



*Citation for published version:*

Parsons, S, Poyntz-Wright, O, Kent, A & McManus, M 2019, 'Green Chemistry for Stainless Steel Corrosion Resistance: Life Cycle Assessment (LCA) of Citric Acid versus Nitric Acid Passivation', *Materials Today Sustainability*, vol. 3-4, 100005. <https://doi.org/10.1016/j.mtsust.2019.01.001>

*DOI:*

[10.1016/j.mtsust.2019.01.001](https://doi.org/10.1016/j.mtsust.2019.01.001)

*Publication date:*

2019

*Document Version*

Peer reviewed version

[Link to publication](#)

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# 1 Green Chemistry for Stainless Steel Corrosion 2 Resistance: Life Cycle Assessment (LCA) of 3 Citric Acid versus Nitric Acid Passivation

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## 9 Abstract

10 Corrosion is a significant problem in many industries, and when using stainless steel,  
11 passivation is undertaken to improve corrosion resistance.

12 Traditionally, nitric acid is used within the passivation step, however, this has some  
13 detrimental environmental and human health impacts during its production and use.

14 Reducing this impact is critical, and because of its toxicity, associated occupational risk and  
15 special disposal requirements, end-users of passivated stainless steels are exploring  
16 alternative passivation methods. However, it is also critical to understand the impact of any  
17 alternatives. Sustainable processing and manufacture embodies many elements, including;  
18 waste reduction, resource efficiency measures, energy reduction and the application of  
19 'green' or renewable chemicals. In order to ensure the most effective system is utilised the  
20 impact, or potential impact of the system must be measured and options compared. The  
21 comparative environmental credentials of bio-based chemicals can be assessed using tools  
22 such as Life Cycle Assessment (LCA).

23 This paper is the first paper to evaluate the environmental impact of passivation using nitric  
24 and citric acid. It uses attributional Life Cycle Assessment (ALCA) to assess the  
25 environmental benefits and dis-benefits of using citric acid - produced biologically via  
26 fermentation, to replace nitric acid, whilst keeping the same level of corrosion resistance.  
27 The work is anticipatory in nature as the process is not yet undertaken on a commercial  
28 basis. The results therefore feed into future manufacturing and design.

29 Citric and nitric acids were compared using three different solutions: 4% and 10% citric acid  
30 solutions, and a 10% nitric acid solution (the conventional case). The results show that a  
31 scenario using a 4% citric acid solution is environmentally preferable to nitric acid across all  
32 impact categories assessed. However, a 10% citric acid solution used on low chromium and  
33 nickel steel was only environmentally preferable for 50% of the environmental impact  
34 categories assessed due to increased electrical energy demand for that scenario.

35 -

## 36 Highlights

- 37 • Citric acid is environmentally preferable to nitric acid for stainless steel passivation
- 38 • Extent is dependent on passivation bath conditions for comparable performance
- 39 • Life cycle approach is key to understanding nuances of environmental impact for  
40 stainless steel passivation

## 41 Key words

42 Stainless steel, passivation, environmental impact, life cycle assessment, LCA

## 43 1.0 Introduction

44 Sustainability has become an increasingly important element in materials manufacture,  
45 leading to focus on process energy reduction and the application of green chemistry and  
46 other eco-design principles. The term 'green chemistry' gained traction during the 1990's  
47 culminating in formal recognition through the publication of the 12 principles of green

48 chemistry [1]. The guiding element to this being 'benign by design'. The principles provide a  
49 toolkit for employing ideas embedded in industrial ecology [2]. The Environmental Protection  
50 Agency (EPA) definition of green chemistry is 'the design of chemical products and  
51 processes that reduce or eliminate the use or generation of hazardous substances. Green  
52 chemistry applies across the life cycle of a chemical product, including its design,  
53 manufacture, use, and ultimate disposal' [3].

54 Metrics for green chemistry include the *Efactor* defined as the amount of waste produced per  
55 kilogram (product) [4], *reaction mass efficiency* or *carbon efficiency* [5], and *Cfactor* which is  
56 the mass ratio of CO<sub>2</sub> to product mass [6], however, it does not distinguish between fossil  
57 and biogenic CO<sub>2</sub> emissions.

58 Given that the overarching aim of green chemistry employs life cycle thinking and a  
59 consideration for the whole chemical product system, techniques like Life Cycle Assessment  
60 (LCA) are often used to quantitatively assess the potential environmental impacts of bio-  
61 based/renewable solvents or resource efficiency measures [7, 8]. LCA evaluates  
62 environmental impact of a chemical process from raw materials production all the way  
63 through to end-of-life [9]. It is a comparative assessment method, meaning that it can be  
64 usefully applied to compare 'green' and conventional production methods. Unlike the green  
65 chemistry metrics, LCA also enables the comparison of production processes across a  
66 number of different environmental impact categories. ISO standards 14040 and 14044 set  
67 out procedures and methodologies for carrying out an LCA study [10, 11]. LCA has four  
68 main components: goal and scope definition, life cycle inventory (LCI), life cycle impact  
69 assessment (LCIA), and interpretation [10]. The goal and scope definition describes the  
70 product or process under assessment and details the purpose of the study. In the life cycle  
71 inventory step data is collected to then be analysed in the impact assessment stage.

72 There are a number of challenges in applying LCA to green chemistry and biotechnology. At  
73 design or process development stages, LCA is often seen as too complex when evaluating  
74 different materials, processing or solvent options – particularly where there is high

75 uncertainty on what the process may look like at scale. Another challenge is the availability  
76 of industrial production data for many biologically derived chemicals and solvents. In order to  
77 overcome some of these issues, key parameters for LCA of green chemicals have  
78 previously been identified in [12]. Never the less, LCA still remains an important assessment  
79 tool in determining comparative impact for bio-based chemicals across a range of  
80 environmental impact criteria.

81 Passivation of stainless steel is an important process to improve corrosion resistance. For  
82 example, within the space industry stainless steels are used in spacecraft and ground  
83 support structures where corrosion risk is high, including the storage and handling of certain  
84 liquids and wastes, propulsion systems, and components and fasteners exposed to harsh or  
85 demanding environments [13]. The effects of corrosion can have substantial economic and  
86 safety impacts, and lead to prolonged periods of asset downtime. The passivation process  
87 removes anodic surface contaminants (e.g. iron compounds) via chemical dissolution and  
88 leads to the formation of a passive oxide layer. The most commonly used acid to do this is  
89 nitric acid. Nitric acid is produced via ammonia oxidation. The process emits nitrous oxides  
90 ( $\text{NO}_x$ ) and ammonia ( $\text{NH}_3$ ) [14]. Nitric acid is highly corrosive and toxic on inhalation, and  
91 whilst it does feature on the EPA's safer chemical choice list for its application as a  
92 processing aid and additive, it is recognised as having some hazard profile issues and is not  
93 necessarily a low level of hazard concern for all human health and environmental endpoints  
94 [15]. Because of its toxicity, associated occupational risk and special disposal requirements,  
95 end-users of passivated stainless steel such as NASA and the European Space Agency  
96 (ESA) have been evaluating the performance of alternative acids, namely citric acid, as a  
97 potential replacement for nitric acid for passivation [13].

