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Commodity chemical production from 3rd generation biomass: A techno-economic assessment of lactic acid production

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Abstract

The unique characteristics and composition of macroalgae offer new possibilities to produce bio-based products such as biofuels and commodity chemicals. Presently, the technologies required for processing macroalgae are not mature enough, and the ones present are primarily oriented towards the production of biofuels. The manuscript explores the production process of Lactic Acid (LA) from brown algae, designed with a capacity of 11 tonnes/hr of product. Four scenarios are simulated in Aspen Plus, for production of polymer-grade LA, utilizing *Laminaria* macroalgae as a feedstock. Techno-economic models are established to investigate the feasibility of these new technologies. Subsequently, configurations for heat recovery are suggested to maximize the productivity, while, minimum viable selling price (MVSP) is calculated for LA to predict an optimal design configuration. The process does not recover investment when using an average composition of *Laminaria sp.* Moreover, the percentage difference between the MVSP and the current selling price (SP) is 34%. Nonetheless, when using *Laminaria digitata*, whose composition of carbohydrates is higher, the percentage difference between the MVSP and the SP is estimated to be 28%. Besides, if the hypothetical fermentation of alginate is considered, the invested capital is recovered by the 11th year. These results highlight the need for an investigation into valorizing the alginate fraction as well, improving microorganism's ability to metabolize alginate to LA or additional products and developing the respective processes would be a justified step that scientific communities should venture into.

1. Introduction

Mankind has been utilizing fossil fuels for centuries. The petrochemical sector is one of the key consumers of a wide range of non-fuel molecules generated in the oil refinery, natural gas processing plants and other coal or co-fired gasifiers. These compounds, in most instances, act as

a building block for numerous products which are used by consumers in our day to day lives. Moreover, this sector is of extreme importance from an economic point of view. Typically, in a petroleum refinery, while a mere 7-10 % of the oil barrel goes to the production of chemical products¹, it accounts for around 50% of the profit, 30% of the energy consumption and 20% of the greenhouse emissions². Recently, with increasing awareness among the end consumers, the bio-based chemical production has emerged as a promising niche, whose market share is expected to grow from 2% in 2008 to 22% in 2025². Targeting the shift from fossil to bio-based raw materials, new research initiatives are focused on finding plant-based feedstocks, with the ability to substitute the non-renewable resources. Implementing new bio-based production routes would result in a radical change in the industry, whose end impacts must be assessed, a priori. Therefore, early-stage economic studies to check the feasibility and environmental impacts of the bio-based processes is vital³.

The first attempt towards substituting the fossil-based commodities with bio-based products was achieved utilizing starchy (1st generation) and lignocellulosic (2nd generation) biomasses.

However, the use of starchy biomass created skepticism due to the competition with food for agricultural land. On the other hand, lignocellulosic biomass requires expensive pretreatments for obtaining their monomers, with high cost and energy requirement³⁻⁵. Thus, algal biomass (3rd generation) emerges as a potential alternative due to their advantages over many terrestrial crops such as growing faster, needing relatively milder pre-treatment and exhibiting higher energy yield per area⁶.

Macroalgae is a 3rd generation algal biomass which possesses a relatively high percentage of carbohydrates, higher biomass production rates (per volume) and higher biomass densities⁷ compared to microalgae. Typically, macroalgae can be classified according to their color as,

green, red and brown algae. Among various types of macroalgae, brown algae emerge as a potential alternative feedstock in a biorefinery. Major reasons being, high yearly production of 9.72 million tons DW (on a Dry Weight basis), largest seaweed source^{7,8}, the high carbohydrate content of 50-60% (DW) and a relatively less amount of lignin⁷⁻¹⁰. Brown algae are largely utilized in East Asian countries such as China, Japan or Korea, as a source for food and biochemical products. Nevertheless, macroalgae species such as *Laminaria digitata* and *Laminaria Lattissima* also grow in the Atlantic waters^{11,12}. Aiming towards the consumption as a feedstock for industrial biotechnology applications, *Laminaria digitata* could be a reasonable selection within brown macroalgae due to its high content of carbohydrates (Mannitol, Laminarin, Alginate, Cellulase and Fucoidan). Figure 1 shows an average composition of *Laminaria* species and elemental analysis is illustrated in Table 1. Also, studies have established the possibility to cultivate various types of brown algae throughout the year to potentially circumvent the storage losses¹³ (see Appendix 1)¹⁴. This considers algal biomass with 20% moisture at the plant gate and harvested throughout the seasons to avoid storage losses. However, it is important to acknowledge that consistent harvest throughout the year is subject to high uncertainties inherited due to regional conditions and requires further investigation. Moreover, the different carbohydrates present in the brown algae are not extracted by following the same procedures. While laminarin and mannitol can be extracted by water, alginate (which accounts for ~ 30%) cannot.

Table 1 The chemical composition of the brown algae *Laminaria* sp., adjusted from¹⁵. Elemental analysis (Ultimate analysis) of brown macroalgae.

Elemental analysis	Dry basis, % (w/w)
C	34.60

H	4.70
O	32.20
N	2.40
S	1.00
P	0.35
K	0.0096

Composition of organic compounds in macro algae (weight % basis)

Figure 1. Macroalgae is a complex feedstock, comprising of various compounds that needs to be processed in order to obtain valuable end-products. The pie chart demonstrates the composition (in percentage) of the brown algae, *Laminaria species*.

To achieve a long-term viable production, selecting the right combination of bio-based feedstock and end-product is of paramount importance. Among several commodity chemicals, lactic acid (LA) has stood out as a prominent alternative in recent years with a steady market growth^{16,17}. It is mainly used in the food industry for the synthesis of base chemicals and for producing biodegradable plastic, polylactic acid (PLA). Among other bio-based polymers (bio-based

polyamides, polyethylene, polypropylene and poly(butylene adipate co-terephthalate)), PLA is predicted to have a significant growth until 2023¹⁸. Also, unlike many contemporary commodity chemicals, production of LA does not directly compete with fossil-based technologies (while PLA could possibly replace some existing fossil-based products in packaging, medical and textile applications¹⁹), making it an ideal bio-based chemical to be produced in large scale²⁰.

