

Environmental Impact Evaluation for Heterogeneously Catalysed Starch Oxidation

Tim M. Hoogstad, Stijn M. Timmer, Anton J. B. van Boxtel, Pieter L. Buwalda, Johannes H. Bitter,* and Lars Kiewidt^[a]

Oxidised starch is currently produced from native starch using sodium hypochlorite as an oxidising agent. The use of hypochlorite has undesired side reactions and produces stoichiometric amounts of waste (salt), thus alternative oxidation methods are desired. In this study, the potential of two catalysed starch oxidation methods to reduce the environmental impact (EI) of oxidised starch production are assessed. We compared the EI of oxidation with molecular oxygen (heterogeneously catalysed) and hydrogen peroxide (homogeneously catalysed) to hypochlorite oxidation through life cycle

assessment (LCA). The results confirm that hypochlorite oxidation is the main environmental hotspot in the current process of oxidised starch production, and that both hydroperoxide oxidation and molecular oxygen oxidation can significantly lower the EI of the process. The impact reduction is most significant in the categories of freshwater eutrophication (~67%), ozone depletion (~66%), climate change (35–60%) and resource use (40%–78%) for peroxide and molecular oxygen oxidation, respectively.

Introduction

Chemical oxidation of potato starch, whereby negatively charged carboxylic acid moieties are introduced, produces anionic starch. Anionic starches are a renewable bio-based alternative for polyacrylates in the paper, textile, and food industry. Anionic potato starch has better pasting and adhesive properties and better shelf life than unmodified potato starch.^[1,2] These properties make anionic starch suitable for applications in the paper and textile industry as surface sizing agents, in the food and feed sector as thickeners, and in various adhesive industries.^[3,4] Worldwide, around 100 kilotons of anionic starch are produced annually.

Various oxidation methods are available to produce anionic starches. Oxidation with sodium hypochlorite (NaOCl) is an established process,^[5] and currently still the standard for the industrial production of anionic starch.^[3] However, the use of hypochlorite as an oxidant has several fundamentally unfavourable characteristics, and the application of new techniques like ultrasonication show potential to improve this process.^[6] During hypochlorite oxidation, small amounts of chlorates are formed and some chloride is built into the backbone of the oxidized

starch (<1%).^[5] These undesired side reactions reduce the applicability of oxidised starches depending on legislation, for example, for food applications.

Next to the formation of chlorates, depolymerisation of starch is another side reaction during hypochlorite oxidation. Using hypochlorite, depolymerisation occurs by oxidation at the C2–C3 carbons,^[5,7] inducing oxidative depolymerisation. The link between the molecular weight of starch and its physicochemical properties, for example, pasting properties and viscosity, is well established.^[8–10] Excessive depolymerisation during the oxidation alters the physicochemical properties, that is, decreases viscosity and retrogradation enthalpy of the product, and thereby reduces suitability of the starch for applications like the production of adhesives.^[1,4] Furthermore, excessive depolymerisation of the starch reduces the reaction yield if small maltodextrins (degree of polymerisation, DP, <6) are formed, which do not contribute to gelling properties of a starch mixture.^[11,12]

In addition to depolymerisation, the use of hypochlorite produces stoichiometric amounts of salt (NaCl) during the oxidation process. Moreover, the production of the sodium hypochlorite for starch oxidation raises concerns of a high environmental impact of the overall process. Homogeneously catalysed hydrogen peroxide oxidation with copper sulphate, iron complexes, or vanadium complexes has been proposed as a more environmentally friendly alternative to hypochlorite oxidation.^[3,4,13–15] The downside of the hydrogen peroxide oxidation, however, is that residues of the catalyst remain in the product, resulting in impurities in the product or higher purification costs. This challenge has thus far hindered the industrial scale application of this process.^[3]

The combination of a potentially high environmental impact (chemicals and salts), undesired side reactions (chlorate formation), catalyst residues, and depolymerisation during oxidation, leads to the need for a new method of oxidising

[a] T. M. Hoogstad, S. M. Timmer, Dr. A. J. B. van Boxtel, Dr. P. L. Buwalda, Prof. Dr. J. H. Bitter, Dr. L. Kiewidt
Biobased Chemistry and Technology (BCT)
Wageningen University & Research
P.O. Box 17
6700 AA Wageningen (The Netherlands)
E-mail: harry.bitter@wur.nl

