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1 **Life cycle assessments of bio-based sustainable polylimonene carbonate production processes**

2

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11

12

Abstract

Biomass is a promising feedstock for the production of sustainable biopolymers, which could offer a significant reduction of the adverse environmental impacts associated with conventional petroleum-based polymers. To further evaluate their potential, this study investigated the environmental impacts associated with the production of the newly proposed biopolymer polylimonene carbonate. Different feedstocks (citrus waste and microalgae) were selected and a conceptual process design from limonene oxidation to polymer synthesis was completed. Using life cycle assessment, the potential for energy integration and the contributions of individual process sections on the overall process environmental impacts were thoroughly analysed. The results showed, that sustainable polylimonene carbonate synthesis was limited by the use of tert-butyl hydroperoxide as the limonene oxidation agent and consequently, a more environmentally-friendly and energy-efficient limonene oxidation method should be developed. Based on the economic analysis, the polymer cost was estimated to range from \$1.36 to \$1.51 kg⁻¹, comparable to the costs of petrol-based polystyrene (\$1.2 to \$1.6 kg⁻¹). Moreover, this study found that both feedstock selection and the biowaste treatment method have significant effects on the process environmental impacts, and a carbon negative process was achieved when applying the waste biomass for electricity generation. Therefore, it was concluded that future process designs should combine polymer production with the co-generation of energy from waste biomass.

Keywords: biomass, cradle-to-gate life cycle assessment, polylimonene carbonate, process simulation, economic analysis, sustainable process design.

1. INTRODUCTION

Polymers, such as polylactic acid (PLA), polyethylene terephthalate (PET) or polystyrene, represent an important global commodity, both industrially and domestically. They can adopt a large variety of configurations, with highly specialised properties, making them applicable to a wide range of areas including electronics, healthcare products, toys, packaging materials, and coatings ^{1,2}. The annual consumption of polymers in the US alone has been estimated at around 31 million tonnes whilst the global production of polymers has exceeded 260 million tonnes since 2009 ^{3,4}. In addition, global polymer production between 2009 and 2015 was reported to have increased by up to 20% , indicating a huge potential global market in the future ⁵.

To improve the sustainability of the polymer production processes, the last two decades have seen increasing efforts to identify renewable and more environmentally friendly raw materials, particularly biomass, to replace the fossil carbon resources used in traditional polymer synthesis ^{2,6}. These include agricultural biomass, citrus wastes, and microorganisms, *e.g.* microalgae and cyanobacteria ⁷⁻¹², which have been used for the synthesis of bio-based polymers such as polycarbonates, polyesters, and polyurethane ^{8,13,14}. To improve the usability of these sustainable feedstocks, new reaction routes have been proposed and compared to the traditional fossil based methods ^{7,15,16}.

Amongst the newly proposed biopolymer candidates, particular attention has been given to polylimonene carbonate (PLC), produced by the reaction of limonene with carbon dioxide ^{13,16,17}. PLC has similar properties to polystyrene ¹⁸, one of the major fossil based polymers with a predicted global production of 700,000 tonnes year⁻¹ by 2020 and annual sales volume of \$28.7 billion ¹⁹. As polystyrene is predominantly made from hydrofluorocarbons (HFC-134a), with global warming potentials around 1000 times that of CO₂ ²⁰, there is a great drive to identify more environmentally friendly alternatives. Limonene, required for PLC synthesis, can be obtained from a range of biomass sources, including orange peels, microalgae and other citrus wastes, with an estimated global

60 production of 70,000 to 100,000 tonnes year⁻¹ ^{17,18,21}, indicating a stable supply for industrial PLC
61 production. Furthermore, as PLC synthesis directly consumes CO₂, the overall process has the
62 potential to actively sequester carbon, and therefore be carbon negative (*i.e.* avoiding greenhouse gas
63 (GHG) emission) ^{13,18}. Consequently, PLC has great potential to replace polystyrene in the near future.

