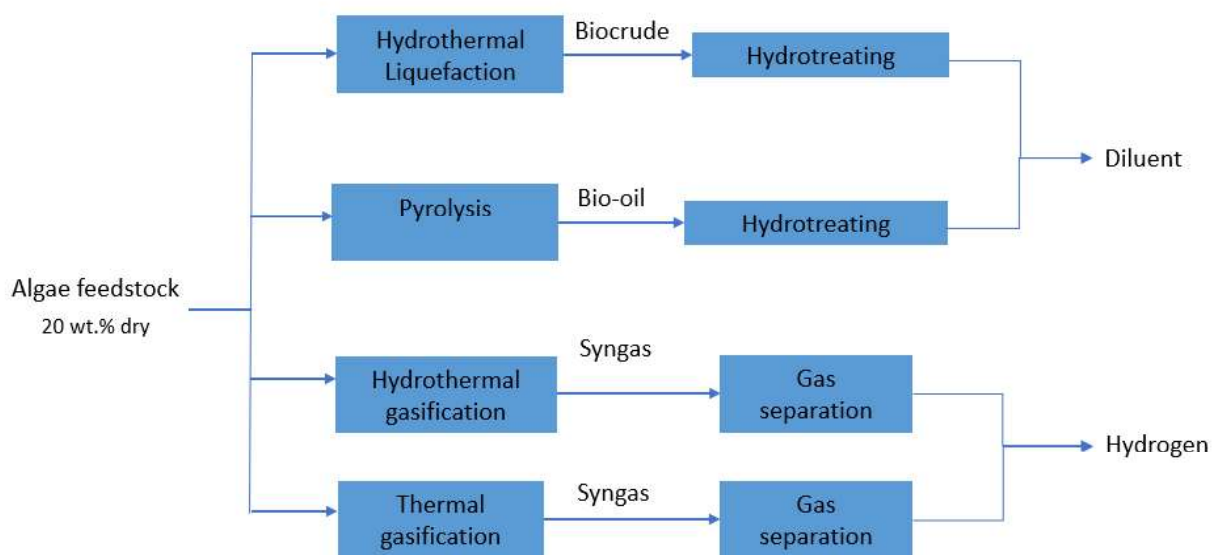


Figure 3: Schematic of the thermochemical conversion pathway for diluent and hydrogen production from biomass

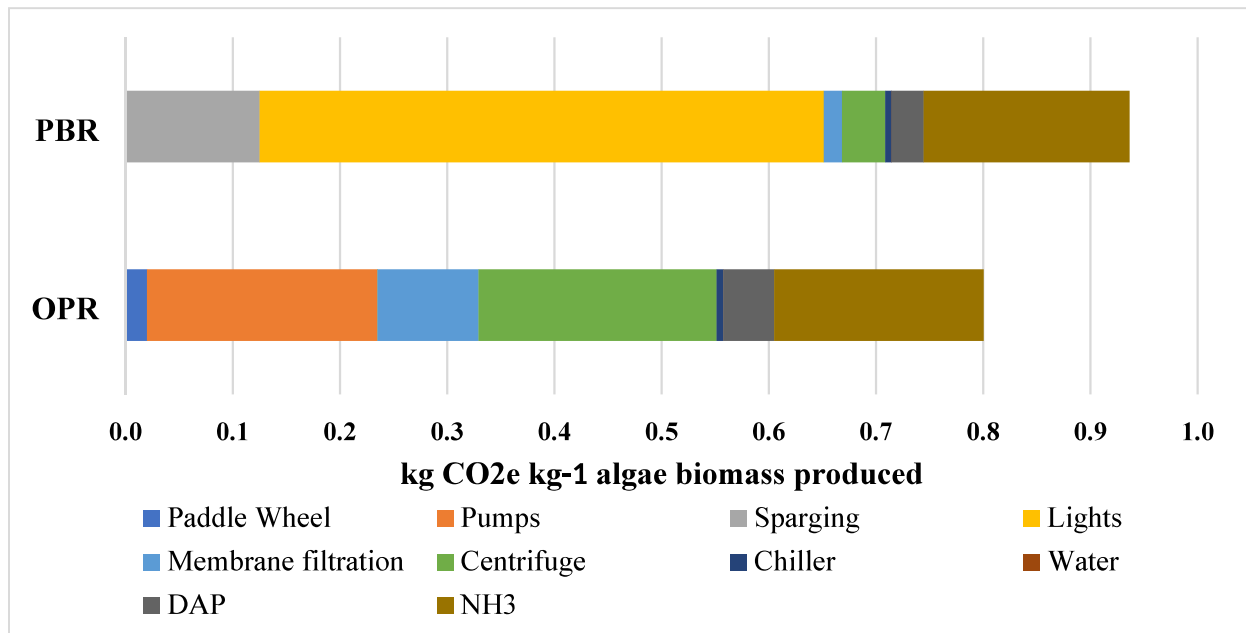


Figure 4. Algae biomass production – CO_{2eq} emissions unit operation for open pond raceway (OPR) and photobioreactor (PBR) (DAP - diammonium phosphate; NH₃ – ammonia)