In past decades, several studies have emerged to assess the economic viability of fermentation-based processes for the 1st and 2nd generation biomass^{21–23}. Moreover, a few studies have been documented pertaining to the techno-economic assessment (TEA) of producing fuels and chemicals^{24–27} with microalgae as a feed source. To the best of our knowledge, no previous TEA has been performed on the 3rd generation, macroalgae biomass, for producing LA. This unique contribution demonstrates the economic impact of macroalgae-based production of LA (a growing bio-based commodity chemical) at a commercial production scale. A detailed techno-economic assessment is performed for the same, which could be used by stakeholders at an early stage, prior to investment, to gain insights into the long-term viability of chemical production, using macroalgae. Also, sensitive parameters have been highlighted and subsequently, its impacts have been explored. The information generated could be used by industry players and the scientific community for not only knowing the limitations but also, to resolve major scientific barriers hindering applications of macroalgae.

2. Background

Macroalgae could be a potential feedstock for producing a large range of bio-based products following thermochemical, chemical and biochemical pathways. Figure 2 illustrates possible production pathways and corresponding end-products that can be produced by macroalgae. Here,

the processes in the lower part (relative to the mechanical pretreatment), represents thermochemical conversion through catalytic conversion and fractionation, while the upper part corresponds to chemical and biochemical conversion. Due to the high water content of the macroalgae, microbial conversion appears to be a logical step (offering a higher potential to lowering the costs), leading to better economic viability compared to direct combustion or thermochemical pathways^{6,8}.

Figure 2. A schematic representation of production scenarios of a macroalgae-based biorefinery to chemicals, fuels and other materials

The carbohydrates present in macroalgae are found to be a promising substrate for fermentation, with the potential of producing a large range of bio-based fuels (such as ethanol, butanol etc.) and chemicals (such as lactic acid, 2-3 butanediol, citric acid etc.)²⁸. Particularly, lactic acid (LA) is an important and widely used organic acid, around the world, due to its wide range of industrial applications^{29,30}. Traditionally, lactic acid production was oriented towards food and

pharmaceutical industry, but lately, its demand is growing due to the interest in producing bioplastics using the bio-compostable and biodegradable³⁰ poly-lactic acid (PLA). Presently, with fifteen major players active in the production of LA, the current production capacity is estimated to be 814300 tonnes per annum (see Appendix 2)^{31–35}. NatureWorks owns the largest production facility with an annual nameplate capacity of 150000 tonnes, while, the other producers cover the rest of production^{16,36}.

The synthesis of lactic acid can follow two different pathways, chemical and microbial. Of which, currently, the most industrially used method worldwide is the microbial fermentation¹⁶. 90% of the commercially available L-lactic acid is produced by submerged fermentation of corn, in which, the feedstock cost accounts for nearly 70% of the overall production cost⁸. However, the ultimate efficiency and economics of LA production are still in doubt, since the process requires a high product specificity and the cost of the raw materials plays an important role. Although lignocellulosic biomass is an abundant renewable feedstock, the harsh pretreatments techniques, long pretreatment time and relatively low yields (compared to thermochemical methods)³⁷, often leads to the high production cost of enzymatic treatment^{38,39}. Therefore, macroalgae as a feedstock, rises as a potential alternative for lactic acid production, although more research in microorganisms able to produce lactic acid from the sugars available in the algae composition is still needed⁸.

Comparing the fermentative production of lactic acid from seaweeds and terrestrial plants, using different *Lactobacillus* bacterial strains, shows that whereas the terrestrial plant carbohydrates can be almost fully fermented, in the case of brown seaweeds, currently it is a mere 61.6% of fermentable carbohydrates. However, lactic acid yields obtained for terrestrial and aquatic plants are similar (0.18-0.19 g/g biomass and 0.16-0.17 g/g biomass, respectively)⁴⁰. Thus, the high

moisture content and the underutilized biomass fractions are linked with the necessity of using large amounts of biomass and, leading to low yields. This, together with the seasonal composition variability, seems to hinder the feasibility of producing lactic acid from macroalgae, at the same capacity as terrestrial plant material, such as corn or lignocellulosic biomasses. Nevertheless, this implies that if the research is oriented towards finding new technologies, capable to process these non-fermentable sugars, the yields of lactic acid for seaweed biomass would increase.

The scope of the study is to investigate the possibilities of algal biomass as feedstock for biorefineries, especially for producing bio-based chemicals. The main focus and contribution of this study lie on the design of a process which produces a commodity chemical (lactic acid with polymer-grade purity) through a fermentative pathway and the performance of a techno-economic evaluation. Various potential configurations are proposed and economically assessed, for eventually determining the boundaries, for an optimal process configuration.

3. Methods and assumptions

A simulation representing a process to produce lactic acid from brown algae is developed utilizing the software Aspen Plus™ V8.8. Rigorous material and energy balances are accomplished to obtain an accurate model which provides inventories that can be used for performing a precise techno-economic assessment of the process. The technical choices and major economic assumptions applied in the design are outlined in Table 2 and Table 3.

Table 2. Technical details and process assumptions

Description	Technical details and process assumptions
Thermodynamic model	The non-random two-liquid model (NRTL), able to handle combinations of

	polar and non-polar compounds up to very strong non-ideality.
Feedstock	<i>Laminaria</i> species.
Plant size	11 tonne of lactic acid per hour, considering 8000 operating hours per year (92.6% optimal). Almost a 10 th of the world expected capacity in 2020 ³⁵ .
Microorganism selection	<i>Lactobacillus casei</i> . facultative heterofermentative anaerobic bacteria able to produce lactic acid by fermentation of glucose and fructose.
Physical pretreatment: biomass washing + drier	<i>Lactobacillus</i> bacteria species are non-halotolerant microorganisms whose growth is limited with salt concentrations higher than 5% ⁴¹ . Washing water enters to the system in a ratio 1:1 (w/w) relative to the input biomass and then is dried till reaching a 20% water content

Table 3. Major economic assumptions. Sources for all the assumptions provided in Appendix 3.

