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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

4 Sophie Parsons^{a†}, Oliver Poyntz-Wright^b, Anthony Kent^b & Marcelle C. McManus^a

5 ^aDepartment of Mechanical Engineering, University of Bath, Claverton Down, Bath BA2 7AY

6 ^bESR Technology Limited, 202 Cavendish Place, Birchwood Park, Warrington, Cheshire,
7 WA3 6WU

8 †Corresponding author: Sophie Parsons, s.c.parsons@bath.ac.uk

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 CO₂ to product mass [6], however, it does not distinguish between fossil
57 and biogenic CO₂ 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 (NO_x) and ammonia (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 cm² 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.

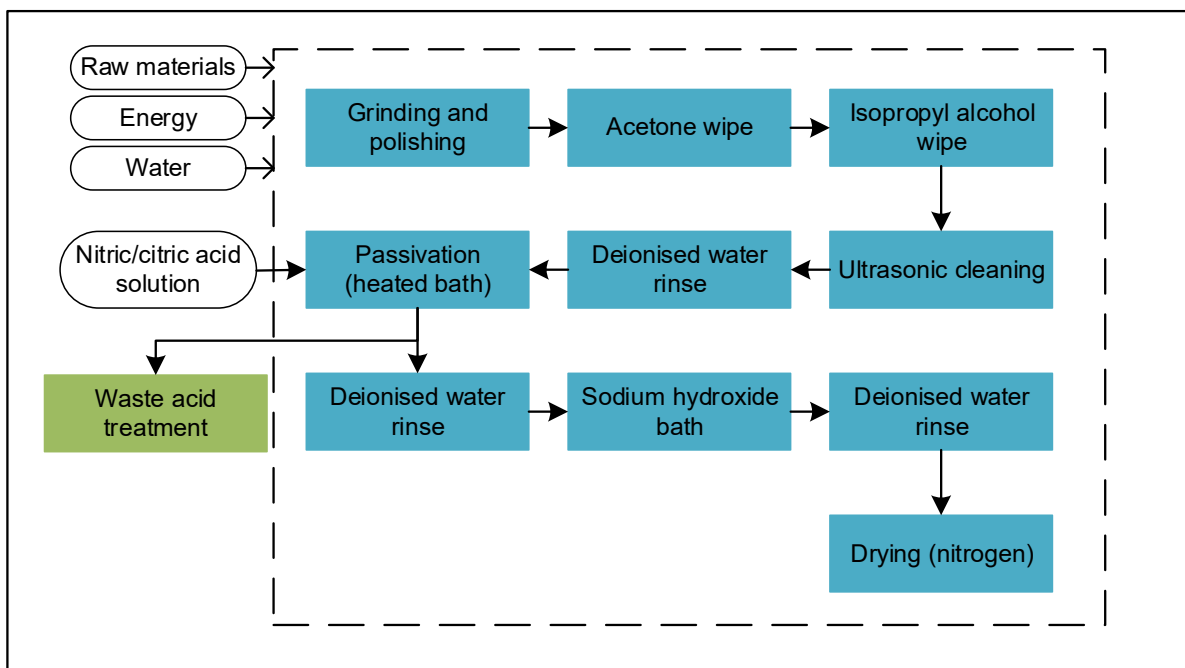
146 The system boundary is given in Figure 1. This includes all activities associated with the
147 cleaning, acid bath passivation, and subsequent washing and drying of samples. Impacts
148 are allocated 100% to the functional unit.

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 cm² 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)
Passivation		
50% nitric acid		
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: http://fumehoodcalculator.lbl.gov/
4% citric acid		
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: http://fumehoodcalculator.lbl.gov/
10% citric acid		
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: http://fumehoodcalculator.lbl.gov/
Sodium hydroxide solution	2l	Primary data (ESR)

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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.