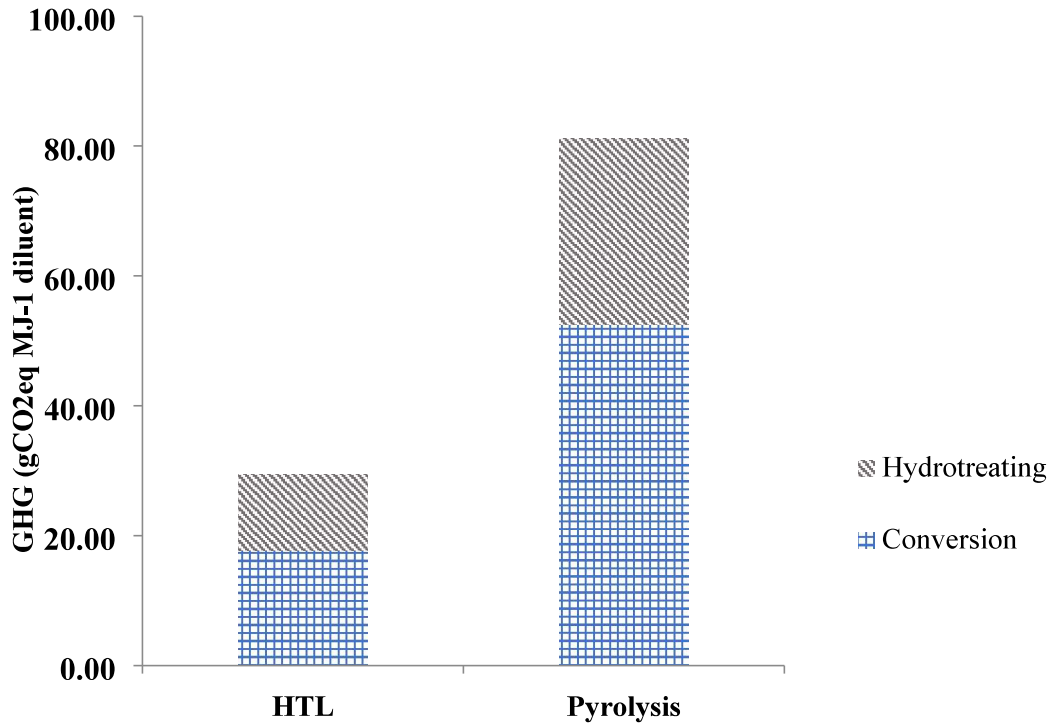


Figure 5. Breakdown of greenhouse gas (GHG) emissions for hydrothermal liquefaction (HTL) and pyrolysis for diluent production