64
65 Previous studies employed life cycle assessments to investigate the potential environmental impacts
66 of limonene production from citrus wastes²² and microalgae ²³, whilst a process design for the
67 oxidation of limonene to PLC was published recently ¹⁸. Moreover, optimal reaction conditions for
68 PLC precursor oxidation and monomer polymerisation have been proposed by different studies ^{13,16,24}.
69 In spite of these achievements, the environmental impacts of the entire PLC production process,
70 ranging from feedstock selection (algae *vs.* citrus) to downstream PLC synthesis, have not yet been
71 explored, and therefore the process sustainability, economic viability, and industrialisation feasibility
72 are unknown.

73
74 To address this open challenge, the current study aimed to design a conceptual PLC production
75 process and conduct a high-level life cycle assessment, facilitating the industrialisation of PLC
76 production at an early stage of the research. In addition, a preliminary economic analysis was carried
77 out to estimate and compare the potential cost of PLC against the price of polystyrene. The next
78 sections will provide a detailed explanation of the design and life cycle assessment of the PLC
79 production process, followed by the results and conclusions discovered in the current research.

81 **2. METHODOLOGY**

82 **2.1 Process description**

83 The overall polylimonene carbonate (PLC) production process can be divided into four distinct
84 operating stages: 1) Production of limonene, 2) Production of the oxidant tert-butyle hydroperoxide
85 (TBHP), 3) Limonene oxidation and 4) PLC synthesis (Figure 1). Moreover, limonene can be

101 the collected citrus oils contain ~ 95% limonene, which is further purified using either vacuum
102 distillation or winterisation (freezing oils) ^{18,22}. As this process has already been analysed in detail in
103 the literature, including orange collection and use of the extracted orange peels as cattle feed ²², it
104 was chosen as the standard route for the production of citrus-based limonene in the current research.

105

106 **2.1.2 Limonene production from algae**

107 An alternative to the conventional, citrus-based limonene production route, is the use of microalgae
108 and cyanobacteria, genetically engineered to produce limonene ^{21,23}. This route promises substantial
109 advantages (*e.g.* high growth rate and solar energy utilisation efficiency) over other solar energy and
110 CO₂ derived biomass ^{25,26}. Recently, a detailed process design for algal limonene and energy co-
111 production was proposed, and the critical limonene productivity, at which the process starts to break
112 even, was identified through process economic analysis ²⁷. The process considers limonene as the
113 major product, whilst algal biomass waste is anaerobically digested for the production of hydrogen
114 and methane, which are subsequently combusted in gas turbines for electricity generation. This
115 configuration was adapted as the standard route for the production of algal limonene in the present
116 work, to allow comparison against the citrus-based process.

117

118 To model algal limonene production, the process was split into five stages (detailed introduction in
119 Supplementary): 1) Algae cultivation in a photobioreactor, 2) limonene recovery via absorption and
120 distillation, 3) algae biomass recovery (including settling, floatation, and electrocoagulation), 4)
121 anaerobic digestion (used for biogas and electricity generation), and 5) wastewater treatment (for
122 water recycle) ^{23,27}. Previous work tested two different algal limonene productivities; a real-case
123 limonene productivity of 1.8 mg L⁻¹ h⁻¹ and a much higher productivity value of 55.5 mg L⁻¹ h⁻¹ ²³.
124 In contrast, the present study adapted a limonene productivity value of 4.5 mg L⁻¹ h⁻¹, consistent with
125 the highest algal limonene productivity reported in the literature ²¹.

126

127 2.1.3 Limonene oxide production

128 Prior to converting limonene into PLC, it must be oxidised into limonene oxide. This can be achieved
129 using a variety of oxidants such as molecular oxygen gas, hydrogen peroxide and epoxides under
130 specific conditions ^{28–30}. However, most available data stem from laboratory scale experiments,
131 requiring numerous assumptions to correlate the reaction selectivity and conversion efficiency to
132 large scale systems (linear scale-up) ³¹. A particularly promising oxidant is tert-butyl hydroperoxide
133 (TBHP), due to its mild operating conditions (room temperature, 1 bar), high single-pass conversion
134 (75%) and selectivity (88%) (Equation 1) ¹⁸. Therefore, TBHP was selected as the oxidant for
135 limonene oxide synthesis in the current study.