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starch.^[16,17] A potential solution to phase out the chlorine chemistry in starch oxidation is the use of molecular oxygen and heterogeneous catalysts. Heterogeneously catalysed oxidation of dissolved polysaccharides with molecular oxygen has been achieved on the lab scale with supported Au and Pt nanoparticles^[18,19] and vanadium complexes.^[20] With heterogeneous catalysis, no chemically produced oxidant is required, since molecular oxygen from air can be used, the catalyst can be separated easily, and the reaction can be more selective towards C6 oxidation,^[19] resulting in less depolymerisation in the process. We, therefore, hypothesise that oxidation of dissolved starch using molecular oxygen and a solid heterogeneous catalyst could alleviate many of the undesired traits of both hypochlorite and peroxide oxidation, and reduce the environmental impact of the process. However, a quantitative analysis comparing the environmental impact of these oxidation methods is not available yet.^[21]

Comparative life cycle assessments (LCAs) of new methods in an early stage of development provide valuable insights into the requirements that these new methods need to meet to be viable and can thereby guide further catalysis research.^[21] In this work, we therefore quantify the environmental impact of the current production of anionic potato starch with sodium hypochlorite through life cycle assessment and investigate potential changes in environmental impact by applying three catalysed oxidation scenarios: two heterogeneously catalysed oxidations with molecular oxygen and one homogeneously catalysed oxidation with hydrogen peroxide. With this analysis, we assess the requirements that a heterogeneous catalyst needs to meet to reduce the environmental impact of anionic starch production in order to guide research and development of this catalyst.

Materials and Methods

Environmental Impact Analysis

Goal and Scope

The goal of the assessment is to identify hotspots in the current production chain of anionic potato starch, and to estimate potential environmental impact reduction of alternative methods of starch oxidation compared to the current industrial standard, for the production of 1 tonne of anionic potato starch. To this end, a gate-to-gate LCA is applied. The production system was divided into 6 modules to assess pre-processing and side-stream processing steps (modules A and B) in combination with four different oxidation methods (modules OCl⁻, H₂O₂, O₂, and O₂DA). Figure 1 gives an overview of the production system.

Mass and energy balances for each unit operation in all modules (see Supporting Information: Process description) are linked to the life cycle assessment (LCA) to compare the different processing options.

System Boundaries

In this gate-to-gate LCA the first gate is at the delivery of fresh potatoes at the processing facility and the end gate for all processing options, with the exception of the O₂DA scenario, is dried anionic starch. In these scenarios, the starch has to be transported and gelatinised before application. For the option with module O₂DA the end gate is the oxidised starch solution from the oxidation step ready for direct application. Transportation of the dry anionic starch powder and gelatinisation are beyond the system boundaries for options OCl⁻, H₂O₂ and O₂ and have equal impact for all options. Therefore, transportation and gelatinisation of the dry anionic starch are

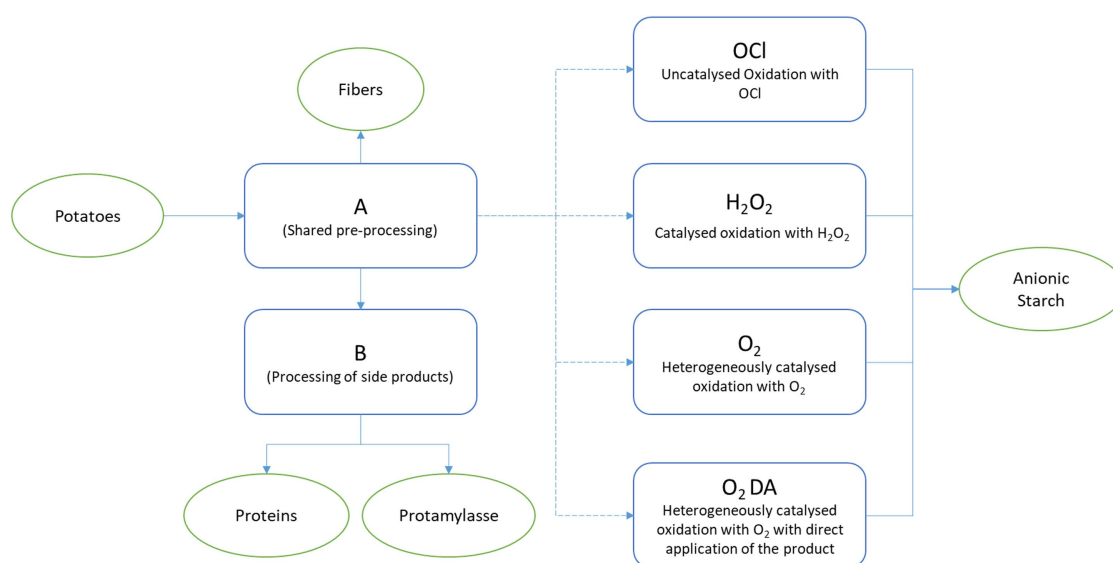


Figure 1. Flowsheet of the overall process to produce anionic starch from potatoes. The dashed lines indicate the four evaluated options for starch oxidation.

omitted from the evaluation of the O₂DA module for an equal comparison. With these system boundaries, the oxidation methods are compared as they would integrate into the current production chain. By doing so, different processing requirements between oxidation and application of the starch are included in the comparison. The LCA is focussed on the unit operations only, other factors like heating and lighting for the facilities, and transport of raw materials to the facilities are excluded.