98 Citric acid is a common metabolite of plants and animals, also present in the juice of citrus  
99 fruits and pineapple. Its biological source and biodegradability make it a renewable and less  
100 toxic alternative to nitric acid. The acid is predominately used for soft drinks, confectionary,

101 medicinal citrates, with smaller quantities used in dyeing and engraving [16]. On an industrial  
102 scale it is predominately produced via fermentation of *Aspergillus* or *Candida*.

103 Despite the introduction of citric acid products such as CitriSurf® for stainless steel  
104 passivation, to date there has lacked rigorous evaluation of chemical performance as a  
105 passivation medium, and comparative assessment of its environmental impact compared  
106 with nitric acid. The goal of this work is to compare nitric and citric acid production across a  
107 range of environmental impact categories to understand whether biologically produced citric  
108 acid can offer a greener, more environmentally friendly alternative to nitric acid passivation  
109 whilst reaching comparable performance levels.

110

## 111 2.0 Methods

112 This study is to contrast the currently applied nitric acid passivation process with the most  
113 suitable citric acid passivation process for selected types of pristine and welded stainless  
114 steels.

115 The process evaluated in this LCA study is based on a laboratory-scale method for stainless  
116 steel passivation. Primary data was collected based on processing methods employed by  
117 ESR Technology Limited. Secondary sources include databases such as Ecoinvent 3.4 [17]  
118 and published literature, which is referenced accordingly in section 2.2. LCA software  
119 package Simapro 8 is used for the study.

120 The LCA evaluates a range of environmental impact categories as part of life cycle impact  
121 assessment, based on the ILCD recommended midpoint impact assessment categories [18].

122 The full range of midpoint categories are reported: climate change, ozone depletion, human  
123 toxicity (cancer and non-cancer), particulate matter, Ionizing radiation HH, Ionizing radiation  
124 E (interim), photochemical ozone formation, acidification, terrestrial eutrophication,

125 freshwater eutrophication, marine eutrophication, freshwater ecotoxicity, land use, water  
126 resource depletion, mineral, fossil and renewable resource depletion.

127

## 128 2.1 Functional Unit and System Boundaries

129 Within LCA it is common for the environmental impacts to be calculated for the same given  
130 service – the functional unit. The functional unit used for this study is *per 2000 cm<sup>2</sup> of*  
131 *stainless steel surface passivated*. This equates to the average surface area exposed during  
132 one passivation process run in the ESR Technology laboratory. Surface area could be used  
133 as a functional unit as it is assumed that each passivation process yielded a comparable  
134 passivation performance. This equivalence was the basis of the ESR and ESA research into  
135 the passivation processes - needing a functionally equivalent output on an area basis.

136 Cut-off rules (relating to environmental significance of certain materials and energy flows)  
137 were not formally applied to the study; however, some inputs to the process were omitted for  
138 both citric and nitric acid passivation. This includes some laboratory disposables used in the  
139 cleaning of the stainless steel samples, such as disposable knitted polyester cloths and pH  
140 testing paper. This is due to an inability to model these inputs to a reasonable level of  
141 accuracy. Also omitted from this work are inputs relating to bagging and storage of samples,  
142 as the conditions for doing this are assumed to be the same for each acid assessment. The  
143 input of the stainless steel into the passivation process is outside the system boundary of  
144 this work. This was done to ensure focus on the passivation process itself, as for nitric or  
145 citric acid the input of stainless steel is assumed to be the same.

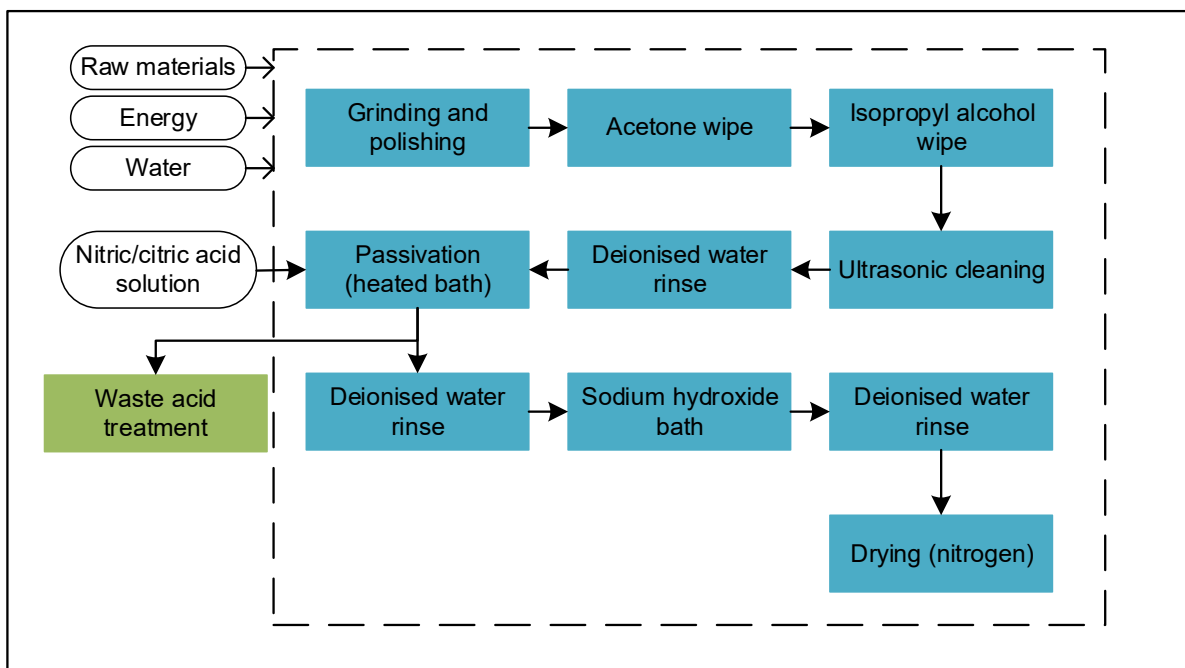
146 The system boundary is given in Figure 1. This includes all activities associated with the  
147 cleaning, acid bath passivation, and subsequent washing and drying of samples. Impacts  
148 are allocated 100% to the functional unit.