136

138

139 Initially, limonene and TBHP are fed to the reactor at a molar ratio of 1:1. The reaction is conducted
140 at room temperature and atmospheric pressure in the presence of catalyst (silica dissolved in solvent)
141 ¹⁸. The resulting product mixture containing limonene oxide, tert-butyl alcohol (TBA), and unreacted
142 limonene and TBHP (side reaction is neglected) is sent to a distillation column (MIDSEP) for the
143 separation of TBA and TBHP from limonene and limonene oxide. Further separation of limonene
144 and limonene oxide and of TBA and TBHP is achieved in two additional columns. Eventually,
145 unreacted TBHP and limonene are recycled back to the reactor, limonene oxide is sent to the PLC
146 production stage, and TBA is returned to the TBHP regeneration stage. Heat exchangers are used to
147 pre-heat the product mixture and cool the outlets from the distillation columns.

148

149 2.1.4 Tert-butyl hydroperoxide regeneration

150 Although tert-butyl hydroperoxide (TBHP) is a commercially available chemical commodity, the
151 environmental and life cycle impacts of its industrial synthesis routes have not yet been analysed. As
152 the current study aims to conduct the life cycle analysis (LCA) for the entire PLC production process,

153 it is necessary to include the TBHP synthesis in this work. Commercial TBHP production follows
 154 one of three different synthesis routes: 1) tert-butyl alcohol (TBA) oxidation by hydrogen peroxide,
 155 2) reaction between peroxymonosulphuric acid and TBA, and 3) auto-oxidation of isobutene with
 156 oxygen³². During limonene oxidation, TBHP is reduced back into TBA, and consequently, the first
 157 two choices are advantageous from the circular economy point of view. Therefore, the limonene
 158 oxidation process only requires hydrogen peroxide or peroxymonosulphuric acid, whilst TBA/TBHP
 159 act as the electron carrier. As reactions involving peroxymonosulphuric acid may yield an explosive
 160 intermediate³², the hydrogen peroxide process, which produces only water, represents the safest and
 161 most environmentally favourable process overall and was chosen for this study.

162
 163 TBA oxidation occurs at room temperature and 1 bar in an acidic environment (Equation 2), with a
 164 high single-pass TBHP yield (approximately 90%)³³. After reaction, the product mixture (unreacted
 165 H₂O₂ and TBA, TBHP, water) is distilled under vacuum, due to the low heat stability of H₂O₂³⁴.
 166 After downstream separation, unreacted TBA and H₂O₂ (recompressed to 1 bar) are recycled back to
 167 the TBA oxidation reactor, whilst TBHP is fed to the limonene oxide production stage, and water is
 168 transported to the utility system (to generate steam or cooling water).

169

171

172 **2.1.5 Polylimonene carbonate production**

173 Finally, the polymerisation reaction of CO₂ and limonene oxide into PLC is conducted in the presence
 174 of homogeneous, zinc-based catalysts at pressures of ~ 7 bar (100 psi) and at ambient temperature
 175 ^{13,18}, with single-pass limonene oxide conversions of 50% (Equation 3)¹⁸.

177

178 After flashing off excess CO₂, PLC is precipitated from the product mixture through the addition of
179 methanol ¹⁸. Subsequently, the solvent is removed via distillation and unreacted limonene oxide is
180 passed to a secondary reaction stage to continue the polymerisation process, followed by renewed
181 PLC precipitation with methanol. This two-reaction stage configuration has been adapted to reduce
182 the energy requirements associated with the gas-liquid mixing in the large, primary reactor ¹⁸.
183 Following distillation, unreacted limonene is recycled to the first reactor whilst the methanol phase
184 is sent to a liquid-solid separation tank, for the collection of the final PLC product.