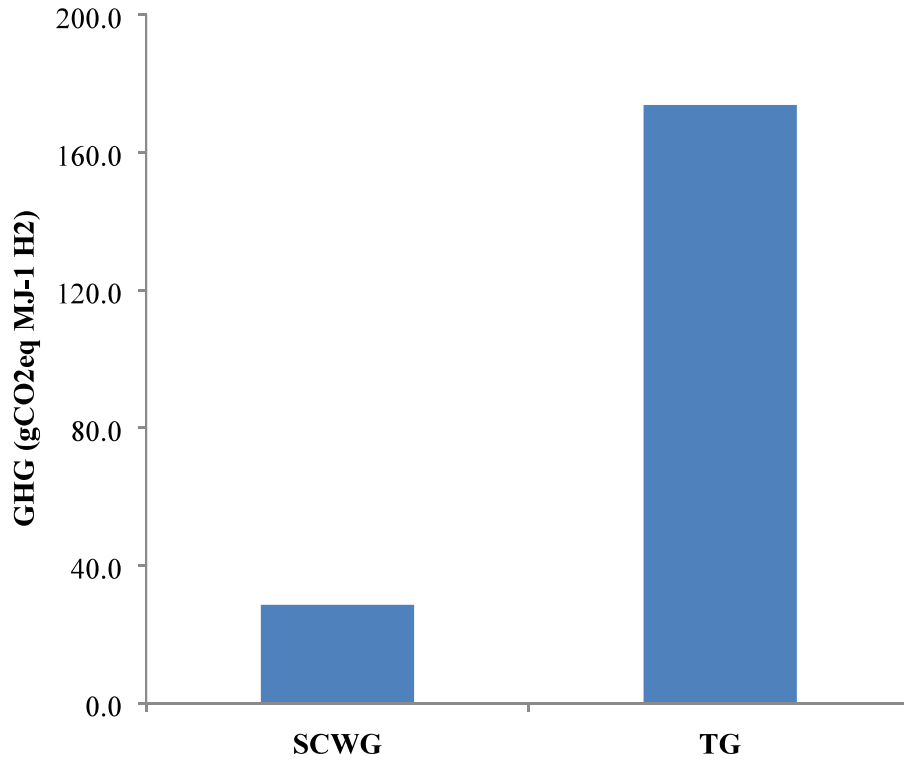


Figure 6. Breakdown of greenhouse gas (GHG) emissions for supercritical water gasification (SCWG) and thermal gasification (TG) for hydrogen production

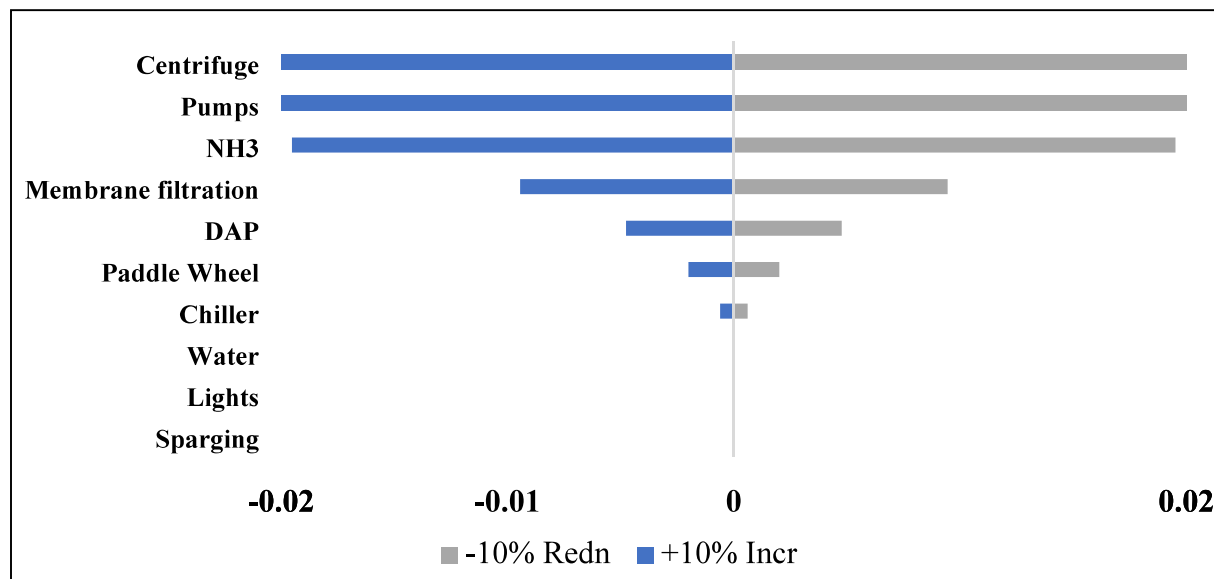


Figure 7. Key factor environmental impact sensitivity for open pond raceway (OPR) algae cultivation systems by kg CO₂-eq kg⁻¹ biomass produced (-10% Redn – 10% reduction in the values of the parameters, +10% Incr – 10% increase in the values of the parameters, DAP - diammonium phosphate, NH₃ – ammonia).