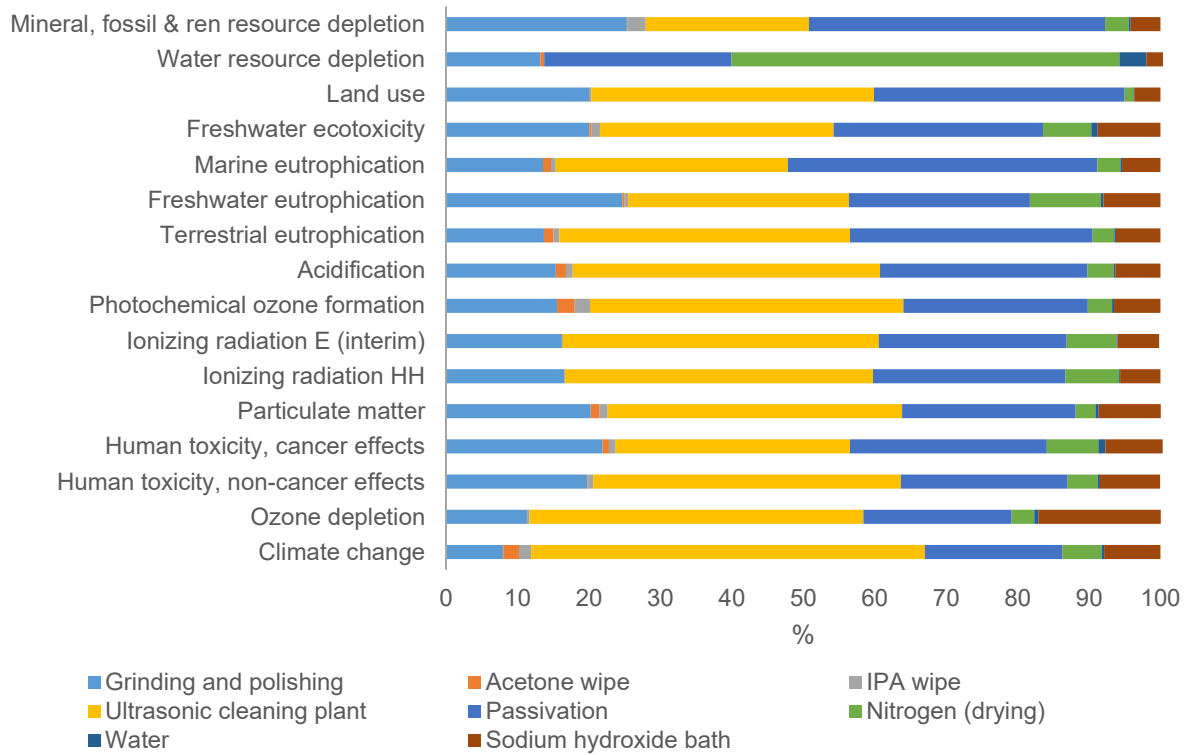
231 The contribution results assess the following 3 scenarios for the passivation bath step:

- 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.

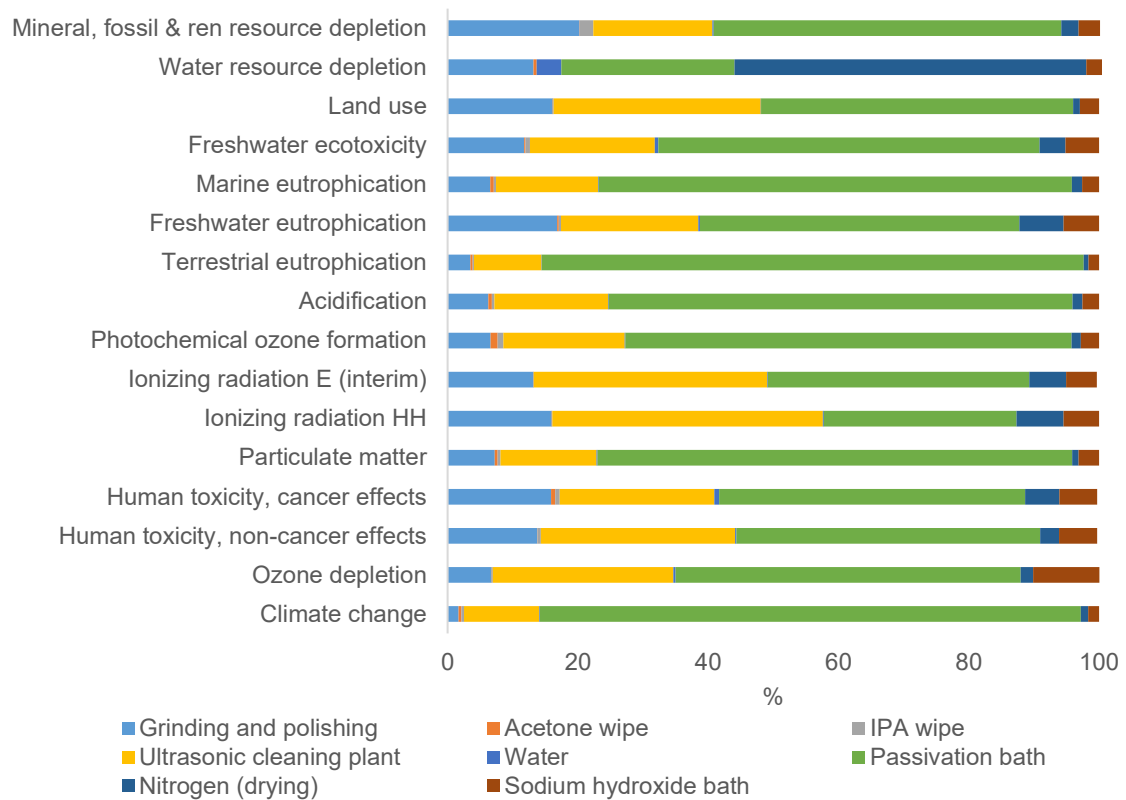
240 [Figure 2](#) shows the contribution to total impact for the 4% citric acid scenario. Major
241 contributors to climate change impact (kg CO₂eq) are the ultrasonic cleaning step (55%) and
242 the passivation step (19%). Within both of these stages the main contribution to impact is
243 from process 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.