149 There are 3 stainless steels evaluated: AISI 410, PH17-7, and AISI 302. This was done in  
150 order to take into account the different processing conditions required for different types of

151 stainless steel based on chromium content. AISI 410 is Martensitic with a lower alloy content  
 152 (~12.5% chromium, 0% nickel content). AISI 302 contains ~18% chromium, 9% nickel, and  
 153 PH17-7 contains ~17% chromium, 7% nickel.

154 The three passivation scenarios were evaluated: 50% nitric acid heated to 55°C and held at  
 155 temperature for 30 minutes (for AISI 302/PH 17-7 and AISI 410 stainless steels); 4% citric  
 156 acid heated to 60°C and held at temperature for 1 hour (AISI 302/PH 17-7 stainless steels);  
 157 and 10% citric acid heated to 80°C and held at temperature for 3 hours (AISI 410 stainless  
 158 steel only – accounting for lower alloying content).

159



160

161 Figure 1. Process flow based flow for stainless steel passivation at laboratory scale (dotted line indicates process  
 162 steps, full line indicates system boundaries)

163

## 164 2.2 Data collection and modelling

165 The LCI was modelled based on primary data from ESR. Material inputs were modelled  
 166 using Ecoinvent 3.4, and are shown in Table 1. An outline of the process is shown in figure



167 1. The abrasive paper used to polish the samples in the first process step was modelled  
168 based on a 3M abrasive paper specification. The acetone wipes used to clean the samples  
169 (3 samples per wipe) excluded the knitted polyester wipe used to apply the acetone. The  
170 same omission was applied to the application of isopropyl alcohol with a polyester wipe.

171 The model for the Lenium® cleaning solution was based on its MSDS data sheet [19]. The  
172 two major components of the solution n-propyl bromide and 2-propanol were modelled using  
173 production data from Ecoinvent (Simpro inputs available in Supplementary Material).

174 For the passivation process direct electricity demand was modelled based on primary data  
175 from ESR. The 3.5l acid bath containing solutions of 4%, 10% w/w citric acid and 50% w/w  
176 nitric acid was modelled using data from Ecoinvent. Subsequent neutralisation with sodium  
177 hydroxide, rinsing with deionised water and drying with gaseous nitrogen was also all  
178 modelled using data from Ecoinvent. Heating of the sodium hydroxide solution to 70°C on a  
179 laboratory hot plate was modelled using energy meter data at the University of Bath. The  
180 bagging and storing of samples is not included in the scope of the study.

181 Electricity production is modelled using the Digest of United Kingdom Energy Statistics  
182 (DUKES) [20]. This assumes a 2015 UK energy mix and assumes a mix broken down in the  
183 following way: 22% coal, 30% natural gas, 21% nuclear, and remaining proportion from  
184 renewables.

185 Within the LCA model, acid waste is treated differently depending on whether it is citric or  
186 nitric acid. Spent nitric acid from the passivation bath (which is assumed to be emptied after  
187 every six samples) is treated by waste solvent incineration. Spent citric acid, emptied from  
188 the passivation bath at the same frequency as the nitric acid, is treated as effluent to waste  
189 water treatment. Within the main LCIA, waste treatment is included as a sub-process within  
190 the passivation step.

191 Waste management is also modelled separately in EcoSolvent [20] to evaluate each acid  
 192 under different waste management scenarios: incineration and waste water treatment.  
 193 Again, this assumes the passivation bath is emptied after each six sample batch.

194 The model assumes a large waste-solvent incineration plant, where the co-products of the  
 195 incineration plant are steam and electricity. Waste water treatment is calculated as a function  
 196 of the waste water composition. The model provides generic and site-specific data ranges  
 197 for mechanical-biological treatment, reverse osmosis and extraction. It is adapted to fit the  
 198 chemical properties of nitric and citric acid.

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Table 1. Inventory for 2000 cm<sup>2</sup> passivation of stainless steel

Item	Process input	Comment
Grit paper	6 pieces	Based on 3M grit paper 12.5% silicon carbide, 87.5% paper backing
Acetone	30 ml	Primary data (ESR)
Isopropyl alcohol	30 ml	Primary data (ESR)
Lenium® solution	0.15 kg	Primary data (ESR) based on 85% n-propyl bromide and 10% 2 propanol
Ultrasonic cleaning bath	1.92 kWh	Primary data (ESR) based on 85% n-propyl bromide and 10% 2 propanol
Deionised water	5.2 kg	Primary data (ESR)
<b>Passivation</b>		
<b>50% nitric acid</b>		
Nitric acid	1.75kg	Primary data (ESR)
Bath heating	0.21 kWh	Primary data (ESR)
Fume hood operation	0.93 MJ	Calculated based on Caltech fume hood energy calculator: <a href="http://fumehoodcalculator.lbl.gov/">http://fumehoodcalculator.lbl.gov/</a>
<b>4% citric acid</b>		
Citric acid	0.14kg	Primary data (ESR)
Bath heating	0.52 kWh	Primary data (ESR)
Fume hood operation	1.8 MJ	Calculated based on Caltech fume hood energy calculator: <a href="http://fumehoodcalculator.lbl.gov/">http://fumehoodcalculator.lbl.gov/</a>
<b>10% citric acid</b>		
Citric acid	0.35kg	Primary data (ESR)

Bath heating	3.3 kWh	Primary data (ESR)
Fume hood operation	5.6 MJ	Calculated based on Caltech fume hood energy calculator: <a href="http://fumehoodcalculator.lbl.gov/">http://fumehoodcalculator.lbl.gov/</a>
Sodium hydroxide solution	2l	Primary data (ESR)

206

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208

## 209 2.3 Assumptions and Limitations

210 There are a number of assumptions and limitations associated with the LCA study. The  
 211 process is based on laboratory scale stainless steel passivation, therefore may not be  
 212 indicative of passivation at industrial scale. The production of steel is not included within the  
 213 scope of the LCA to allow direct comparison between passivation acids (with the production  
 214 of citric and nitric acid included in the scope of the study). Some laboratory consumables are  
 215 omitted from the study, such as polyester wipes used for initial degreasing of the samples,  
 216 as it has proved difficult to obtain inventory data to accurately represent these. These form  
 217 only a very small part of the study and are their omission is therefore thought to have  
 218 minimal impact on the results. As per standard LCA practice, the production of laboratory  
 219 equipment is also not included within the scope of the assessment.

220 In the LCA study it is assumed that nitric and citric acid undergo different waste treatment  
 221 options. Nitric acid is treated via waste solvent incineration, and citric acid via waste water  
 222 treatment. There is uncertainty as to what would be the case at an industrial scale, and  
 223 therefore waste treatment was also modelled separately in Ecosolvent.

## 224 3.0 Results and Discussion

### 225 3.1 Contribution analysis

226 The contribution of each processing step to the overall environmental impact of the whole  
 227 passivation process was assessed using the ILCD recommended midpoint impact  
 228 assessment categories. In this analysis everything is analysed as a percentage contribution

229 of the individual process. This indicates within each option which impact has the most  
230 significant contribution.