185

186 **2.2 Life cycle assessment**

187 Life cycle assessment (LCA) is a norm-based methodology to estimate the environmental impacts of
188 a specific product over its entire life cycle ³⁵. It consists of four key steps: goal and scope definition,
189 life cycle inventory, life cycle impact assessment, and interpretation ³¹. LCAs can be applied across
190 different system boundaries, such as cradle-to-grave, cradle-to-gate, and gate-to-gate analysis ^{14,23,36}.
191 Amongst these, cradle-to-gate (from feedstock collection to final production of the investigated
192 product, excluding transportation to the local market) is the most common, as the transportation and
193 end use of the final product are usually similar ¹⁴. As the current work covers the process from the
194 preparation of the raw material (fertilising orange trees or cultivating algae biomass) to the final
195 production of PLC before it is transported to customers, the cradle-to-gate analysis was applied.

196

197 **2.2.1 Goal and scopes**

198 The primary goal of this LCA was to investigate the net CO₂ emissions or consumption of the newly
199 proposed biopolymer (PLC) manufacturing process and identify any potential adverse environmental
200 impacts (*e.g.* ozone and water deletion). In this context, the term “carbon negative” specifically refers
201 to eliminating GHG emission during the product synthesis route. To provide a comprehensive
202 analysis for PLC production at this early stage of research, the LCA covered limonene production
203 from both algal and citrus waste resources. Moreover, although algal biomass was sent for energy

204 regeneration in the previous study, in this work to explore the carbon footprint and solar energy
205 utilisation efficiency of each process, two different scenarios were considered for the disposal of
206 waste biomass, namely energy generation via anaerobic digestion (“PLC from algae”) and use of
207 biowaste as animal feed (“PLC from algae without electricity”).

208

209 **2.2.2 System boundaries and function units**

210 In this study, two sets of LCA boundaries were used: the boundaries between the entire production
211 system (from algae cultivation or citrus plantation to PLC production) and the environment, and the
212 boundaries between each of the four separate processing stages (production of limonene, limonene
213 oxide, TBHP, and PLC). It should be noted, that the supply chain of raw materials and transportation
214 of products were not included in this study. The first boundary set was applied to analyse the
215 environmental impacts of the entire system, whereas the latter set was employed to allow correlation
216 of major environmental burdens to specific processing stages.

217

218 The current global production of limonene has been estimated between 70,000 and 100,000 tonnes
219 year⁻¹ ¹⁹. Considering its predominant use in other industries (*e.g.* perfume and food), the present
220 study assumed an annual limonene consumption of 15,000 tonnes for the production of PLC in a
221 single plant, as recommended previously ³⁷. As a result, the function unit for this LCA was set to the
222 equivalent PLC production (21,600 tonnes) from a single plant.

223

224 In addition, in this study methanol is used as a solvent to precipitate PLC, and TBHP is used as the
225 direct oxidant for limonene oxidation. As introduced before, both of them are recycled inside process
226 without being emitted, meaning they are confined in the system. Moreover, their purchase is one-off
227 (other materials have to be supplied continuously) and their required amount is much lower than other
228 chemicals. As a result, it is plausible to exclude the environmental impact of these chemicals in the

229 preliminary LCA. However, to verify the validity of this simplification, different cases were designed
230 and compared in this work and presented in Section 3.3.

231

232 **2.2.3 Life cycle inventory**

233 The life cycle inventory was calculated from mass and energy balances. The environmental impacts
234 of limonene production from both citrus wastes and microalgae were previously evaluated in LCA
235 studies ^{23,22 27}, and were directly adopted in the current study, except for the increased algal limonene
236 productivity of 4.5 mg L⁻¹ h⁻¹ instead of 1.8 mg L⁻¹ h⁻¹ as described above (Section 2.1.2). To account
237 for this change, the original inventory was revised by interpolation (shown in Supplementary
238 Information). For the production of limonene oxide, TBHP, and PLC, both mass balances and energy
239 consumptions were estimated through process simulation. LCAs for the production of H₂O₂ and TBA,
240 the two starting materials for TBHP synthesis, are available from the Ecoinvent 3.2 database and
241 previous research ³⁶. Hence, combining this information, allowed the completion of the LCA for the
242 PLC production process. The full inventory from raw materials consumption to PLC production can
243 be found in the Supplementary Information.