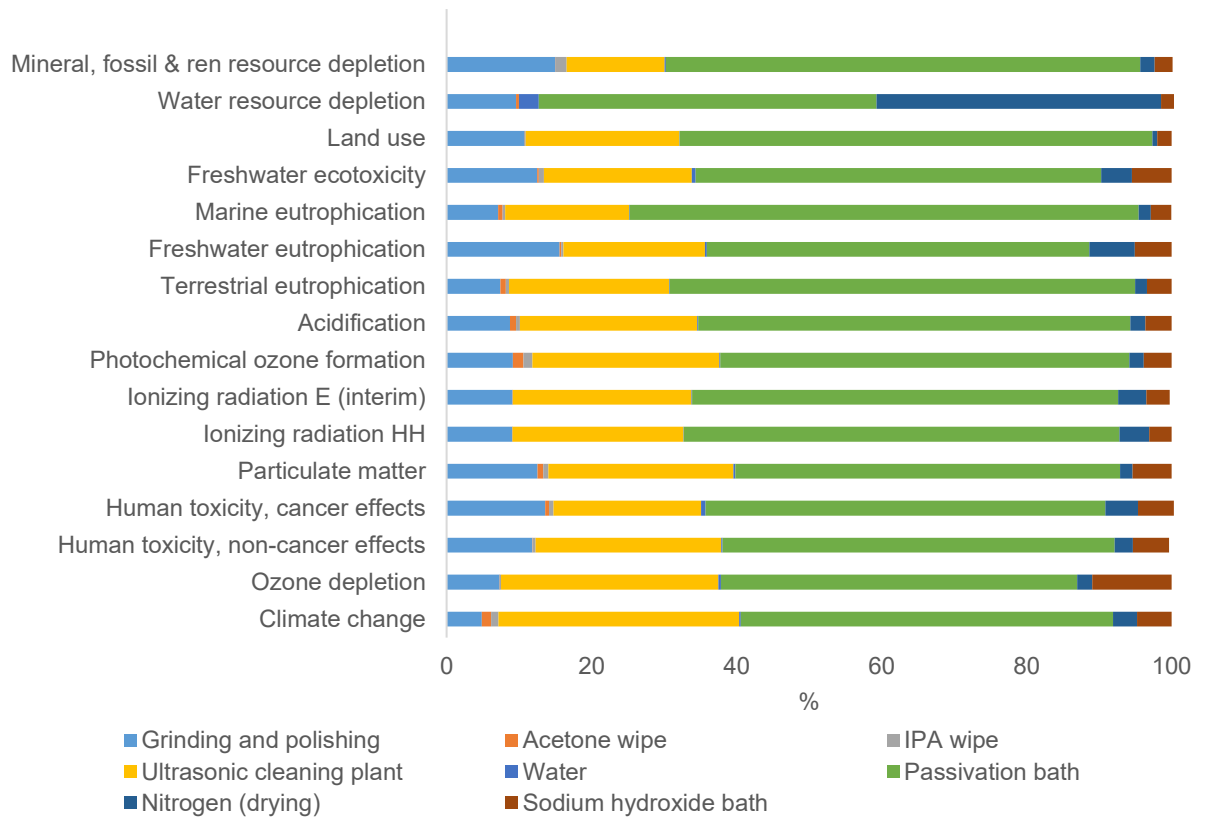


253

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

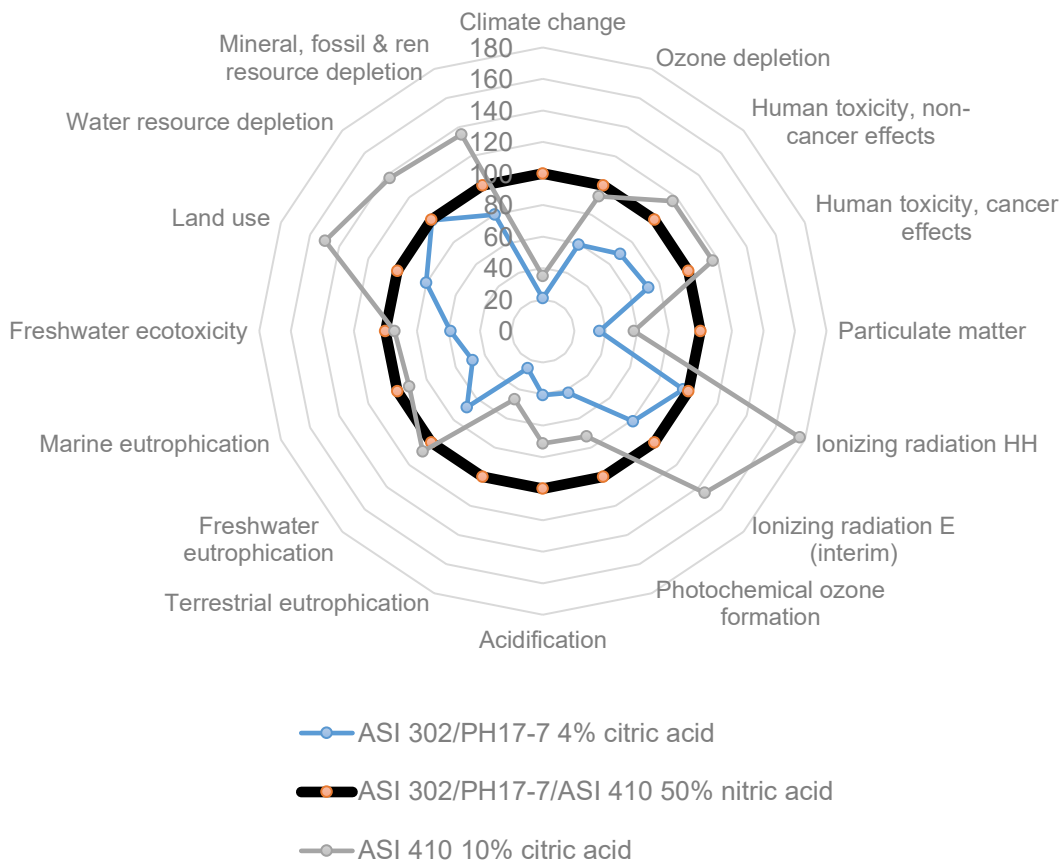
273 All three passivation scenarios can be compared against each other (figure 5). All impacts
 274 are compared with nitric acid as the reference, which is shown as 100% impact. Therefore,
 275 effectively the two citric acid options are compared to nitric acid as the base case.

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

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307 3.3 Acid waste treatment