LCA Methods

Since the LCA is used to compare different processing options for the same product, that is, anionic starch suitable for application, internal normalisation (i.e. relative impact) is used as the main tool for comparison (equations 1 and 2).

Internal normalisation in comparative LCA studies helps avoid macroscopic mistakes, for example, use of datasets that are not scale-calibrated, while providing easily interpretable results.^[22,23] No subsequent weighing step is applied as this can distort the results.^[23,24] Because the quality and quantity of the side streams remain equal for all processing options, allocation of impact to side products is not required. All quantities are expressed per tonne of produced anionic potato starch.

The LCA calculations have been performed with openLCA 1.10.2.^[25] The Life Cycle Inventory (LCI) was based on the Product Environmental Footprints (PEF) database, and impact and category choice follow the International Reference Life Cycle Data System (ILCD 2011 midpoint) method in accordance with the guidelines of the European platform on life cycle assessment made by the Joint Research Centre of the European commission.^[26,27] The categories on ionising radiation and the category water use were omitted from the LCI and ILCD 2011 midpoint method due to limited data availability for some flows, which would result in an incomplete analysis in these categories. Water use was instead evaluated based on total amount of clean water required within the different processes. The list of indicators and their units is given in Table 1. The LCI is given in the Supporting Information.

From all mass and energy streams of each operation (see Supporting Information), the total environmental impact per

unit operation for each impact category is calculated [Eq. (1)]. This results in a matrix with the impact from each unit operation in each impact category:

$$EI_{k,i} = \sum_j F_{k,j} \cdot EIF_{j,i} \quad (1)$$

Where $EI_{k,i}$ is the Environmental Impact of unit operation k in impact category i , $F_{k,j}$ is a quantity of mass or energy j going into unit operation k , and $EIF_{j,i}$ is the environmental impact factor associated with F_j in impact category i .

To compare the different oxidation scenarios, internal normalisation is applied. Hereby, the total impact in a category is calculated by summation of all the impacts across the unit operations. Then, the impact per category for each unit is expressed as a percentage of the total impact [Eq. (2)].

$$NEI_{k,i} = \frac{EI_{k,i}}{\sum_k EI_{k,i}} \cdot 100 \% \quad (2)$$

Where $NEI_{k,i}$ is the normalised environmental impact of unit operation k in impact category i expressed as a percentage of the total impact of all unit operations in category i .

Process Description

For the environmental impact analysis, the production process of anionic starch described by Grommers and van der Krogt, and Rutenberg and Solarek^[5,28] was used as a case study as it closely resembles the current process used in industry. Flowsheets and process description of modules A and B are shown in the Supporting Information. Flowsheets of the different oxidation modules are shown in Figures 2 and 3. The corresponding mass and energy balances of the different unit operations, as well as the implemented efficiencies are given in the Supporting Information (Supporting Information). The mass and energy balances of all modules were scaled to relevant industrial scale to evaluate their potential as a large scale replacement for the current industrial process.

The process steps for oxidation with hypochlorite (NaOCl) or hydrogen peroxide (H₂O₂) are given in Figure 2. First, dry native starch is dispersed in water to make a slurry of 39% (w/w) starch. Then either NaOCl (a) or H₂O₂ plus a catalyst (b) is added in a stirred tank batch reactor. During the oxidation acidic compounds are formed and the pH decreases. To avoid depolymerisation due to acidification, which would result in decreased pasting properties, NaOH is added to keep the pH > 6.^[3,12,28] The mixture from the hypochlorite oxidation has a high NaCl concentration, which is produced in stoichiometric amounts. The NaCl is washed out in hydro-cyclones after oxidation (starch refining step). A sieving centrifuge recovers the starch loss from the hydro-cyclones. The anionic starch is dewatered by a drum filter and dried in a pneumatic dryer. Finally, the dry anionic starch powder is separated with cyclones. The anionic starch has a dry matter content of 80% (w/w).

Table 1. Summary of analysed impact categories and units.