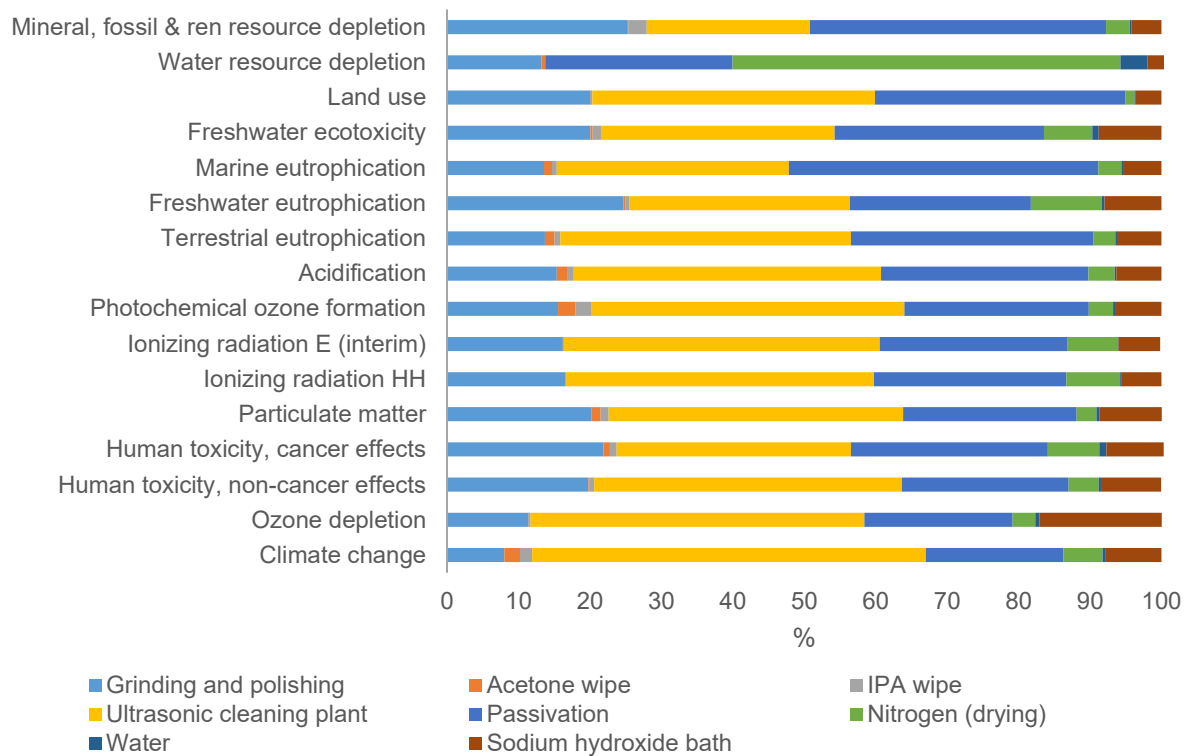
231 The contribution results assess the following 3 scenarios for the passivation bath step:

- 232 • 50% nitric acid heated to 55°C and held at temperature for 30 minutes (AISI 302/PH  
233 17-7 and AISI 410 stainless steels)
- 234 • 4% citric acid heated to 60°C and held at temperature for 1 hour (AISI 302/PH 17-7  
235 stainless steel)
- 236 • 10% citric acid heated to 80°C and held at temperature for 3 hours (AISI 410  
237 stainless steel)

238

239 Impact relating to acid usage and waste disposal is included as part of the passivation step.

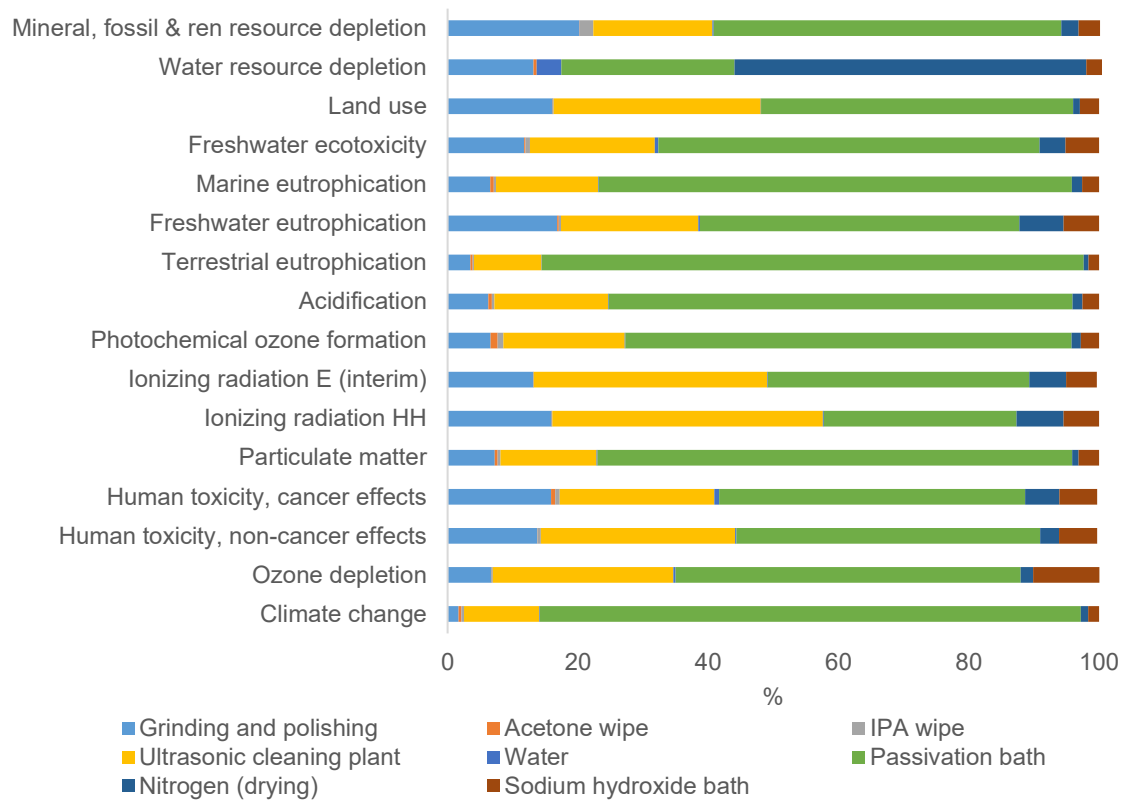
240 [Figure 2](#) shows the contribution to total impact for the 4% citric acid scenario. Major  
241 contributors to climate change impact (kg CO<sub>2</sub>eq) are the ultrasonic cleaning step (55%) and  
242 the passivation step (19%). Within both of these stages the main contribution to impact is  
243 from process energy use – the operation of the cleaning bath or the passivation bath.  
244 Further impact categories show a similar trend with ultrasonic cleaning and passivation step  
245 dominating.