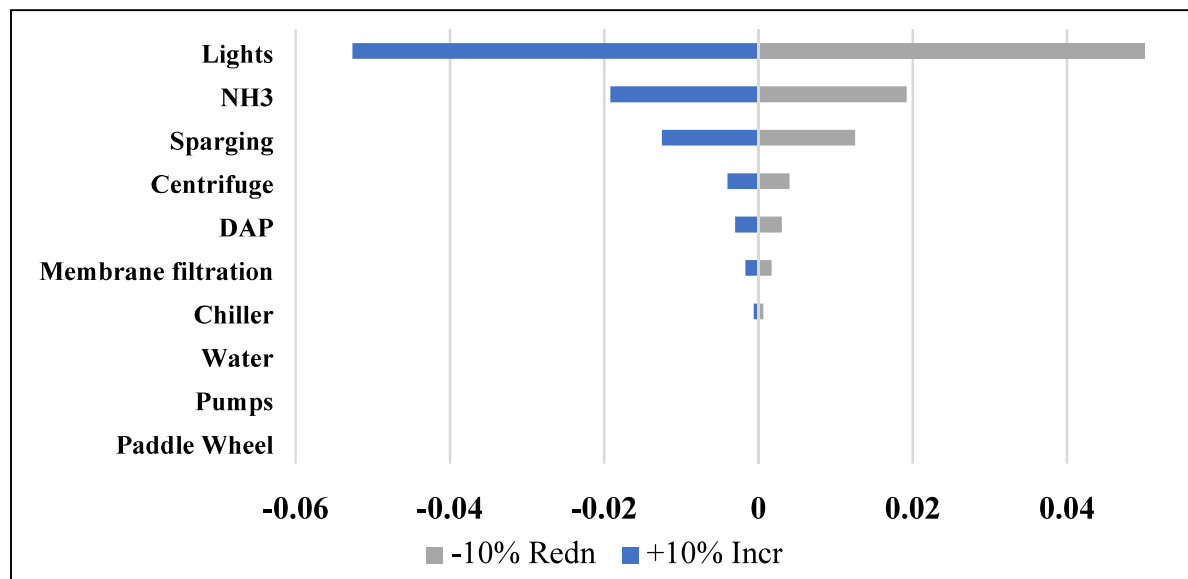


Figure 8. Key factor environmental impact sensitivity for photobioreactor (PBR) algae cultivation systems by kg CO₂-eq kg⁻¹ biomass produced (-10% Redn – 10% reduction in the values of the parameters, +10% Incr – 10% increase in the values of the parameters, DAP - diammonium phosphate, NH₃ – ammonia).

TABLES

Table 1: Data related to the production of 1 kg of algal biomass with open pond raceway (OPR) and photobioreactor (PBR) systems

Parameters	OPR	PBR	Units	References and notes
Productivity	5.8	1825	g L ⁻¹ yr ⁻¹	• OPR system – modeled growth at Fort Saskatchewan, harvest at 5 g L ⁻¹ for 203 growing days [70]
				• PBR system – modeled growth at Fort Saskatchewan, harvest at 5 g L ⁻¹ for 330 growing days [79]
Land	1.24	0.00048	m ² kg ⁻¹ yr ⁻¹	• OPR system – modeled growth at Fort Saskatchewan, harvest at 5 g L ⁻¹ for 203 growing days [70]
				• PBR system – modeled growth at Fort Saskatchewan, harvest at 5 g L ⁻¹ for 330 growing days [79]
Water	1.06	0.023	m ³ or T	• OPR system – modeled growth at Fort Saskatchewan, harvest at 5 g L ⁻¹ for 203 growing days [70]
				• PBR system – modeled growth at Fort Saskatchewan, harvest at 5 g L ⁻¹ for 330 growing days [79]
Cultivation period	203	330	d yr ⁻¹	• OPR system – modeled growth at Fort Saskatchewan, harvest at 5 g L ⁻¹ for 203 growing days [70]
				• PBR system – modeled growth at Fort Saskatchewan, harvest at 5 g L ⁻¹ for 330 growing days [79]
Water loss - evaporation	0.5	0	% d ⁻¹	• OPR system – from NREL [68] and adjusted for pond depth of 25 cm
				• PBR system – system enclosed. Therefore, no water loss due to evaporation
Water loss - blowdown	0.5	0.5	% d ⁻¹	• OPR system - from NREL [68]
				• PBR system - from NREL [68]
Water loss - harvesting	0.2	0.2	% harvest ⁻¹	• OPR system - from NREL [68]
				• PBR system - from NREL [68]

Harvests	11	330	# yr ⁻¹	<ul style="list-style-type: none"> • OPR system - modeled growth at Fort Saskatchewan, harvest at 5 g L⁻¹ for 203 growing days [70] • PBR system - modeled growth at Fort Saskatchewan, harvest at 5 g L⁻¹ for 330 growing days [79]
Potential for cultivation crash	5	1	%	<ul style="list-style-type: none"> • OPR system - from NREL [68] • PBR system – working assumption. Literature concurs that open pond systems are much more susceptible to pond crashes