244

245 **2.2.4 Allocation of by-products**

246 The previous LCA for limonene production from citrus feedstocks stated that only 1% of the
247 environmental impacts of the process should be allocated to limonene (economic based), as it is a
248 waste-derived by-product with a much lower production volume than orange juice, whilst the
249 remaining citrus waste after limonene production is sold as cattle feed ²². This is different to limonene
250 production from the algae-based process, which has been particularly designed for the co-production
251 of biomass and limonene ²³. In this case, the allocation factor for limonene was set between 64% and
252 98% according to the algal limonene productivity (1.8 mg L⁻¹ h⁻¹ to 55.5 mg L⁻¹ h⁻¹), based on the
253 economic value of limonene and biomass residue. As the assumed limonene productivity in the
254 present study was 4.5 mg L⁻¹ h⁻¹, the allocation factor was increased to 66% by linear interpolation.

Hence, the remaining environmental impacts of 34% was allocated to the biomass waste which was either anaerobically digested for electricity generation or sold directly as animal feed. Although the electricity generated from the algae biomass could be used internally, this would be inefficient as the PLC synthesis requires mostly lower grade heat energy. Consequently, the generated electricity was fed into the electricity grid instead, whilst the heating requirements were met using industrial steam. As the only by-product from the limonene oxidation and PLC production is water, the environmental impacts associated with these stages are fully allocated to PLC.

2.3 Impact assessment methodology

The production stages for limonene oxide, TBHP and PLC were simulated in Aspen Plus V9 to estimate both the energy consumption and mass balances for each process section. In addition, the models were used to evaluate the potential for energy integration to reduce the heating and cooling utilities, and obtain estimates for the process capital and operation costs. LCA was performed in Simapro 8.1, using the Ecoinvent 3.2 LCA database and ReCiPe Midpoint method. This method has been widely applied in previous studies^{22,38}, and has the advantage of breaking down environmental impacts into specific criteria. The criteria chosen for this study were ‘climate change’, ‘ozone depletion’, ‘terrestrial acidification’, ‘freshwater eutrophication’, ‘human toxicity’, ‘particulate matter formation’, ‘terrestrial and freshwater ecotoxicity’, ‘agricultural land occupation’ and ‘water and fossil depletion’, all of which are commonly used in the literature^{22,38}.

3. RESULTS AND DISCUSSION

3.1 Process simulation results

The modelling results for the PLC production process (from limonene oxide synthesis to PLC production) are presented in Table 1. These mass balance and energy consumption data form the life cycle inventory for this study. Electricity is mainly used in the utility system and pump system. Moreover, the results includes the energy consumption data after process energy integration.

281 Table 1: Process simulation result for the production of 21.6 kt PLC (1 function unit). “Heat integrated”
 282 and “Cooling integrated” represent the external energy required for heating and cooling after process
 283 energy integration.

	Limonene oxide production section			
Flow rate	Limonene	THBP	Limonene oxide	TBA
	1764.7 kg h ⁻¹	1164.8 kg h ⁻¹	1972.3 kg h ⁻¹	957.2 kg h ⁻¹
Energy use	Heat (steam)	Heat integrated	Cooling	Cooling integrated
	4.20 MW	3.24 MW	5.15 MW	4.18 MW
	Electricity: 633.6 kW (143 kW after energy integration)			
	TBHP production section			
Flow rate	H ₂ O ₂	TBA	H ₂ O	TBHP
	439.3 kg h ⁻¹	957.2 kg h ⁻¹	232.2 kg h ⁻¹	1164.3 kg h ⁻¹
Energy use	Heat (steam)	Heat integrated	Cooling	Cooling integrated
	2.66 MW	2.60 MW	2.81 MW	2.76 MW
	Electricity: 1040 kW (949 kW after energy integration)			
	PLC production section			
Flow rate	Methanol	Limonene oxide	CO ₂	PLC
	833.0 kg h ⁻¹	1927.8 kg h ⁻¹	585.2 kg h ⁻¹	2542.0 kg h ⁻¹
Energy use	Heat (steam)	Heat integrated	Cooling	Cooling integrated
	1.95 MW	1.80 MW	0.17 MW	10.1 KW
	Electricity: 5.65 kW (0.35 kW after energy integration)			

284

285 3.2 Effect of limonene source and biomass use on process environmental impacts

286 To explore the effect of the limonene source (citrus waste and algal biomass) and use of waste
 287 biomass (cattle feed or electricity production) on the environmental impacts of the PLC production
 288 process, three scenarios were selected for comparison (Figure 2). The two scenarios using biomass

for animal feed are both CO₂ positive, with net emissions of 1.21 kg (CO₂ eq.) kg⁻¹ (PLC) and 11.99 kg (CO₂ eq.) kg⁻¹ (PLC), for the citrus and algae based processes, respectively.