Description of assumption	Assumed value
No subsidies for the capital investment are considered and thus, the entire amount is depreciated.	Debt: 70% and Equity: considered 30% IRS's MACRS schedule for 20 years
Salvage value	A salvage value of 0 is assumed
Plant life	20 years
Interest rate	10% on the debt amount
Income tax rate	35% of estimated profit
Annual capital charge ratio (ACCR)	0.16
Plant construction expenditure schedule	3 years, the capital cost is shared as follows: Year 1- 30%, Year 2- 50%, Year 3- 20% + working capital.

The production process consists of different steps beginning with the procurement of the fresh biomass and culminating when the lactic acid is obtained with a polymer grade purity. The

technologies for producing bio-products from 3rd generation biomasses are not mature.

Therefore, the novel process design for algal feedstocks is based on the National Renewable Energy Laboratory (NREL) studies for ethanol production from lignocellulosic and microalgae as biomass feedstock^{42,43}. However, steps such as pretreatment or downstream have important differences due to the usage of a different feedstock and the production of a different final product.

The process design has mainly five stages of processing (physical pretreatment, chemical pretreatment, fermentation, concentration and downstream). However, since it is a non-validated procedure, which has not been experimentally tested, different potential scenarios for each step are simulated, resulting in 8 scenarios, as depicted in Figure 3. Thus, the performance of various technologies is assessed. Two physical pretreatments and two downstream configurations are specifically designed for the brown macroalgae process while the two thermochemical pretreatments are adjusted from the process from lignocellulosic biomass. Figure 4 illustrates a schematic/configuration of the simulations performed.

Figure 3. Potential processing scenario for producing LA from macroalgae (*Laminaria digitata*)

*REED/EDBM: Reverse Electro Enhanced Dialysis and Electrodialysis with Bipolar Membrane

Figure 4. A simple process flow diagram illustrating a typical process configuration (hereby the scenario of dilute acid pretreatment with reactive distillation) used to produce LA from 3rd generation biomass.

3.1 Pretreatment

The handling of the biomass before entering the fermenter can be differentiated into physical and chemical pretreatment. The aim of the physical pretreatment is conditioning the biomass to improve the reaction efficiency in the subsequent steps, whereas the chemical (thermochemical and enzymatic pretreatment) pretreatment hydrolyzes the carbohydrates into sugars, making the sugars accessible for efficient fermentation.

3.1.1 Physical pretreatment

Physical processing involves washing of the biomass with fresh water to remove the high content of salt, sand and other traces which can affect the efficiency of microorganisms during the fermentation⁴⁴. As previously mentioned, the feedstock has high water content, making it suitable for fermentation processes⁴¹. Thus, ideally, a drying step would not be required, implying the possibility of skipping this stage in the physical pretreatment (as shown in Figure 5). However, currently, in processes where algal biomass is handled, a drying step is performed to reduce the high moisture content, due to the following reasons:

- Firstly, because the dried feedstock opens up the possibility to be stored and transported more economically (moisture content reduced to around 20%⁴²).
- Secondly, enabling drying the biomass provides the possibility of storing the feedstock in the desired composition conditions and utilizing it during the year.

Thus, although both scenarios are considered, the one set as a baseline is the scenario where the biomass is dried using a rotary drier as depicted In Figure 6⁴².

Figure 5. 1st physical pretreatment: Washing and crushing

Figure 6. 2nd physical pretreatment: Washing, drying and crushing

3.1.2 Thermochemical and enzymatic pretreatment

Two different thermochemical and enzymatic pretreatments are suggested. The first one implemented is a dilute acid pretreatment (ACTH), inspired by the one used for 2nd generation biomasses. This consists of adding sulfuric acid in an autoclave at 121 °C with 20% solids loading solution to reach pH 1 (22 g H₂SO₄/kg dry biomass)⁴² as depicted in Figure 7. However, the lack of lignin (polymer responsible for the conversion of lignocellulosic biomass into products) in brown algae structure, implies that such harsh pretreatment is not needed in algal biomasses. Thus, another scenario based on a hot water wash is set-up as a second chemical pretreatment. Thereby, water at 50 °C (HWW) is added until reaching a solid loading of 20%⁴² as shown in Figure 8.

Reactions occurring during this step are the mild hydrolysis of laminarin and cellulose into glucose. However, since the thermo-chemical pretreatment is not able to fully hydrolyze the algal polymers laminarin and cellulose an enzymatic treatment is performed in a separate reactor.

For simulation purposes, a common industrial enzyme (cellulase) is considered for performing the saccharification step ($0.02 \text{ kg cellulase/ (kg cellulose + laminarin)}$). Mannitol, though, before being fermented must be oxidized to fructose by mannitol dehydrogenase, enzymes which appears in microorganisms such as *Lactobacillus*. However, before including the enzymes in the saccharification reactor, a conditioning step is required to adjust the flow to specific conditions for the enzymes to work as intended (pH 5-6 and temperature 48°C). This step differs between both pretreatments described. In dilute acid pretreatment, the temperature needs to be lowered from 121°C in the hydrolysis reactor and, therefore, a heat exchanger is needed. Then, to neutralize the H_2SO_4 added in the prior reactor and raise the pH to 6, ammonia is added in a ratio of 4.8 g/l of hydrolysate. The scenario with HWW presents a heat exchanger which reduces the temperature and H_2SO_4 is added to lower the pH to 6⁴².

Figure 7. Dilute acid hydrolysis and enzymatic pretreatment

Figure 8. Hot water wash and enzymatic hydrolysis

All reactions are included in the simulation as presented in Table 4 summarizes the conversions for each case⁴² and their heat of reaction calculated with the enthalpy of formation of each one of the components⁴⁵ (data on the Heat of Formations provided in Appendix 4).