Impact categories	Units
Acidification	mol H ⁺ eq
Climate change	kg CO ₂ eq
Ecotoxicity freshwater	CTUe
Eutrophication freshwater	kg P eq
Human tox. - cancer	CTUh
Human tox. Non-cancer	CTUh
Land use	kg C deficit
Eutrophication marine	kg N eq
Resource use mineral and metals	kg Sb eq
Ozone depletion	kg CFC11 eq
Particulate matter	kg PM _{2.5} eq
Photochemical ozone formation	kg NMVOC eq
Eutrophication terrestrial	mol N eq

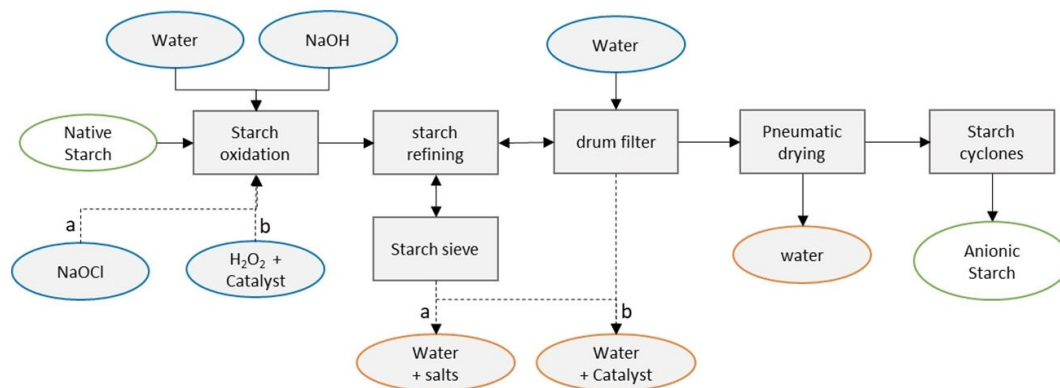


Figure 2. Flowsheet of modules OCl^- (a) and H_2O_2 (b) from figure 1 for the oxidation of native potato starch to anionic starch with sodium hypochlorite (a) and hydrogen peroxide (b), respectively.

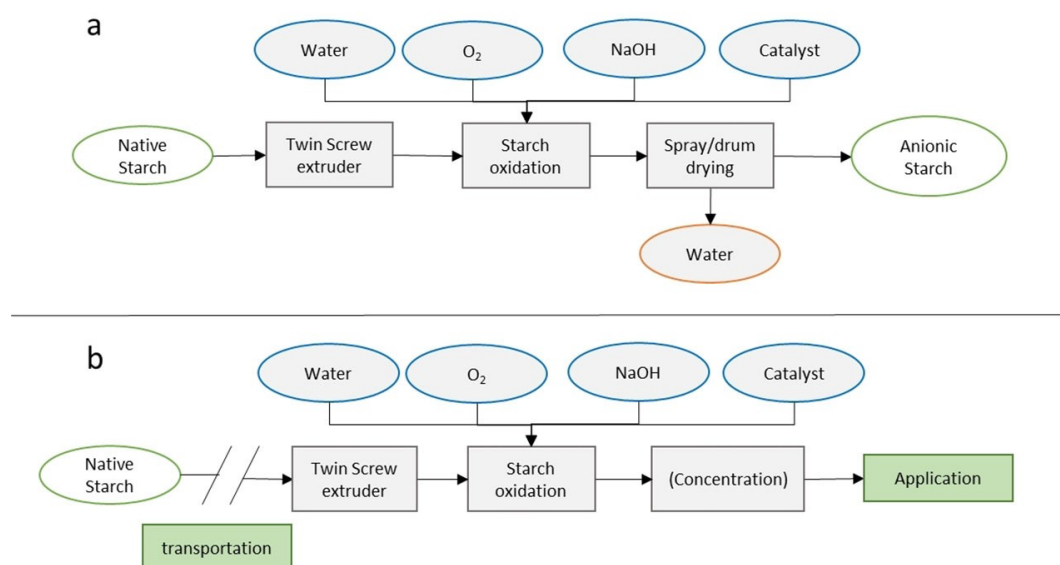


Figure 3. Flowsheets of modules O_2 (a) and O_2DA (b) for the oxidation of native potato starch with molecular oxygen and a heterogeneous catalyst. In the O_2DA scenario, the oxidation is performed on-site the user location to enable direct application of the product and omit the energy-intensive drying step

Hydrogen peroxide oxidation (Figure 2, route b) proceeds similarly to hypochlorite oxidation, but H_2O_2 is added as oxidant instead of NaOCl . Because of the lower oxidation strength of H_2O_2 compared to NaOCl , a catalyst (e.g. iron complexes, copper sulphate, or vanadium complexes) is used. As the catalyst is homogeneous, it can be difficult to separate as some catalysts form complexes with carboxylated starch.^[29] As a result, traces of the catalyst appear in the side streams and in the final product.