Figure 2: Effect of feedstock and use of biowaste on LCA results (without energy integration and accounting for recycled chemicals) for PLC production process. “PLC from citrus waste” and “PLC from algae without electricity” denote processes where biomass is sold as animal feed, and “PLC from algae” denotes the process where algae biomass is used for energy generation.

In contrast, combining limonene production with energy generation from the algal residue resulted in a carbon negative process together with mostly environmentally favourable indicators (negative values in 7 of 11 categories). This finding can be attributed to the high amount of recoverable solar energy stored inside the biomass, previously estimated at 109.2 MJ kg⁻¹ (PLC), which greatly exceeds the energy requirements of the PLC production process (approximately 22.0 MJ kg⁻¹ (PLC), mainly heat)²³. Hence, from the energy balance point of view, recovering this energy through the combined anaerobic digestion / electricity generation process, allows the exporting of excess electricity to the

304 grid, displacing carbon-based electricity (although in this study industrial steam is directly used for
305 PLC synthesis, and the electricity required for PLC synthesis is negligible compared to that generated
306 from anaerobic digestion). This is not possible, however, when the biomass is sold as animal feed, as
307 the stored solar energy remains unused. Consequently, the system energy demands must be met with
308 alternative, fossil resources, increasing the net carbon emissions of the process.

309

310 When comparing the citrus- and algae-derived PLC processes, the latter performs worse in terms of
311 water depletion, land occupation and ozone depletion, regardless of the biomass treatment method.
312 Considering the ethical implications of diverting land and water for fuel generation, these results
313 appear to favour limonene from citrus wastes over algal limonene for PLC production. Nonetheless,
314 it is important to consider the different allocation factors used during the evaluation of these processes.
315 Limonene from citrus waste is considered as a by-product with an allocation factor of only 1%, while
316 limonene from algae was allocated 66%. It is therefore unsurprising that citrus derived limonene is
317 less water or land intensive than algae based limonene. However, as the demand for limonene
318 increases in the future, its allocation factor to the citrus-based process could increase, increasing the
319 associated environmental impacts. For instance, from the current LCA study, it was estimated that
320 increasing the limonene allocation factor to 10% for citrus derived PLC, results in the same climate
321 change and fossil fuel depletion impacts as the algae derived PLC scenario (without energy
322 generation).

323

324 **3.3 Effect of solvent and oxidant used during PLC production**

325 To evaluate the effect of the solvent (methanol) and oxidant (TBHP) on the overall life cycle impacts
326 of the PLC process, the system was modelled with and without these chemicals (Figure 3). It was
327 assumed, that all the TBHP required during the first year was purchased externally, whilst in all
328 subsequent years, 90% of the required TBHP was regenerated internally from TBA, requiring only
329 10% of new TBHP. The results show that methanol has a very minor effect on the system, whereas

the inclusion of TBHP significantly increases the impacts on climate change, human toxicity, and ecotoxicity. For instance, for the citrus-based process the climate change and human toxicity impacts increase by 156.7% and 1603.4%, respectively, even though the use and replacement of lost TBHP is much lower than for any of the other feedstocks.

In the case of algal PLC production, including TBHP production changes the values for human toxicity, terrestrial ecotoxicity and freshwater ecotoxicity from negative to positive, indicating a change from a net positive to a net detrimental environmental impact. This clearly suggests that even though TBHP/TBA is recycled internally within the process, and only employed as an electron carrier for the redox reaction between limonene and hydrogen peroxide, its current external synthesis route (TBA is a co-product from commercial propylene oxide synthesis ³⁶) could significantly aggravate the environmental impacts of the PLC production process, depending on how much is actually consumed in the process. As a result, more environmentally friendly routes should be developed for the synthesis of TBHP/TBA, whilst more research effort should be focused on the direct reaction between limonene and hydrogen peroxide.