Table 4. Reactions, conversions and heat of reaction used in the simulation

	Reactions	ATH + enzymatic conversion	HWW + enzymatic conversion	Heat of reaction (J/kmol)
Laminarin	$(C_6H_{10}O_5)_n + H_2O \rightarrow C_6H_{12}O_6$	92.5%	75%	-4.8012e+7
Cellulose	$(C_6H_{10}O_5)_n + H_2O \rightarrow C_6H_{12}O_6$	92.5%	75%	-4.8012e+7
Mannitol	$(C_6H_{14}O_6) \rightarrow (C_6H_{14}O_6)_{aq}$	95%	95%	-3.0457e+9 *
Neutralization	$2 (NH_3) + H_2SO_4 \rightarrow (NH_4)_2SO_4$	100%	-	-3.53013e+8

* Heat of solution used

3.2 Fermentation

Fermentation is a core step of the process, where, the glucose generated in the previous step from the hydrolysis of laminarin and cellulose and mannitol, oxidized to fructose, are fermented to lactic acid by the bacteria *Lactobacillus Casei*. The study of Khanifatun et al.⁴⁶ shows the dependence of the bacteria performance on the concentration of sugars (glucose and fructose) in the broth that leads to different lactic acid yields and presents 159 g/l as the optimum concentration⁴⁶. The concentration of sugars after the pretreatments is lower than this value in every scenario. Therefore, before fermentation, the hydrolyzed slurry is taken to an evaporator which concentrates the sugars to ~150 g/l and an inoculum of 10% of the fermentation volume (v/v solution) is added to the reactor to have enough cells for the fermentation to take place⁴⁶.

The conditions in both reactors, seed production and main fermenter, are the same, the temperature is kept 37 °C with cooling water and pH 6 is maintained by the addition of calcium carbonate (150 g/l broth⁴⁷). Calcium carbonate acts as a buffer in controlling the pH drop due to the acid production by reacting with the lactic acid, producing calcium lactate. This addition is required since a lower pH would inhibit the production of lactic acid in the fermenter. The cells growth in fermentation requires nitrogen and phosphorus nutrients. In this case, the high amount of proteins present in the feedstock are considered as nitrogen source whereas diammonium phosphate (DAP) is added as P source⁴².

The equations for the lactic acid production, lactic acid neutralization with calcium carbonate and cells growth are represented in Table 5 with the conversions and the calculated heat of reaction. The amount of sugar converted into biomass is considered small and does not significantly affect the production of lactic acid⁴⁷.

Table 5. Reactions and conversions in the fermentation step. The conversion fraction (%) is derived from^{8,30,48} documented in Appendix 5, while the heat of reactions were calculated as shown in the Appendix 4^{8,43}).

	Reaction	Conversion	Component	Heat of reaction (J/kmol)
Oxidation	$\text{C}_6\text{H}_{14}\text{O}_6 \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2$ <p><i>Mannitol</i> <i>Fructose</i></p>	100%	Mannitol	1.78e+9
LA production	$\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2 \text{C}_3\text{H}_6\text{O}_3$ <p><i>Fructose</i> <i>Lactic Acid</i></p>	88.25%	Fructose	-1e+8
Cells growth	$\text{C}_6\text{H}_{12}\text{O}_6 + 0.3704 \text{ Proteins} + (\text{NH}_4)_2\text{HPO}_4 \rightarrow$ <p><i>Fructose</i> <i>Diammonium phosphate</i></p> $6 \text{ Lactobacillus} + 2.4 \text{ H}_2\text{O}$	1.76%	Fructose	-5.07e+9

LA production	$C_6H_{12}O_6 \rightarrow 2C_3H_6O_3$ <i>Glucose Lactic Acid</i>	85.02%	Glucose	-1e+8
Cells growth	$C_6H_{12}O_6 + 0.3704 \text{ Proteins} + (NH_4)_2HPO_4 \rightarrow$ <i>Fructose Diammonium phosphate</i> $6 \text{ Lactobacilus} + 2.4 H_2O$	1.79%	Glucose	-5.07e+9
Ca-Lac from LA	$2C_3H_6O_3 + CaCO_3 \rightarrow$ <i>Lactic acid Calcium carbonate</i> $C_6H_{10}CaO_6 + CO_2 + H_2O$ Calcium lactate	100%	CaCO ₃	8.48e+7

3.3 Concentration and solids removal

Before going to the downstream, the non-reacted fraction of the algae in the solution (such as alginate, lipids, proteins and cells) must be removed. Firstly, the cells, whose particle size is bigger are removed with a filter (micrometres scale). Then, the solids with smaller particle size (alginate, lipids, proteins, non-reacted laminaria, mannitol and cellulose) present in the solution are removed with a decanter (nanometer scale). However, at this point, it is important to notice that the calcium lactate formed in the fermenter is in solution since its concentration is lower than 8.5 g/100 ml⁴⁹) and so, it does not decant, avoiding the loss of lactate.

Subsequently, to recover the lactate in form of calcium lactate, the aqueous solution is acidified by the addition of sulfuric acid, which reacts with the calcium lactate producing lactic acid and calcium sulphate salt as Table 6 shows. It must be noted that the conversions are based on optimistic small-scale experiments derived from the literature and may reduce in a scaled-up

production facility. This salt, also known as gypsum, is subsequently separated by a decanter, leaving the solution free of solids before the separation step.

Table 6. Lactic acid recovery. The conversion fraction (%) is derived from³⁰.

<i>Reaction</i>	<i>Conversion</i>	<i>Heat of reaction</i>
$\text{H}_2\text{SO}_4 + \text{C}_6\text{H}_{10}\text{CaO}_6 \rightarrow \text{CaSO}_4 + \text{C}_3\text{H}_6\text{O}_3$ <p>Sulfuric acid Calcium lactate Calcium sulfate Lactic acid</p>	100%	-2.109e+8 (J/kmol)

The last step before the separation stage is an evaporator used to decrease the amount of water in the solution and increase the concentration of lactic acid before the distillation as Figure 9 illustrates.

Figure 9. Concentration step

Instead of simulating solid separations with Aspen Plus™, which lacks biological solids properties, the software SuperPro Designer was used since it is more accurate handling biological solids.