Table 2. Open pond raceway (OPR) and photobioreactor (PBR) system assemblies with input/output operations

ASSEMBLIES	OPR	PBR	Units kg ⁻¹ *	References and notes
ALGAE INOCULUM SYSTEM				
Inputs				
Makeup water	3.98		m ³ or T	
Land for inoculum	0.12		m ²	
Nutrients	0.24		kg	
Energy - electrical	0.0257		kWh	
Outputs				
Oxygen gas (O ₂) from hydrolysis of water	0.14		kg	From photosynthetic stoichiometric equation. Start with algae biomass composition. Calculate weight of carbon as percentage of biomass and for 1 MJ of biomass energy at lower heating value of 24.3 MJ kg ⁻¹ dry biomass. Convert weight of carbon for 1 kg biomass. Calculate moles of carbon. Since equal, moles O ₂ produced for each mole of C, can then calculate amount of O ₂ kg ⁻¹ dry biomass.
Inoculum media moved to cultivation	2.14		m ³ or T	Make up water – restart every 2 nd harvest
Water loss	1.84		m ³ or T	<ul style="list-style-type: none"> Sum of water loss = evaporation + photosynthetic hydrolysis + blowdown Evaporation = Volume to cultivate 1 kg biomass * cultivation days * % evaporation d⁻¹ (0.36% [68]) Photosynthetic hydrolysis = H₂O calculation from reaction stoichiometry

ASSEMBLIES	OPR	PBR	Units kg⁻¹*	References and notes
Carbon dioxide (CO ₂) lost to air	0.038		kg	<ul style="list-style-type: none"> Blowdown = Assumed avg. 0.63 mm L⁻¹ d⁻¹ / 25 cm* 100 = 0.252% d⁻¹ * Vol (m³) kg⁻¹ biomass yr⁻¹ * # cultivation days From photosynthetic stoichiometric equation. Assume 20% surplus
N loss to water blowdown / air	0.0016		kg	N loss = 20% surplus excess beyond the stoichiometric requirement.
ALGAE CULTIVATION SYSTEM				
Inputs				
Inoculum media with water	2.14		m ³ or T	
Makeup water	21.5	0.011	m ³ or T	
Land for cultivation	12.4	0.00048	m ²	
Nutrients	2.4	2.4	kg	
Energy – electrical	0.257	0.785	kWh	
Outputs				
Oxygen gas (O ₂) from hydrolysis of water	1.4		kg	
Water loss	18.4	0.011	m ³ or T	
Carbon dioxide (CO ₂) lost to air	0.38	0.38	kg	

ASSEMBLIES	OPR	PBR	Units kg⁻¹*	References and notes
Nitrogen (N) loss to water blowdown / air	0.016	0.016	kg	
Cultivation media (10 g/L – 1% solids)	0.155	0.0005	m ³ or T	
ALGAE DEWATERING - Ultra / micro filtration membrane				
Inputs				
Cultivation media (10 g/L – 1% solids)	0.155	0.0005	m ³ or T	
Energy - membrane filtration	0.11	0.020	kWh	
Outputs				
Algae biomass (130 g/L – 13% solids)	0.012	3.8E-05	m ³ or T	
Water for recycling	0.143	0.00046	m ³ or T	
ALGAE DEWATERING - Centrifuge				
Inputs				
Algae biomass (130 g/L – 13% solids)	0.012	3.8E-05	m ³ or T	
Energy - centrifuge	0.27	0.048	kWh	
Outputs				
Algae biomass (200 g/L - 20% solids)	0.0078	2.5E-05	m ³ or T	

ASSEMBLIES	OPR	PBR	Units kg⁻¹*	References and notes
Water for recycling	0.0042	0.000013	m ³ or T	
ALGAE STORAGE - Chilling				
Inputs				
Energy - chilling biomass / kg	0.0073	0.0073	kWh	
<ul style="list-style-type: none"> • Units kg⁻¹ dry biomass (nitrogen surplus) under lower heating value calculations. Inoculum based on 10% of cultivation values. 				