Heterogeneously catalysed starch oxidation, that is, by using a solid catalyst, is currently under development. Therefore, the described process is hypothetical, but based on realistic parameters published by Verreast et al.^[19] Since solid starch granules do not interact with solid catalyst particles, the starch needs to be gelatinised before oxidation. Starch gelatinisation is achieved in twin screw extruders or jet cookers, where the

granules are broken and solubilised by a combination of shear stress and temperature.^[28] The gelatinised starch is then oxidised using molecular oxygen, a supported Pt catalyst, and sodium hydroxide to keep the pH of the reaction constant.^[19] The energy use in this oxidation with oxygen from air is estimated based on the energy used in aerated reactors in wastewater treatment.^[30,31] Similarly, the required oxygen for this reaction is expressed as chemical oxygen demand (COD), and the activity of the catalyst is expressed in terms of oxygen uptake rates (OUR). Energy use for separation of the catalyst is excluded since the catalyst can be fixed in the reactor in either a fixed bed or trickle bed configuration. Impact for the production of the catalyst is not considered as catalyst production generally accounts for <1% of the environmental impact.^[32]

Table 2. Process conditions for different oxidation methods.

Oxidant	OCI ⁻	H ₂ O ₂	O ₂ (from air)
Starch concentration (w/w) Granular/gelatinised	39 % granular	39 % granular	max. 5 % gelatinised
Oxidant consumed (g oxidant/g starch)	0.2	0.092	~
Electrical energy use	0.785 kWh per m ³ starch slurry	0.785 kWh per m ³ starch slurry	3.4 kWh per m ³ starch solution
Oxygen uptake rate	~	~	0.3 mg O ₂ L ⁻¹ min ⁻¹

After oxidation with air over a heterogeneous catalyst, the oxidised starch is drum-dried or spray-dried,^[33,34] see Figure 3a. After drying, the anionic starch is transported to the user location for application. As an alternative, the energy-intensive spray/drum drying of the anionic starch is circumvented by transporting the native starch to the user location where the native starch is oxidised on-site and then directly applied after further concentration (Figure 3b). Table 2 gives the process conditions for each oxidation method. Oxidised starches are generally applied in a concentration range of 2–10 wt.%,^[35] which partially overlaps with the concentration range of the oxidation reaction.

Results and Discussion

Identification of Environmental Hotspots

The contributions of the eight unit operations with the highest impact in each category are shown in Figure 4; the contributions of all remaining unit operations is combined in the 'other' category. Hotspot analysis showed that these eight unit operations were responsible for more than 90% of the total

environmental impact in each category for the OCI⁻ reference case (modules A,B, and OCI⁻).

Figure 4 shows that the unit operations pneumatic drying of native and of anionic starch, preheating, protamylasse concentration, fibre dewatering, steam injection, and starch oxidation, are the main contributors to the overall environmental impact of the process. Starch oxidation is the main contributor in the categories of freshwater eutrophication, ozone depletion, climate change, acidification, and resource use. The impacts of the oxidation step are linked to the use of chemicals (NaOCl, NaOH) in the oxidation process.^[36–38] Starch oxidation contributes only marginally to marine and terrestrial eutrophication and photochemical ozone formation. These results show that the oxidation step is the main hotspot in the production of anionic starch. The other seven highlighted unit operations from Figure 4 are considered secondary hotspots.

The high environmental impact of the preheating, fibre dewatering, pneumatic drying of native and anionic starch, steam injection, and protamylasse concentration units is due to the high energy use for heating and drying in these steps.^[39,40] The impact profile of these units, that is, the ratio of the contributions to a category, is similar across all impact categories because these unit operations use the same type of energy (heat and electricity from a combined heat-power plant utilising natural gas). A full table of the calculated normalised impact indicators for all unit operations is given in the Supporting Information.

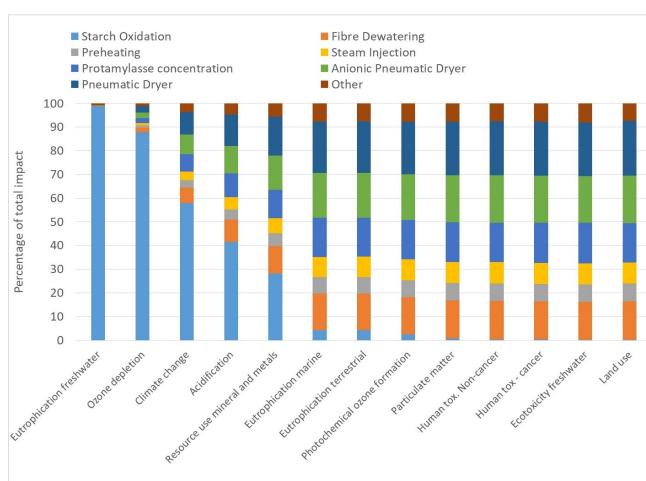


Figure 4. Normalised environmental impacts of the eight highest scoring unit operations that account for more than 90% of the total impact in each category. The contribution of the remaining unit operations is combined in the 'other' category.