3.4 Separation and purification

The final stage of the process is for separating the lactic acid from the fermentation broth and purifying it to its polymer grade variant (99 wt% dry basis³⁰). The components that reach this stage are mainly lactic acid and water. Nevertheless, there are also some sugars which did not

react in the fermentation stage (glucose and fructose). Thereby, the lactic acid purification presents some difficulties since it is a nonvolatile compound (its boiling point at atmospheric pressure is 210 °C) mixed with nonvolatile impurities and other organic acids and also undergoes self-polymerization at high temperatures.

Thus, several methods such as crystallization, solvent extraction, evaporation, adsorption, electrodialysis, membrane separation or reactive distillation have been applied to facilitate this separation. Although all of them present pros and cons, the two-step process consisting of esterification of lactic acid with alcohol followed by the separation of the lactate ester by distillation and its hydrolysis to lactic acid rises as a good option to obtain high purity lactic acid^{29,30}. The process depicts a configuration chosen by current commercial player Purac® (now Corbion®, Netherlands) hence further warranting this selection⁵⁰. Thus, although performing this method requires high capital cost, it can be improved by executing these steps simultaneously using a reactive distillation column.

The present work implements this configuration. The reactive distillation is simulated with a RADFRAC unit in Aspen Plus™ which is fed from the bottom part with the liquid phase from the evaporator (60 wt. % lactic acid) and methanol. The column is designed in a way that the esterification reaction takes place in the lower stages of the column (Table 7, reaction (1)) whereas the upper ones are for the separation of the products of the reaction, water and methyl lactate (distillation section). This presents a continuous system where the products leave the reaction section towards the separation stages as soon as they are produced. According to Le-Chatelier's principle, the equilibrium reaction shifts toward enhancing product formation.

The hydrolysis reactor follows the reactive distillation column. There, methyl lactate reacts with water giving lactic acid and methanol that are finally sent to a final distillation column which separates the methanol giving as a result pure lactic acid (Table 7, reaction (2)).

Table 7. Reactions in the reactive distillation, downstream step.

Unit	Reaction	No.
Reactive distillation column	$\text{C}_3\text{H}_6\text{O}_3 + \text{CH}_3\text{OH} \rightarrow \text{C}_4\text{H}_8\text{O}_3 + \text{H}_2\text{O}$ <p><i>Lactic acid Methanol Methyl lactate</i></p>	(1)
Hydrolysis reactor	$\text{C}_4\text{H}_8\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_6\text{O}_3 + \text{CH}_3\text{OH}$ <p><i>Methyl lactate Lactic acid Methanol</i></p>	(2)

However, the glucose and fructose present in the solution, due to the incomplete carbohydrate fermentation of the algal biomass cannot be removed by this process, as these do not evaporate with water or methanol. Hence, to reach the required purity (99% lactic acid), a simplification was assumed (for simulation purposes), where a component separator (an Aspen Plus™ unit operation module) is used in the simulation, before the downstream purification. The downstream process is illustrated in Figure 10.

Figure 10. Reactive distillation downstream.

The presence of non-reacted sugars hinders the separation since conventional methods are not able to separate particles with this particle size. However, since glucose and fructose do not have charge and are in solution with lactic acid, which is charged, the possibility of being separated by electrodialysis rises. Thus, the Reverse Electro Enhanced Dialysis (REED) and Electrodialysis with Bipolar Membrane (EDBM) method have been reported^{51,52} to separate the lactic acid with an efficiency of 100%⁵³ and so, it is implemented in the current study.

The solution of lactic acid, water and sugars (glucose and fructose) enters the system and is subsequently separated by an anion-exchange membrane as, comes in sodium hydroxide, illustrated in Figure 11. This membrane is connected to an electrical current that extracts the lactate from the incoming solution, reacting with the sodium cation from the alkaline solution and producing sodium lactate (Table 8, reaction (1)). Likewise, the hydroxide anions flow back to react with the cations in the inlet solution. The sodium lactate solution goes to the electrolysis unit (EDBM) where the lactate reacts back with the protons producing lactic acid. The sodium hydroxide is also regenerated and is recirculated to the REED unit. The reactions of this process are shown in Table 8.

Figure 11. REED/EDBM + distillation column downstream

Table 8. Reactions in the REED/EDBM downstream set-up

Unit	Reaction	No.
REED	$\text{C}_3\text{H}_6\text{O}_3 + \text{NaOH} \rightarrow \text{C}_3\text{H}_5\text{NaO}_3 + \text{H}_2\text{O}$ <p><i>Lactic acid Sodium lactate</i></p>	(1)
EDBM	$\text{C}_3\text{H}_5\text{NaO}_3 + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_6\text{O}_3 + \text{NaOH}$ <p><i>Sodium lactate Lactic acid</i></p>	(2)

4. Process optimization

4.1 Capital cost assessment

The aim of performing a thorough process design, accomplishing a simulation model with accurate mass and energy balances is to eventually complete a techno-economic assessment of lactic acid production from brown algae. The cost obtained will position the production process

of lactic acid via this pathway in the market: This will allow the assessment of which changes in the process could improve the economics and direct research efforts.

The first step of the process is sizing the equipment. Although Aspen Process Economic Analyzer V8.8. provides this information, to obtain the costs as precise as possible, some equipment is sized according to the method shown in Biegler et al [63]. This is the case of reactors and ash columns whose sizes are obtained taking into account the flow and the residence time. Besides, since the equipment materials also have a big influence in the capital cost, the selection of the adequate materials is based in the report of the national renewable energy laboratory (NREL) and introduced manually to Aspen Process Economic Analyzer V8.8. Thus, together with the design information extracted from the process simulation and cost related to procuring and installing the equipment, the inside the battery limits (ISBL) costs are estimated. Besides, some costs (such as the dryer for similar unit operation) are obtained from literature^{42,43} while others (such as the decanters or the filters which handle solids whose properties are not available in Aspen Plus™) are obtained from the software SuperPro Designer®. Then, to calibrate this cost values to the scale of the current facility, Equation 1 is applied:

$$\text{New cost} = \text{Base cost} \times (\text{New size}/\text{Base line})^n \text{ ----- (1)}$$

Where, “n” is the scaling exponent that depends on the type of equipment.