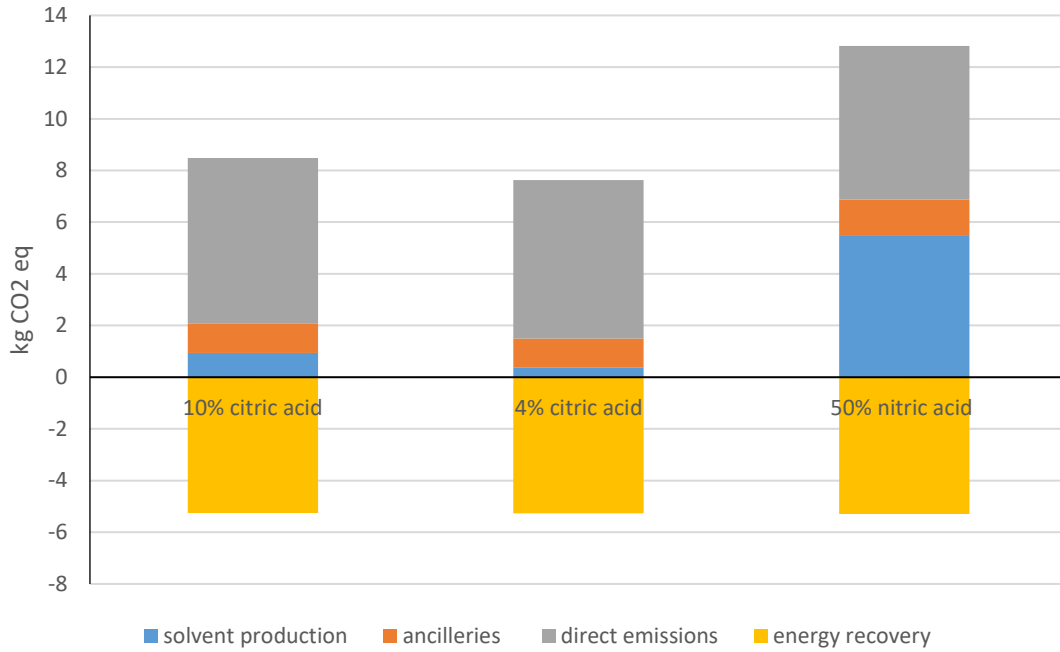
308 Aside from potentially different processing conditions for citric (4%, 10% scenarios) and nitric
309 acid during the stainless steel passivation process, the methods for acid disposal also differ.
310 Nitric acid is highly corrosive and a strong oxidiser meaning that the 50% nitric acid solution
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 CO₂eq 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 CO₂eq.

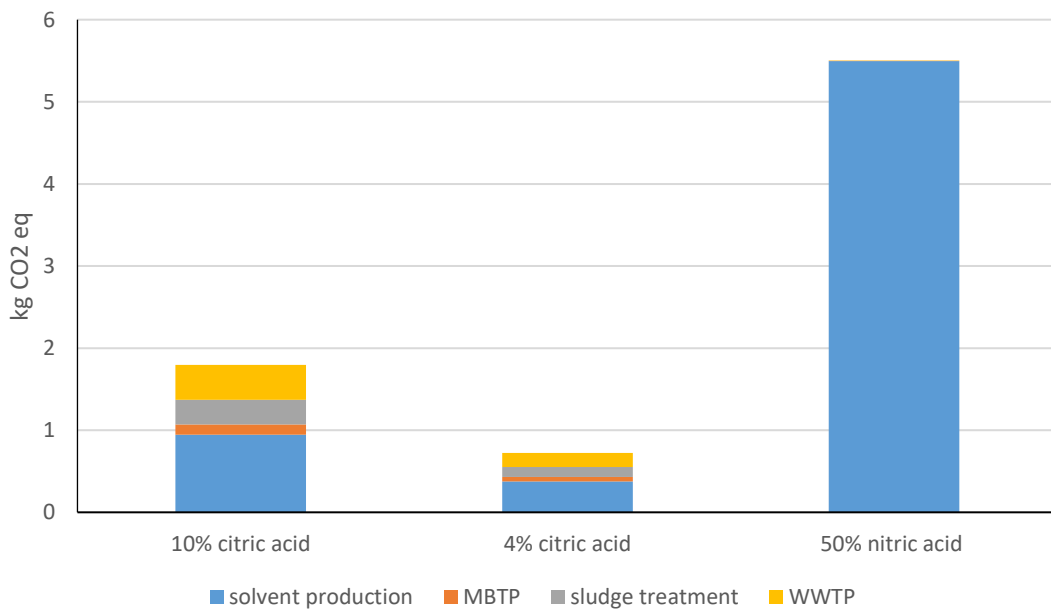
336 The results from modelling of waste treatment show that for both waste treatment options
337 nitric acid has the higher GWP potential compared with both 4% and 10% citric acid
338 scenarios. However, much of this additional impact comes from nitric acid production
339 (particularly for waste water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

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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.

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