246

247 Figure 2 Contribution analysis for AISI 302/PH 17-7 4% citric acid

248 The passivation step is far more dominant for the 50% nitric acid scenario (Figure 3  
 249 3). Here contribution to climate change impact is 83% of the total score. Passivation  
 250 dominates other environmental impact categories. The dominance of the passivation step  
 251 relates to the production of nitric acid. Nitric acid in Ecoinvent via the Ostwald process is  
 252 dominated by ammonia production.

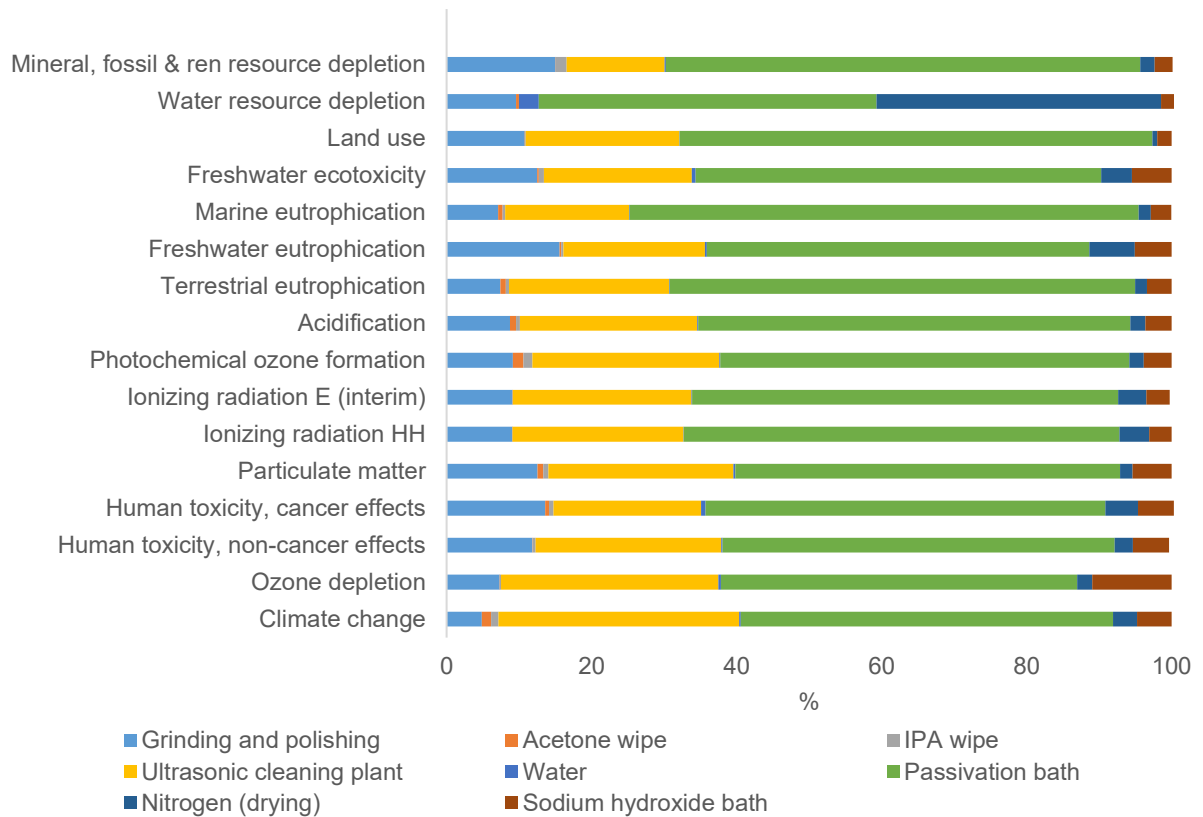


253

254 Figure 3 Contribution analysis for AISI 302/PH 17-7 and AISI 410 50% nitric acid

255 The 10% citric acid scenario is used for the AISI 410 steel type only (figure 5). This has a far  
 256 lower chromium and nickel alloy content (12.5% chromium, 0% nickel). Here the passivation  
 257 step dominates impact for the majority of impact categories assessed. For climate change it  
 258 contributes to 51% of overall impact. For freshwater ecotoxicity it contributes 56%, and for  
 259 human toxicity (cancer and non-cancer) it contributes 55%. Sub-processes leading to the  
 260 significant contribution of the passivation bath step to total impact are energy demand (bath  
 261 operation) and production of citric acid. In this case citric acid is assumed to be produced via  
 262 the fermentation of microorganism *Aspergillus niger*. Fermentation data is provided by a  
 263 European citric acid producer, but the dataset aggregated by Ecoinvent to protect process  
 264 confidentiality. Due to the contribution of the citric acid, further exploration undertaken in this  
 265 area showed that although the process is widely known there is no published disaggregated  
 266 data available on this. However, based on analysis of ecoinvent proxies (and previous

267 evaluation by [22]) indicate that the impacts in citric acid production result predominantly  
 268 from the feedstock and any energy used in associated fermentation.



269  
 270 Figure 4 Contribution analysis for AISI 410 10% citric acid

### 272 3.2 Comparisons

273 All three passivation scenarios can be compared against each other (figure 5). All impacts  
 274 are compared with nitric acid as the reference, which is shown as 100% impact. Therefore,  
 275 effectively the two citric acid options are compared to nitric acid as the base case.