The value obtained from Aspen Process Economic Analyzer V8.8 assumes that the location of the plant in North America. Thus, a location factor which estimates the cost in relation with the cost in U.S. Gulf Coast (USGC) is used, in order to account for the effect of the location, as shown in Equation 2. Since the current assessment assumes a production facility located in the USA, it acts as a base case, with location factor as 1.00. Whereas, **Germany** and China, are

assigned a location factor of 1.11 and 0.61 (relative to the base case described in Appendix 9), respectively⁵⁴.

Cost of plant in location A = cost of plant in USGC x LF_A ----- (2)

Outside battery limits (OSBL) costs, such as, electricity, power stations and other facilities that the plant requires for its proper functioning, are calculated as a percentage (40%) of the direct costs (ISBL), added up with the ISBL the fixed capital cost (FCC) is obtained. Likewise, the **working capital is obtained as a percentage (15%) of the ISBL + OSBL costs⁵⁵**. After deducing the capital investment, the total cost of production is calculated with the fixed and variable operating costs for eventually doing the cash-flow analysis⁵⁵. The fixed operating costs (FCOP) are independent to the output of the plant since they refer to the labor and maintenance costs, the overhead charges and the taxes and are summarized in Table 9.

Table 9. Fixed operating costs⁵⁴⁻⁵⁶. Find all the detailed assumptions in Appendix 3.

Labor	
Shift position	Fluids + Solids continuous process: 3 shift positions + 1/every solid handling = 6
Operating labor	50000 \$/shift (States Gulf Coast)
Supervisor	25% operating labor ⁵⁵
Direct overhead	50% (operating + supervisor labor) ⁵⁵
Maintenance	
Maintenance cost	5% of ISBL (processes where handling of solids is involved) ⁵⁵
Overhead expenses	

Plant overhead	65% (labor + maintenance) ⁵⁵
Tax & insurance	2% (ISBL + OSBL) ⁵⁵

The variable operating cost (VCOP) is proportional to the production rate of the plant and they refer to the costs of raw materials, utilities, consumables and effluent disposal^{55,56}. These usually are a big share of the total cost of production and thus, optimizing their usage in the process is a main target in the process design. Decreasing the consumption of raw materials and consumables without affecting the production is, in many cases, something not susceptible to change.

However, the usage of utilities and the effluent disposal can be managed in the way the costs are reduced and the heat is recovered leading to optimizing the design. Finally, the cash flow is calculated as a record of flows in and out in a business project throughout its lifetime.

4.2 Heat integration (HENS)

The optimization of process simulations is done with an objective to maximize the profitability of a plant and to reduce utility usage. In order to reach these objectives, many parameters of the project can be considered in the optimization. A well-known method of reducing the utility consumption is through optimizing the utility network by means of heat integration.

Furthermore, streams of waste can be considered as an energy input for the system (from waste to energy byproduct) as a way to recover calorific value from waste streams.

Heat integration is performed with Aspen Energy Analyzer™ V8.8. Aspen Process Economic Analyzer V8.8 used to estimate the capital costs and is a tool available in the Aspen Engineering Suite that is able to extract the design details from the simulation. The heat exchanger network designs are built with an objective of minimizing the total annualized cost. Among the five steps

of the process simulation, the physical pretreatment is excluded from the heat integration and two heat integration analysis were accomplished; for the scenario with dilute acid pretreatment and for the scenario with hot water wash, both with reactive distillation downstream. Then, these two optimization designs are applied with slight modifications in the downstream section to the scenarios with REED/EMDS downstream.

Besides, it is thought to give it a second value to the non-reacted solids separated in the concentration step by incinerating it, instead of just disposing of it. Hence, the incineration of this biomass will produce energy that can be considered a byproduct of the process. This is calculated as Equation 3 shows.

$$P_{WFV} = P_F \times H^o_C \quad (41) \quad \text{-----} \quad (3)$$

Where PWFV = waste value as fuel (\$/kg), P_F = price of fuel (\$/MMbtu or \$/GJ) and H^o_C is the heat of combustion (MMBtu/lb or GJ/kg).

Thus, the waste stream that comes out from the decanter has non-reacted carbohydrates, lipids, proteins and ash. Knowing the flow of the waste stream (taken from each of the simulations in kg/h), the price of the fuel (7.402 \$/kJ⁸) and the low heating value (LHV) of *Laminaria* sp. (12.1 MJ/kg⁸), the revenue per time (\$/h or \$/year) is obtained using the conversion factor 9.48E+04 MMBtu/MJ. LHV is used since there is not enough energy to release due to the water evaporation. This process is assumed to happen in a burner with efficiency of 100%. However, the incineration unit is not modelled individually but it is assumed to be included in the OBLS cost of the project.

4.3 Techno-economic assessment

Thus, the overall techno-economic assessment is performed while assuming the price of lactic acid as the sensitive parameter. Thus, the selling price is varied to achieve a zero cumulative cash-flow in a set period. This represents the break-even point, moment from which the plant starts giving benefits. Thus, the cumulative cash-flow analysis is applied for each of the scenarios to see if the investment can be recovered in 15 or 20 years, respectively, or if the selling price must be changed to have the break-even point in the year 15 or 20.

The methodology for evaluating the feasibility of each of the 4 scenarios follows a sequential framework. The procedure entails the simulation design, equipment sizing and economic evaluation with the calculation of the minimum viable lactic acid selling price, MVSP, and the maximum feedstock price. Subsequently, to improve the feasibility of the project, the optimization of the plant with heat recovery is approached. The first run considers the heat integration configuration given by Aspen Energy Analyzer, which is implemented in the simulation and assessed as shown in the diagram (Figure 12). If the minimum viable selling price (MVSP, the minimum possible selling price of the product for the economic viability of the project) is lower than one of the base cases, it is considered as the optimum configuration and the rest of the analysis are performed referring to it, else they are done to the base case (production facility located in the USA).