Comparison of Oxidation Methods

Four different oxidation methods were investigated. It became evident that the O₂-oxidation scenario without direct application of the anionic starch solutions performs poorly compared to the other scenarios (see Figure SI5 in the Supporting Information). In the O₂-oxidation scenario, a significant increase in environmental impact is seen for several categories (Climate change + 400%, acidification + 600%, resource use + 700%; the full data is given in the Supporting Information). The high increase in environmental impact is the indirect result of practical limitations. Gelatinised (oxidised) starch cannot feasibly be transported or stored since it is susceptible to microbial decay and retrogradation, which severely reduces the robustness of the supply chain. Moreover, since the concentration of such a solution is low (<5% w/w), the added volume and weight of water substantially increases the cost of trans-

portation. Due to these limitations, the gelatinised starch would need to be dried before transportation and/or storage. In the O_2 -oxidation scenario, the starch is in solution and highly viscous after oxidation so that mechanical dewatering or pre-concentration before drying is technologically unfeasible. To dry the oxidised starch solution from the 5% (w/w) to a powder, approximately 9 tonnes of water need to be evaporated per tonne of starch. At a theoretical minimum of 2.3 GJ of energy used per tonne of water evaporated, the energy use for spray or drum drying the anionic starch solution thus becomes infeasibly high.^[41] For these reasons, the O_2 -oxidation scenario is deemed unviable and is omitted from further analysis and graphical representations to increase readability of the viable alternatives. Since the O_2DA scenario performs the oxidation directly before application, no transport, storage or drying of the oxidised starch is required and as a result these limitations of the O_2 scenario do not apply to the O_2DA scenario. For the remaining oxidation methods (H_2O_2 and O_2DA), two comparisons were made. First, the achievable reduction in environmental impact was investigated relative to OCl^- oxidation itself (without including the pre-processing modules A and B). Second, the achievable reductions in environmental impact were placed in context of the complete process chain (including the pre-processing modules A and B).

Figure 5 shows the relative reductions of environmental impact of anionic starch production by employing H_2O_2 oxidation or molecular oxygen oxidation with direct application of the gelatinised anionic starch (O_2DA).

The H_2O_2 and O_2DA scenarios reduce the environmental impact of starch oxidation step compared to hypochlorite oxidation for most categories and increase it in none of the categories (Figure 5). Both the H_2O_2 and O_2DA scenario strongly reduce the impact in the freshwater eutrophication (63% and 75%, respectively) and ozone depletion category (65% and 68%, respectively). Eutrophication in this process is caused mainly by the chemicals NaOH and NaOCl. Since NaOH use is equal in all processes, the difference in the environmental impact reduction between the H_2O_2 and O_2DA scenario represents the impact of the H_2O_2 itself. The reduction in ozone

depletion is a result of the elimination of the use and production of chlorinated compounds (NaOCl) from the process. Chlorine and chlorinated compounds are strong contributors to ozone depletion.^[36,37] The H_2O_2 scenario further reduces impact in the categories climate change (35%), resource use (41%), and leads to small improvements (5–10%) in marine and terrestrial eutrophication, and photochemical ozone formation. In comparison to the H_2O_2 scenario, the O_2DA scenario overall shows a higher reduction of environmental impact. In addition to the reduction in freshwater eutrophication (75%), ozone depletion (68%), climate change (60%), and resource use (78%), which is also observed in the H_2O_2 scenario to a slightly lower extend, the O_2DA scenario reduces the environmental impact across all the remaining categories by 75% to 85%. This reduction is attributable to reduction in energy demand through the elimination of the drying step for the oxidised potato starch. In both, the O_2DA scenario and the H_2O_2 , the impact reduction for the category acidification is the lowest. The impact in this category is mainly caused by the usage of NaOH,^[42] which is required to compensate the pH drop of oxidising starch, regardless of oxidation method.

Variations in water use between the OCl^- , H_2O_2 , O_2 , and O_2DA scenarios were minimal with the initial washing step being the main contributor for all scenarios. Water used in the oxidation step is recovered during the subsequent drying of the oxidised starches and recycled. For this reason, the differences in water use between the analysed scenarios do not significantly impact the results.