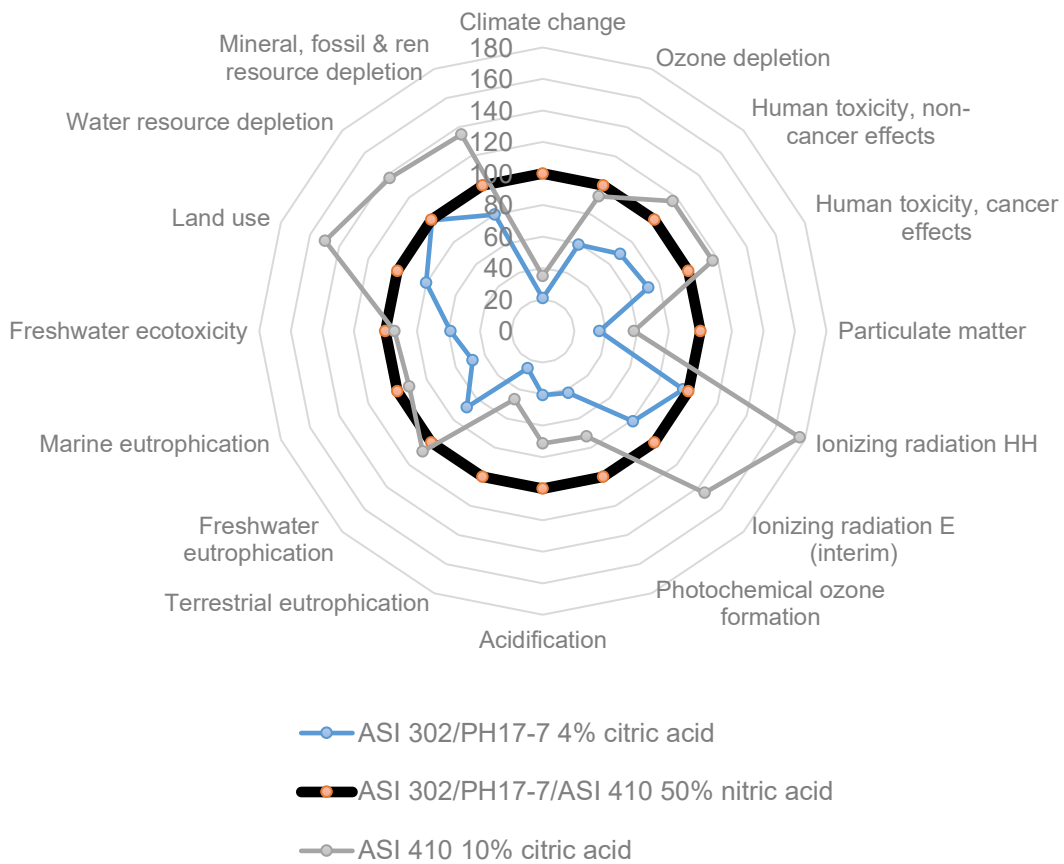
276 Comparing the 4% citric acid scenario used for AISI 302 and PH17-7 stainless steels against  
 277 the 50% nitric acid scenario used for all steels, the 4% scenario performs better across all  
 278 ILCD impact categories. For 8 out of the 16 ILCD impact categories for the 10% citric acid  
 279 scenario (AISI 410 stainless steel) has a higher environmental impact than the 50% nitric

280 acid scenario. This is due to the production of electricity required to heat the passivation bath  
281 for three hours. Options to reduce this would include using a higher penetration renewable  
282 technology for the heating, or heating in a more efficient way, if possible.

283 The comparisons made here show that despite the increased toxicity and environmental  
284 impact from use of nitric acid as opposed to bio-based citric acid to passivate stainless steel,  
285 where the process requires longer heating periods (10% citric acid scenario) and hence  
286 higher process energy inputs this reduces some of the environmental gains made through  
287 use of bio-based chemicals. The findings here highlight why multi-impact category  
288 assessment methods like LCA are valuable for assessing green manufacturing alternatives.

289 Table 2 shows the characterised data in terms of absolute total values. The same data as in  
290 Figure 5 is shown here, but not in terms of a percentage of the largest impact in each  
291 category. Therefore, here one can compare the impact across the scenarios all the  
292 scenarios in absolute terms for each scenario.





293

294 Figure 5. Comparison of each acid passivation scenario across all ILCD Recommended impact categories (nitric  
 295 acid = 100%)

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305 Table 12. Breakdown of individual ILCD impact scores for each passivation scenario

Impact category	Unit	AISI 302/PH17-7 4% citric acid	AISI 302/PH17-7/AISI 410 50% nitric acid	AISI 410 10% citric acid
Climate change	kg CO2 eq	2.42E+00	1.15E+01	4.02E+00
Ozone depletion	kg CFC-11 eq	4.92E-07	8.29E-07	7.67E-07
Human toxicity, non-cancer effects	CTUh	8.39E-07	1.21E-06	1.41E-06
Human toxicity, cancer effects	CTUh	1.26E-07	1.74E-07	2.03E-07
Particulate matter	kg PM2.5 eq	1.89E-03	5.27E-03	3.04E-03
Ionizing radiation HH	kBq U235 eq	8.75E-01	9.07E-01	1.60E+00
Ionizing radiation E (interim)	CTUe	2.42E-06	2.99E-06	4.34E-06
Photochemical ozone formation	kg NMVOC eq	8.46E-03	1.99E-02	1.44E-02
Acidification	molc H+ eq	2.04E-02	5.02E-02	3.58E-02
Terrestrial eutrophication	molc N eq	3.40E-02	1.34E-01	6.27E-02
Freshwater eutrophication	kg P eq	1.17E-03	1.71E-03	1.85E-03
Marine eutrophication	kg N eq	3.73E-03	7.73E-03	7.10E-03
Freshwater ecotoxicity	CTUe	1.89E+01	3.22E+01	3.03E+01
Land use	kg C deficit	1.03E+01	1.28E+01	1.91E+01
Water resource depletion	m3 water eq	2.25E-02	2.26E-02	3.11E-02
Mineral, fossil & ren resource depletion	kg Sb eq	1.80E-04	2.25E-04	3.04E-04

306

### 307 3.3 Acid waste treatment

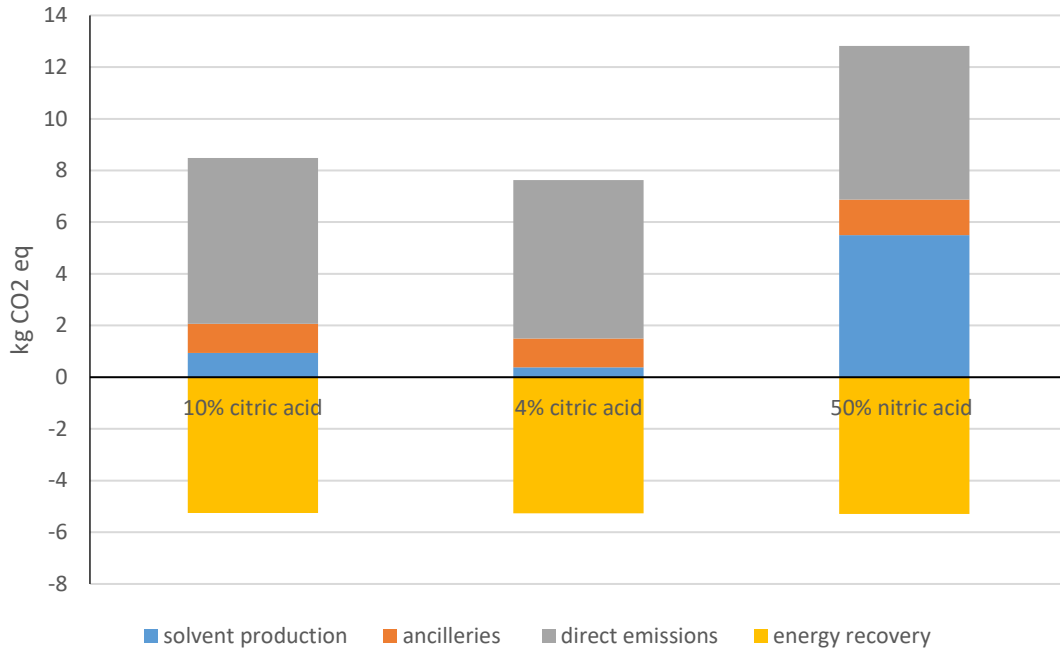
308 Aside from potentially different processing conditions for citric (4%, 10% scenarios) and nitric  
309 acid during the stainless steel passivation process, the methods for acid disposal also differ.  
310 Nitric acid is highly corrosive and a strong oxidiser meaning that the 50% nitric acid solution  
311 within the passivation bath will require special handling. It is likely that it would be disposed  
312 of via a formal solvent disposal route as opposed to an industrial waste water treatment  
313 system. Within the LCA model itself the nitric acid is assumed to be incinerated, whereas the  
314 citric acid is treated via waste water treatment. For transparency, the disposal methods are  
315 compared using Ecosolvent, which is a life cycle assessment tool developed by ETH Zurich  
316 to quantify impacts relating to waste solvent treatment [20]. The tool models a hazardous  
317 waste solvent incineration plant, and an industrial waste water treatment plant. Coproducts  
318 from the incineration plant are steam and electricity, with environmental credits granted for  
319 these.