Figure 12. Methodology followed for each scenario.

A similar scheme is followed when applying the new configuration options suggested as a sensitivity analysis. As Figure 13 shows, in these cases, the base case will be the most feasible case after the heat recovery, and its MVSP is compared with the ones obtained after changing the selected parameters for performing the sensitivity analysis.

Figure 13: Methodology followed for the sensitivity analysis scenario

5. Results and discussions

5.1 Incurred process costs

Once all the cases are rigorously simulated, economic evaluations are performed before and after the optimization. This is carried out to observe, if there is a tradeoff between the savings in utilities (impacting the variable operating cost) and the capital cost due to the implementation of the optimal designs. To initiate the analysis, the breakdown of the cost contributors of different scenarios is illustrated in Figure 14 (a-d). The cost contributors considered are raw materials, consumables, utilities, labor, annualized capital and maintenance cost.

Figure 14 (a-d). A summary of cost contributions of various scenario's studied: a. Acid chemical pretreatment and reactive distillation downstream, b. Acid chemical pretreatment and REED/EDBM downstream, c. Hot water wash pretreatment and reactive distillation, d. Hot water wash pretreatment and REED/EDBM downstream.

The pie charts for all the scenarios depict two major cost contributors; raw materials and utilities. The usage of raw materials is linked to the yield of the process, which is an indication of the fraction of solids utilized for the LA production. The utility cost is the second largest contributor in the total cost. Due to the impact of utility in the variable cost of production and the project cash flow, the optimization is focused on reducing utility consumption. Thus, the results of the economic analysis before and after the heat integration of different scenarios are assessed. Table 10 summarizes the results from simulations and analysis of the 4 different scenarios, with drying of biomass as a unit operation, in the physical pretreatment.

Table 10. Results of the simulation and techno-economic assessment for the scenarios with drying of biomass in the physical pretreatment. A detailed information for the economic parameters is provided in Appendix 7.

Pretreatment scenario	Dilute acid pretreatment (ACTH)		Hot water was pretreatment (HWW)	
Downstream Configuration	Reactive distillation	REED/ EDBM	Reactive distillation	REED/ EDBM
Fresh biomass (kg/h)	317293	317293	353555	353555
LA (kg/h)	10911	11127	10967	11005
Yield (%) kg LA/kg carbohydrates	49.83	50.82	44.95	45.11
Yield (%) kg LA/kg solids	28.65	29.22	25.85	25.94
Capital cost, annualized (\$)	3.23E+07	2.93E+07	3.00E+07	2.91E+07
Variable cost of production (\$)	2.31E+08	2.34E+08	2.33E+08	2.27E+08
Fixed cost of production (\$)	2.14E+07	1.95E+07	1.99E+07	1.94E+07
Total cost of production (\$)	2.85E+08	2.83E+08	2.83E+08	2.76E+08

At a first glance, it is evident that a substantial quantity of fresh biomass is required to produce the 11 tonnes/hour lactic acid set as plant capacity. The large amount of macroalgae required, together with the low yield obtained (it does not reach the 30 % (kg LA/ kg solids), highlights the difficulty of building a feasible lactic acid plant, with comparable capacity as corn or lignocellulosic biomass. Regarding the availability of biomass, the annual production of brown algae is estimated to be 9.42 MT (dry basis)⁸. The geographic locations, where brown algae are grown, are primarily in Asia. In this region, China produces more than 4 MT/year of *Laminaria* seaweed where 90% is cultivated via aquaculture⁵⁷. Although this amount satisfies the feedstock demand of the lactic acid plant, with the set capacity, it would require a big percentage of the annual brown algae production. Thus, to envision the implementation of such a process,

obtaining higher amounts of biomass from countries, which have barely implemented macroalgae cultivation techniques, would be required⁵⁷.

Moreover, the large quantities of algae needed are aligned with the fact that a mere 12% of the biomass is a solid fraction, of which 28.5% is ash (Table 1). Thus, although the carbohydrate content in brown algae is higher than in lignocellulosic biomass, the yield of lactic acid from brown algae turns to be comparable (yield of 269 kg LA/dry ton), when using corn stover as feedstock⁵⁷. This is a direct consequence of not being able to metabolize alginate to lactic acid using the microbial strains currently available.

Apart from the global output gleaned from the amount of biomass required and the yields obtained, Table 10 gives an overview of the four base cases simulated. The two cases with dilute acid pretreatment present higher yields of lactic acid production than the two with hot water wash pretreatment. The yield difference is due to higher polymer hydrolysis achieved when using the acid pretreatment compared to HWW (as previously illustrated by the conversion fractions in Table 4). This leads to higher availability of sugars to be metabolized to lactic acid, during the fermentation. On the other hand, scenarios with electrodialysis applied to the downstream configuration resulted in a lower capital cost. This agrees with the fact that the reactive distillation needs two distillation columns and one reactor while the REED/EDBM scenario needs less equipment; system with two membranes connected to an electric field and a distillation column.

According to these results, the scenario with dilute acid pretreatment and electrodialysis downstream is determined to be the best option. However, the fact that the scenario with dilute acid pretreatment uses more consumables (more sulfuric acid and ammonia) and utilities (it

reaches higher temperatures) relative to the scenarios with hot water wash, it is important that the later must not be ruled-out without a thorough analysis.

To relate all the income and expenses over the project life and, obtain the time when the project starts having benefits (break-even point), a discounted cash flow analysis is performed for each scenario. The results for the four scenarios are displayed in Figure 15. Detailed parameters and assumptions pertaining to the cash flow (Operational and capital expenses) are documented in Appendix 7.

Figure 15. Discounted cash flow of the four base case scenarios. Appendix 7 provides details pertaining to parameters used to estimate the cash flows for the 4 scenarios illustrated here.