Overall reduction of environmental impact

Plotting the relative reductions in environmental impact of the investigated oxidation methods provides a good comparative tool, but this comparison alone lacks a broader context since it gives no information on the absolute orders of magnitude of the environmental impacts of the process. To put the results into a broader perspective, the environmental impacts of the different oxidation methods were expressed as a contribution to the total system impact as defined by the system boundaries. Hereby, the significance of the reduction of environmental impact of each category can be estimated without the pitfalls of using external normalisation for internally normalised LCA.^[22] The environmental impact reduction of the H_2O_2 and O_2DA scenarios expressed in reduction to the environmental impact of the entire processing chain is given in Figure 6.

The reduction in freshwater eutrophication (~65%) and ozone depletion (~69%), present in both the H_2O_2 and O_2DA scenarios, remains high in the overall process chain. The reduction in environmental impact in the categories resource use and climate change became moderately more relevant compared to others. In the categories marine and terrestrial eutrophication, land use, acidification, and photochemical ozone formation, the O_2DA scenario still provides relevant reductions in environmental impact of 10–20%. The significance of the reduced environmental impact of H_2O_2 oxidation compared to OCl^- oxidation, however, seems to be limited to

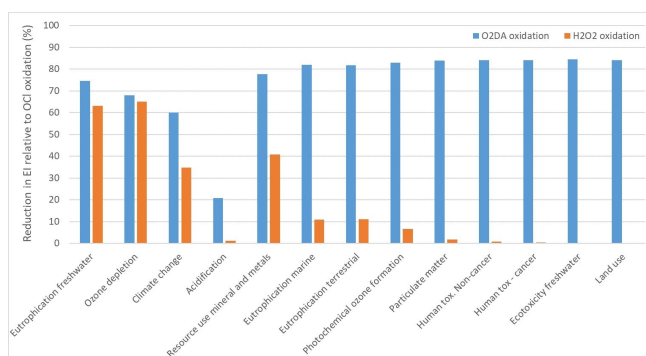


Figure 5. Achievable reduction in environmental impact (EI) by H_2O_2 oxidation or molecular oxygen oxidation with direct application (O_2DA) relative to the OCl^- reference case. Higher values indicate a higher reduction and thus lower environmental impact.

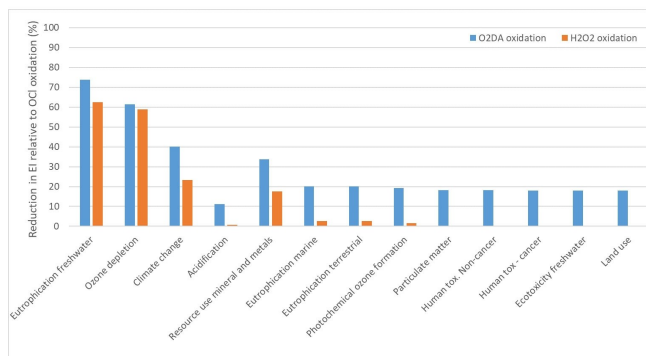


Figure 6. Comparison of the reduction in environmental impact (EI) of the H_2O_2 and O_2DA scenarios expressed in reduction of environmental impact of the overall process

freshwater eutrophication, ozone depletion, climate change, and resource use.

From an environmental perspective, both homogeneously catalysed H_2O_2 oxidation and heterogeneously catalysed O_2 oxidation (O_2DA) are preferred over OCl^- oxidation. The O_2DA scenario provides substantially higher reductions in environmental impact over a broader range of categories than H_2O_2 oxidation.

Evaluation of Assumptions in the Heterogeneously Catalysed Oxidation

The analysis showed that the heterogeneously catalysed oxidation of starch using molecular oxygen with direct application (O_2DA) has the potential to significantly reduce the environmental impact of anionic starch production. However, since the data is based on the estimated performance of a conceptual process, the robustness of these findings needs to be evaluated. The most influential assumptions that affect the results for the O_2DA scenario are: 1) the yield of the reaction, and 2) the energy use for aeration.

First, the OCl^- oxidation has a yield of approximately 97% in the currently employed industrial process.^[28] The losses during this reaction are mainly due to oxidative depolymerisation through C2–C3 diol cleavage.^[1,5,7] Heterogeneous catalysts for polysaccharide oxidation that are selective towards C6 oxidation have been developed on lab scale.^[19] Because of the selectivity towards C6 oxidation, the effect of oxidative depolymerisation is attenuated.^[17,19,20] It is thus reasonable to assume that the yield of a well-developed heterogeneous catalyst for starch oxidation is at least equal to or greater than that of OCl^- oxidation.