320 Ecosolvent holds data for 26 solvents based on their elemental composition, heat of  
321 vaporisation, and heating value. The model for these was adapted for nitric and citric acid  
322 using their chemical property information. The incineration model calculates inventory data  
323 for solvent combustion as a function of chemical composition. The model is based on data  
324 for a Swiss incineration plant with a capacity of 35,000 tonnes per year. Results from each  
325 waste scenario are reported in terms of their global warming potential

326 For the incineration scenario (figure 6), incineration energy recovery for all 3 scenarios is not  
327 enough to counter direct emissions from the process. Per functional unit impact from solvent  
328 production is far higher for nitric acid than for both citric acid scenarios. GWP totals for 10%,  
329 4% citric acid and 50% nitric acid were 3.23, 2.37 and 7.52 kg CO<sub>2</sub>eq respectively.

330 Impact from treatment at a waste water treatment plant (figure 7), despite not including any  
331 energy recovery, is environmentally favourable for all acid passivation scenarios. Impact is  
332 separated between solvent production, electricity and ancillaries in mechanical-biological  
333 treatment and associated emissions (MBTP), sludge treatment, and waste water treatment  
334 (WWTP). Impacts relating to reverse osmosis and extraction are zero. The relative GWP for  
335 10%, 4% citric acid and 50% nitric acid scenarios is 1.79, 0.72, and 5.5 kg CO<sub>2</sub>eq.

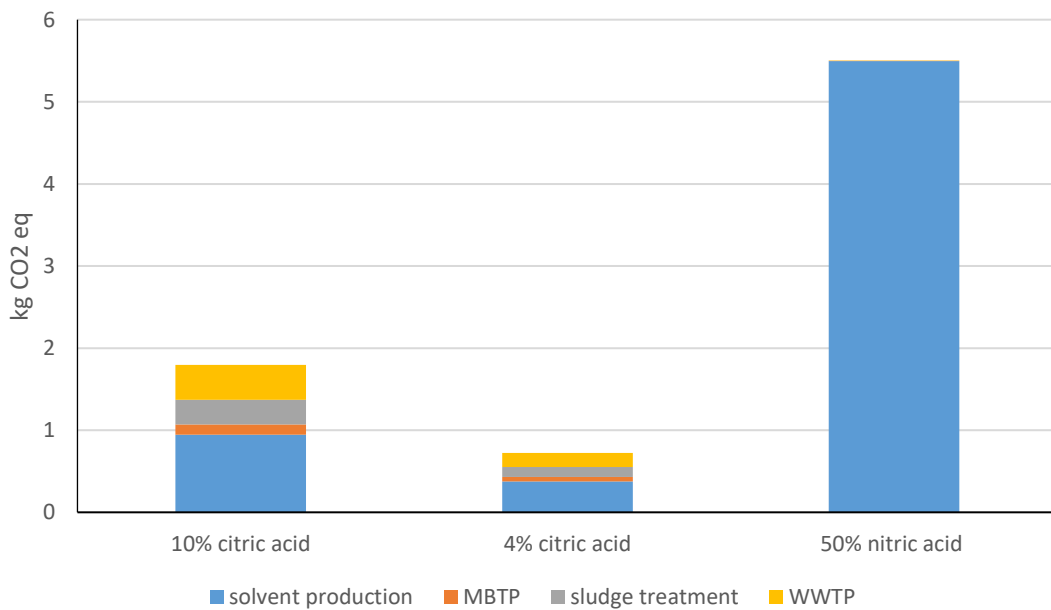
336 The results from modelling of waste treatment show that for both waste treatment options  
337 nitric acid has the higher GWP potential compared with both 4% and 10% citric acid  
338 scenarios. However, much of this additional impact comes from nitric acid production  
339 (particularly for waste water treatment), rather than the waste disposal method selected.



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Figure 6 Waste solvent treatment - Incineration. Global Warming Potential (GWP) per functional unit



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Figure 7 Waste solvent treatment. Waste water treatment plant. Global Warming Potential (GWP) per functional unit

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## 348 4.0 Conclusions

349 The use of green chemicals in manufacture and materials treatment processes, increases  
350 sustainability and helps to avoid difficult scale-up issues relating to chemical health and  
351 safety implications. Bio-based, renewable chemicals have the potential to be safer and have  
352 lower environmental impacts associated with both production and disposal stages of their life  
353 cycle than many conventional chemicals and solvents. However that is not always the case,  
354 and using Life cycle assessment (LCA) is a useful quantitative method for determining the  
355 comparative benefits or dis-benefits when selecting certain 'green' chemicals.

356 When treating stainless steel for corrosion resistance, there is increasing interest in  
357 passivating them using citric acid as opposed to nitric acid. Nitric acid is highly corrosive and  
358 toxic on inhalation, requiring heightened EHS criteria. This paper provides the first LCA of  
359 the potential benefits of citric acid over nitric acid as a passivation technique. This is based  
360 on the required conditions for passivation in order to generate the same corrosion resistance  
361 performance.