346 Figure 3: Effect of solvent (methanol) and oxidant (TBHP) on LCA results (without energy
 347 integration) for PLC production process.

348

349 3.4 Effect of energy integration on PLC production process

350 For many chemical processes, heat exchange between hot and cold streams is an effective method of
 351 reducing the energy requirements of the utility system. Therefore, the current research conducted a
 352 preliminary estimation of the energy integration potential of the PLC production process (Table 1).
 353 This resulted in total energy savings (heat and electricity) of 20.8%, mostly associated with the
 354 reduction of electricity used for the recycling of cooling water in the limonene oxide production
 355 section (77.4%) and PLC production section (93.8%). Except for the limonene oxide production
 356 section, energy integration had little impact on the heat requirements (steam) of the PLC production
 357 process, as most of the reactions take place at room temperature, and their product mixtures are easily
 358 separated by distillation.

359

360

361

Figure 4: Effect of energy integration on LCA results (including impacts of recycled chemicals) for PLC production process. “PLC from citrus (full)” and “PLC from algae (full)” represent results without energy integration; “PLC from citrus (energy saving)” and “PLC from algae (energy saving)” represent the cases where energy integration has been included.

Including the energy integration savings within the life cycle assessment results in small improvements on climate change (6.2%) and ozone depletion (15.2%), but has a marginal impact on the other environmental categories, regardless of limonene feedstock (Figure 4). This indicates that energy integration may not be an effective method of improving the environmental-friendliness of the PLC process, whilst increasing the capital investment due to the addition of heat exchangers and other auxiliary equipment. However, it is important to stress that in the current process most of the reactions are room temperature, limiting the potential for energy integration to the cooling water system. As cooling water does not represent a significant environmental burden, energy integration has no significant impact on the overall environmental impacts of the process. In contrast, for processes involving high-temperature reactions, the findings may be different, and energy integration may still represent an effective solution.

3.5 Contribution of individual process sections to overall environmental impacts of PLC process

To discover the contribution of each individual process section to the overall environmental impact of the PLC process, the impacts were evaluated separately for each processing stage (Figure 5). For the citrus based PLC production process, limonene production carries the lowest environmental burden (in most cases less than 10%), indicating that the use of biowaste for the production of biorenewable precursors could offer a sustainable processing route.

(a)

(b)

Figure 5: Contribution of individual process sections to the overall environmental impact of the PLC

390 process (after energy integration and consideration for recycled chemicals). (a): citrus derived PLC
391 production process. (b): algae derived PLC production process.

392

393 Consistent with the results from section 3.3, the TBHP regeneration section makes a major
394 contribution to the overall system environmental impacts, even though the consumption of externally
395 supplied TBHP is much lower than for the other chemicals. This result emphasizes the need to
396 develop more environmentally friendly reaction pathways that eliminate the use of TBHP. The
397 production of limonene oxide has the second highest environmental impacts, in many cases more
398 than twice the impacts attributed to the PLC production section. This can be related to the high energy
399 requirements of this section, representing 58% and 47% of the total respective electricity and heat
400 consumption of the PLC production process. Consequently, it is recommended that more energy-
401 efficient synthesis routes should be developed for the limonene oxide production step.

402

403 Different to the citrus derived PLC production process, the PLC production and limonene oxide
404 production sections make a relatively minor contribution to the algae derived PLC processes.
405 Although the impacts of TBHP production are still significant, it is noteworthy that limonene
406 production carries large environmental burdens in a number categories, particularly ozone depletion,
407 land occupation, and water depletion. Once again, the difference to the citrus based process can be
408 attributed to the much higher factor allocated to limonene production, as it is the primary economic
409 driver for this scenario. Nonetheless, the results also show great positive impacts associated with algal
410 limonene (negative values), in categories such as climate change and fossil resource depletion. Recall
411 that in this process, biomass waste is sent to anaerobic digestion for energy generation, and more
412 energy is produced than required for the whole PLC production process. As a result, the net fossil
413 fuel consumption is negative and no CO₂ is emitted to the environment. It should be emphasized,
414 however, that the present study does not include the supply chain of the raw materials or

415 transportation of products. The above result should therefore be verified further using entire life cycle
416 assessments.