Second, the uncertainty in energy use for aeration, which has two causes: First, the energy use for aeration of the reactor is influenced by varying oxygen transfer rates based on the viscosity of the reaction mixture.^[43–46] Second, variances in catalyst activity would result in different reactor size and/or

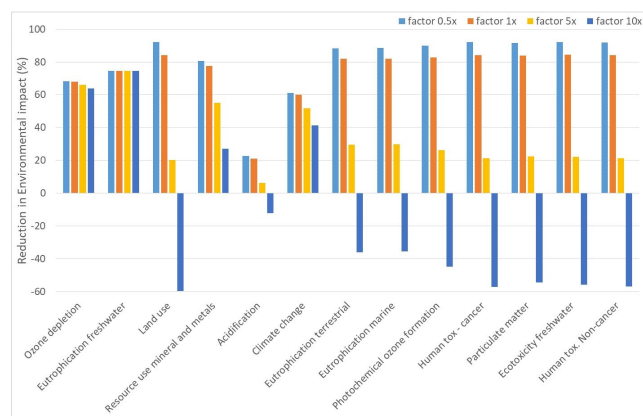


Figure 7. Reduction in environmental impact (oxidation step only) for multiples of estimated energy use (0.5 ×, 1 ×, 5 ×, 10 ×) for heterogeneously catalysed starch oxidation (O_2DA) compared to the OCl^- reference. Negative values indicate an increase in environmental impact rather than a reduction.

residence time, thus increasing or decreasing energy use for aeration.^[31]

To evaluate the effect of the energy use for aeration on the results, several scenarios with multiples of the estimated energy consumption (0.5 ×, 5 ×, and 10 ×) for the reactor have been computed (Figure 7) to estimate the critical point where the O_2DA method no longer provides substantial benefits over the OCl^- scenario.

Figure 7 shows that the potential for impact reduction in all categories apart from ozone depletion, freshwater eutrophication, and climate change, decrease significantly with increasing energy use. In most of the categories in which the reduction of impact decreases with increased energy use, the threshold for exceeding the environmental impact of the reference case is between a five- and ten-fold increase in energy use. However, for the categories climate change and mineral and metal resource use, the threshold is higher than factor 10.

From this data, we conclude that even at a five-fold increase of the estimated energy consumption, the heterogeneously catalysed oxidation of starch with oxygen with direct application (O_2DA) will still reduce the overall environmental impact compared to OCl^- oxidation. This shows that the technology change remains viable, from an environmental impact perspective, for energy requirements up to 17 kWh m^{-3} which provides an estimation for the required performance of heterogeneously catalysed oxygen oxidation reactions. At higher energy consumption levels ($> 17 \text{ kWh m}^{-3}$), a trade-off needs to be made between the different impact categories, and the benefit of the O_2DA scenario compared to the OCl^- oxidation is debatable.

Conclusions

Hotspot analysis showed that the oxidation step in the production chain of anionic starch as a renewable alternative for polyacrylates is the main contributor to environmental

impact in the categories freshwater eutrophication, ozone depletion potential, climate change, acidification, and resource use. In addition, unit operations to concentrate or dry products have high energy use and contribute as secondary hotspots in the remaining categories.

Homogeneously catalysed hydrogen peroxide oxidation and heterogeneously catalysed oxidation with molecular oxygen and direct, on-site product application both reduce the environmental impact of the process due to the elimination of OCl^- as an oxidising agent. The greatest reduction is found in the category freshwater eutrophication (~67%), and ozone depletion (~66%). In the categories climate change and resource use, both methods reduce the environmental impact, but homogeneously catalysed hydrogen peroxide oxidation achieved less reduction (35% and 41%, respectively) than heterogeneously catalysed oxygen oxidation with direct, on-site product application (60% and 81%, respectively).

Since the heterogeneously catalysed oxidation of starch requires the starch to be gelatinised before oxidation, this method is only viable if the starch can be applied directly after oxidation without intermediate drying. As a result of the omission of the drying step, heterogeneously catalysed starch oxidation with direct product application has the potential to further reduce impact in the categories marine and terrestrial eutrophication, photochemical ozone formation, particulate matter emission, human toxicity (cancer and non-cancer effects), freshwater ecotoxicity, and land use by approximately 80%.

As demonstrated, heterogeneously catalysed starch oxidation with molecular oxygen has the potential to substantially reduce the environmental impact of anionic potato starch production. Additionally a performance requirement for the energy use in this process has been estimated at a maximum of 17 kWh m^{-3} for a 5% starch solution to maintain improvements over the current process from an environmental perspective. However, further research into the process and into developing a catalyst with sufficient activity, selectivity, and stability is required to eventually phase out the chlorine chemistry.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: anionic starch · comparative life cycle assessment · environmental impact · starch oxidation · sustainable chemistry

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