Table 3. Energy requirements for the pyrolysis of algae

Operation	Value [70]	Unit
Dryer	5.68	MJ/kg diluent
Heater	3.15	MJ/kg diluent
Reactor	31.4	MJ/kg diluent
Hydrotreat pump	0.40	MJ/kg diluent
Compressor	0.32	MJ/kg diluent
Hydrotreat heater	1.58	MJ/kg diluent
Column-reboiler	0.07	MJ/kg diluent
Flash separator	0.11	MJ/kg diluent
Hydrotreater	7.85	MJ/kg diluent

Table 4. Energy requirements for the hydrothermal liquefaction (HTL) of algae

Operation	Value [70]	Unit
HTL Pump	0.36	MJ/kg diluent
Reactor	12.23	MJ/kg diluent
Hydrotreat pump	0.47	MJ/kg diluent
Hydrotreat compressor	0.25	MJ/kg diluent
Hydrotreater	0.64	MJ/kg diluent
Column reboiler	0.28	MJ/kg diluent

Table 5. Energy requirements for the supercritical water gasification (SCWG) of algae

Operation	Value [70]	Unit
SCWG pump	1.44	MJ/kg H ₂
Heater	56.7	MJ/kg H ₂
Selexol pump	1.66	MJ/kg H ₂
Compressor	7.6	MJ/kg H ₂
Gas purification pump	5.4	MJ/kg H ₂

Table 6. Energy requirements for the thermal gasification of algae

Operation	Value [70]	Unit
Reactor	57.24	MJ/kg H ₂
Dryer	5.51	MJ/kg H ₂
Selexol pump	2.56	MJ/kg H ₂
Compressor	12.89	MJ/kg H ₂
Gas purification pump	6.62	MJ/kg H ₂

Table 7. LCA of thermochemical technologies for diluent and hydrogen production via two alternative cultivation systems (open pond raceway [OPR] and photobioreactor [PBR]) and four different thermochemical production platforms (hydrothermal liquefaction [HTL] and pyrolysis for diluent production and supercritical water gasification [SCWG]) and thermal gasification [TG] for hydrogen production) (gCO₂eq MJ⁻¹)

Cultivation Process	PBR		OPR		PBR		OPR	
	HTL	Pyrolysis	HTL	Pyrolysis	SCWG	TG	SCWG	TG
Hydro Thermal Process								
Production of diluent (Base case)	-5.90	45.65	-11.5	40.05				
Production of diluent (Scenario)	-5.90	15.8	-11.5	10.2				
Production of hydrogen (Base case)					-7.0	138.3	-12.56	132.68
Production of hydrogen (Scenario)					-7.0	97.7	-12.56	92.1

Statement of Informed Consent, Human/Animal Rights

“No conflicts, informed consent, human or animal rights applicable”

Statement of Novelty

This work evaluates the environmental sustainability of open pond raceway and photobioreactor algae cultivation systems in a cold climate with downstream processing to hydrogen and diluent with commercial biomass production of 2000 T/day. This has not been investigated earlier and hence is a novel contribution in this area.

Appendix

Algae Biomass Production – CO₂ Emissions Calculations

Table A1 – Open pond raceway (OPR) calculations (kg CO₂e kg⁻¹ biomass produced)

	+10% increase	Calculated emissions	-10% Reduction	+10% increase	Normalized to zero	-10% Reduction
Paddle Wheel	0.022	0.020	0.018	-0.002	0	0.002
Pumps	0.236	0.215	0.193	-0.021	0	0.021
Membrane Filtration	0.104	0.094	0.085	-0.009	0	0.009
Centrifuge	0.245	0.222	0.200	-0.022	0	0.022
Chiller	0.007	0.006	0.005	-0.001	0	0.001
Water	0.000	0.000	0.000	0.000	0	0.000
Diammonium phosphate (DAP)	0.052	0.048	0.043	-0.005	0	0.005
Ammonia (NH ₃)	0.215	0.195	0.176	-0.020	0	0.020

Table A2 – Photobioreactor (PBR) calculations (kg CO₂e kg⁻¹ biomass produced)

	+10% increase	Calculated emissions	-10% Reduction	+10% increase	Normalized to zero	-10% Reduction
Sparging	0.138	0.125	0.113	-0.013	0	0.013
Lights	0.579	0.526	0.474	-0.053	0	0.053
Membrane Filtration	0.019	0.017	0.015	-0.002	0	0.002
Centrifuge	0.044	0.040	0.036	-0.004	0	0.004
Chiller	0.007	0.006	0.005	-0.001	0	0.001
Water	0.000	0.000	0.000	0.000	0	0.000
Diammonium phosphate (DAP)	0.033	0.030	0.027	-0.003	0	0.003
Ammonia (NH ₃)	0.211	0.192	0.173	-0.019	0	0.019