417

418 **3.6 Process economic analysis**

419 To assess the financial viability of the citrus- and algae-based PLC production routes, the capital and
420 operating costs were estimated in Aspen Plus V9 for a single PLC production plant (Table 2). Prices
421 for the raw materials were obtained from manufacturer websites and recent studies (CO₂ price was
422 assumed to be zero as it is a general industrial waste which can be collected from different processes
423 at little cost)^{18,27}. It can be seen that the cost of PLC ranges from \$1.36 kg⁻¹ for the citrus-based route
424 to \$1.51 kg⁻¹ for the algal route. Whilst these values exceed the market price for polyethylene (\$0.91
425 kg⁻¹), they fall within the price range of polystyrene (\$1.2 to \$1.6 kg⁻¹), a traditional commercial
426 polymer with similar properties to PLC but based on conventional fossil resources. Consequently,
427 based on the results from the life cycle assessment and process economic analysis, it can be concluded
428 that the proposed process has great potential to replace fossil based polystyrene with biomass derived
429 PLC.

430 Table 2: Results from economic analysis of the PLC production processes

Process capital and operating cost (21.6 kton PLC annually)			
	THBP production	Limonene oxide production	PLC production
Capital cost	\$1.15 million	\$5.87 million	\$5.62 million
Operating cost	\$0.33 million yr ⁻¹	\$1.80 million yr ⁻¹	\$1.69 million yr ⁻¹
Raw material price (\$ kg ⁻¹) ^{18,27}			
Limonene (citrus)	1.35	Hydrogen peroxide	0.40
Limonene (algae)	1.57	Methanol	0.30
Tert-butyl alcohol	1.48	CO ₂	0.0
PLC cost (\$ kg ⁻¹)			
PLC from citrus	1.36	PLC from algae	1.51

431

432 **4. Conclusion**

433 The current study designed and assessed a process for the production of the polystyrene substitute
434 PLC from biomass-derived limonene. Particular attention was given to the source of limonene (citrus
435 waste or engineered algae), the use of waste biomass (animal feed or electricity generation) and the
436 potential of energy integration, to minimise the life cycle impacts of the process.

437

438 Compared to citrus waste, adverse life cycle impacts of algal limonene production were significantly
439 enhanced, particularly with respect to ozone depletion, agricultural land use and water depletion. This
440 could be mostly attributed to the high allocation factor given to limonene production from the algal
441 route (66%) compared to the citrus route (1%). At the same time, algal limonene production offers a
442 number of significant advantages, most notably the potential for gasification and electricity
443 generation from waste biomass, which was found to significantly outweigh the energy requirements
444 of the process. Consequently, the algal route, incorporating electricity production, had a substantial
445 net positive impact on a number of life cycle categories, most notably climate change and fossil
446 resource depletion. This highlights the importance of identifying the most effective ways to maximise
447 the utilisation efficiency of the huge amount of solar energy stored inside biowaste.

448

449 By analysing the individual stages of the PLC production process, it was found that the use of TBHP
450 as an electron carrier for the redox reaction between limonene and hydrogen peroxide had a
451 significant negative impact on the overall process despite its low quantities compared to the other
452 reaction chemicals. More research should therefore be focused on the development of alternative
453 limonene oxidation routes, such as applying hydrogen peroxide directly, as well as quantifying the
454 actual TBHP losses from the process.

455

456 Interestingly, energy integration had only a limited positive impact on the overall life cycle
457 assessment, which was attributed to the ambient reaction temperatures employed in this process.
458 Finally, cost estimates for PLC production ($\$1.36 \text{ kg}^{-1}$ to $\$1.51 \text{ kg}^{-1}$) were comparable to the cost of
459 polystyrene, and it was therefore concluded that the proposed process has great potential to replace
460 fossil based polystyrene with biomass derived PLC.

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