362 The LCA results show that the 4% citric acid scenario using AISI 302 and PH17-7 stainless  
363 steels, is environmentally preferable to 50% nitric acid across all ILCD recommended  
364 environmental impact categories. However, for the lower chromium and nickel content  
365 stainless steel AISI 410, the environmental benefits of moving to citric acid are less  
366 pronounced with only 50% of the ILCD impact categories assessed having a lower impact  
367 score than the nitric acid case. Impact associated with ionising radiation, resource depletion,  
368 and human toxicity were higher for the 10% citric acid scenario than for the nitric acid  
369 scenario. This is due to the increased time required within the heated passivation bath for  
370 the 10% citric acid scenario over the 4% citric acid, and 50% nitric acid scenarios.

371 This work demonstrates the importance of LCA as a method for evaluating processes which  
372 contain 'green' or bio-based chemicals. Evaluation across a number of different impact  
373 categories reveals a more nuanced picture of comparative environmental impact than that

374 given through use of singular assessment metrics. This is despite modelling approach  
375 having been carried out at a laboratory scale and lead to potential misalignment with actual  
376 processing at industrial scale. Process energy provision during passivation has been shown  
377 to strongly influence the scale of environmental gains made by switching to a 'greener' acid  
378 alternative.

## 379 Acknowledgements

380 This work was carried out as part of the activity "Citric Acid as a Green Replacement for  
381 Steel Passivation", funded by the European Space Agency (ESA) under the Technology  
382 Research Programme, Contract no. 4000114892/15/NL/KML. ESR (Oliver Poyntz-Wright  
383 and Anthony Kent) provided the data and technical guidance in constructing the process  
384 model for passivation used in the LCA. The University of Bath (Parsons and McManus)  
385 undertook the LCA modelling and analysis. We also thank ESA (Advenit Makaya, Julian  
386 Austin) for their technical input and direction on goal and scope definition of the LCA study  
387 itself.

## 388 Data availability

389 Primary data was provided by ESR Technology Limited. The raw data required to reproduce  
390 these findings is available in the Supplementary Material. Processed data produced using  
391 Simapro 8 and Ecosolvent is presented within the body of this paper.

## 392 References

- 393 1. Anastas, P.T. and J.C. Warner, *Green chemistry: theory and practice*. 1998, New  
394 York: Oxford University Press.
- 395 2. Lankey, R.L. and P.T. Anastas, *Life-Cycle Approaches for Assessing Green*  
396 *Chemistry Technologies*. Industrial and Engineering Chemistry Research, 2002.  
397 **41**(18): p. 4498–4502.

- 398 3. EPA. *Basics of Green Chemistry*. 2018 05/2018]; Available from:  
399 <https://www.epa.gov/greenchemistry/basics-green-chemistry>.
- 400 4. Sheldon, R.A., *Organic synthesis; past, present and future*. Chemical Industry, 1992:  
401 p. 903-906.
- 402 5. Curzons, A.D., et al., *So you think your process is green, how do you know?—Using*  
403 *principles of sustainability to determine what is green—a corporate perspective*. Green  
404 Chemistry, 2001. **3**: p. 1-6.
- 405 6. Voss, B., et al., *C factors pinpoint resource utilization in chemical industrial*  
406 *processes*. ChemSusChem, 2009. **2**: p. 1152–1162.
- 407 7. Capello, C., U. Fischer, and K. Hungerbühler, *What is a green solvent? A*  
408 *comprehensive framework for the environmental assessment of solvents*. Green  
409 Chemistry, 2007. **9**: p. 927-934.
- 410 8. Slater, C.S., et al., *Environmental analysis of the life cycle emissions of 2-methyl*  
411 *tetrahydrofuran solvent manufactured from renewable resources*. Journal of  
412 Environmental Science and Health, Part A 2016. **51**(6): p. 487-494
- 413 9. Burgess, A. A., Brennan, D. J., *Application of life cycle assessment to chemical*  
414 *processes*. Chemical Engineering Science, 2001, **56**(8), 2589-2604
- 415 10 ISO, *Environmental management -- Life cycle assessment -- Principles and*  
416 *framework*. 2006, International Organization for Standardization.
- 417 11 ISO, *Environmental management -- Life cycle assessment -- Requirements and*  
418 *Guidelines*. 2006, International Organization for Standardization
- 419 12. Tufvesson, L.M., et al., *Life cycle assessment in green chemistry: overview of key*  
420 *parameters and methodological concerns*. The International Journal of Life Cycle  
421 Assessment, 2013. **18**(2): p. 431–444.
- 422 13. Yasensky, D., et al. *Citric Acid Passivation of Citric Acid Passivation of Stainless*  
423 *Steel*. 2011 08/2017]; Available from:  
424 <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20110001362.pdf>.

- 425 14. EPA. *Nitric acid*. 2018 05/2018]; Available from:  
426 <https://www3.epa.gov/ttnchie1/ap42/ch08/final/c08s08.pdf>.
- 427 15. EPA. *Safer Chemical Ingredients List*. 2018 05/2018]; Available from:  
428 <https://www.epa.gov/saferchoice/safer-ingredients>.
- 429 16. Angumeenal, A.R. and D. Venkappayya, *An overview of citric acid production*. LWT -  
430 Food Science and Technology, 2013. **50** (2): p. 367-370.
- 431 17. Wernet, G., et al., *The ecoinvent database version 3 (part I): overview and*  
432 *methodology*. The International Journal of Life Cycle Assessment, 2016. **21**(9): p.  
433 1218–1230.
- 434 18. ILCD, *Recommendations for Life Cycle Impact Assessment in the European context*,  
435 European Commission-Joint Research Centre - Institute for Environment and  
436 Sustainability, 2011, EUR 24571 EN. Luxemburg
- 437 19. Petroferm Inc. *MATERIAL SAFETY DATA SHEET* 08/2017]; Available from:  
438 <http://www.cleansolutions.org/downloads/msds/610/Lenium%20GS%20MSDS.pdf>.
- 439 20. BEIS. *Digest of UK Energy Statistics (DUKES)*. 2015 05/2017]; Available from:  
440 [https://www.gov.uk/government/collections/digest-of-uk-energy-statistics-](https://www.gov.uk/government/collections/digest-of-uk-energy-statistics-dukes#2015)  
441 [dukes#2015](https://www.gov.uk/government/collections/digest-of-uk-energy-statistics-dukes#2015).
- 442 21. Capello, C., et al. *Ecosolvent*. 2018 05/2017]; Available from:  
443 [http://www.emeritus.setg.ethz.ch/research/downloads/software---](http://www.emeritus.setg.ethz.ch/research/downloads/software---tools/ecosolvent.html)  
444 [tools/ecosolvent.html](http://www.emeritus.setg.ethz.ch/research/downloads/software---tools/ecosolvent.html).
- 445 22. Griffiths, O.G., *Environmental Life Cycle Assessment of Engineered Nanomaterials in*  
446 *Carbon Capture and Utilisation Processes*, in *Faculty of Engineering and Design*.  
447 2014, University of Bath.

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