Figure 15 illustrates that none of the cashflows converge to the x-axis, implying break-even point cannot be achieved within the 20 years of operation. The cumulative cash flow of the four scenarios follows the same trend. In the first three years, the cumulative cash flow decreases sharply due to the cost related to construction, while not fetching any revenue from the operation

(Table 3). From the fourth year onwards, the intensity of drop reduces. This reduction is a result of revenue generation countering the outgoing expenses. Moreover, starting the fourth year, the cash cost of production ($CCOP = VCOP + FCOP$) and the depreciation is also accounted for, contributing to the decline of the cumulative cash flow. The CCOP is constant during the whole project but, as mentioned previously, the debt payment is accounted for during the first ten years. Thus, once the debt payment stops (10 years of operation), the trend of the cumulative cash flow changes. While the scenarios a, b and c continue to have a negative slope (showing no recovery), scenario d with hot water wash pretreatment REED/EDBM starts compensating the losses with marginal recovery. The plot reveals that the scenario with hot water wash pretreatment and REED/EDBM (d) is the most feasible case. Since none of the presented scenarios has a breakeven point within the 20 years of the lifetime of the facility, the minimum viable selling price (MVSP) for LA is calculated for each scenario, to see the price at which the product must be sold to get a payback within 15 to 20 years.

Therefore, by optimizing the process by applying heat integration, the outcomes are expected to be better. Subsequently, the techno-economic evaluation is performed on each scenario and an MVSP is calculated for recovering the initial investment in 15 and 20 years of operation, respectively.

By displaying the different MVSP's (for various combinations of process configurations and payback period) in Figure 16, it is expected to clearly identify, how the changes reflect in the economic performance of the plant.

Figure 16. Minimum viable selling price (MVSP in \$/kg, with pay off scenarios in 15 and 20 years) comparison of the scenarios with drying of biomass in the physical pretreatment.

Figure 16 illustrates how various MVSP's change, depending on the simulation design applied. As seen previously, in Figure 15, none of the base case scenarios recovers the investment in 15 or 20 years with the actual lactic acid selling price (2.86 \$/kg)⁵⁸. Therefore, to recover the initial investment within this period, the lactic acid selling price is increased until the break-even point appears. Moreover, heat integration is applied to the four scenarios to observe the potential of optimizing utility usage. Figure 16 shows that depending on the pretreatment utilized, the results change. For the scenarios of acid pretreatment, heat integration results in a lower minimum selling price than the base case, the investment in equipment (increase in the capital cost) is recovered due to utility savings. However, in the scenarios with hot water wash pretreatment, the MVSP is higher for the HENS design and thus, the heat integration is not worthy from an economical perspective.

Since the HENS configuration applied in the scenarios with hot water wash downstream is not economically viable, theoretically, another configuration could be tried to check if utility savings are achieved. However, since the composite curves diagram performed by Aspen Energy Analyzer for this scenario (Appendix 8) displays insignificant potential for internal heat exchange, the heat integration of this scenario is discarded. Thus, for the scenarios with dilute acid pretreatment, the optimum configuration is with heat integration and for the scenarios with hot water wash the optimum configuration is the base case. In summary, least MVSP is obtained for hot water pretreatment and REED/EDBM (d) with MVSP of 4.05 \$/kg for a pay off in 15 years (42 % higher than the current selling price of lactic acid) and 3.83 \$/kg for a pay off in 20 years (34 % higher than the current selling price of lactic acid).

5.2 Sensitivity analysis

Although the calculations made with the presented techno-economic framework for obtaining the minimum lactic acid selling price can be already considered as a sensitivity analysis to the price of the product, other relevant parameters are also appraised for sensitivity analysis, which affects the economic operation of the plant. The parameters considered are listed in Table 11 and are evaluated in the current section.

Table 11. Sensitivity analysis scenarios

	Parameter	Changes
Financial	Location	China; Germany ; United states (Gulf coast)
Processing	Physical pretreatment	Drying biomass; Biomass not dried
Composition	Biomass composition (I)	Carbohydrates % in the feedstock (Mannitol & laminaria)
Composition	Biomass composition (II)	Including alginate in the fermentation

5.2.1 Location

As mentioned before, the location of the plant has a major effect on the economics of the plant since prices such as equipment purchases, commodities, utilities or taxes change according to the region where the plant is operating. In the base case calculations, USA (gulf coast) is the selected region but to see how much the location affects, two more regions are considered; **Germany** and China.

To perform a sensitivity analysis, the parameters considered are the location factor, which affects the capital cost as Equation 2 shows, and the cost of the commodities and utilities, which affects to the variable cost of production. Appendix 9 lists all the various location cost factors used for the calculations. In addition, Appendix 9 lists various regional inflation rates applied for the region specific discounted cashflow calculations. Thus, the changes are implemented in the techno-economic model and new MVSP's are calculated for each scenario.

Firstly, the MVSP for each configuration, on the four scenarios, are calculated for **Germany** and China as shown in Figure 17, to observe, if the performance of scenarios depending on the place where the plant is located. The regional MVSP's (to payback in 20 and 15 years) are plotted together with the best minimum selling prices obtained for each scenario (for Base and HENS configurations).

Figure 17. Minimum viable selling price (MVSP, \$/kg) comparison of the scenarios with drying of biomass in the physical pretreatment in the *Germany* and China (20 years pay off).

At first glance, Figure 17 shows results similar to the ones obtained for the USA (Figure 16), as none of the configurations has a cost below the respective regional selling price. However, in contrast to the USA, the most profitable configuration in *Germany* (hot water wash and REED/EDBM downstream (d)) is 43.5% higher than the respective selling price.

The trend exhibited by China is in somewhat similar in comparison to that of the USA. However, in contrast to the USA, the difference between the current selling price in China and the MVSP obtained is very different (109.6 % of the difference in the best case and 113.5% for the base case). However, since the current selling prices are quite different in particular countries, comparing their MVSP in the same plot would not give a proper overlook of the process. The lowest MVSP for each region (which represent the best scenario for this region) is compared with its current selling price, as listed in Table 12.

Table 12. Difference between the minimum viable selling price (regional base case and heat integrated configuration) and the current selling price of each country

Base Case					
Location	Pretreatment	Downstream	Selling Price (\$/kg)	MVSP (\$/kg)	Difference (%)
Germany	HWW	REED/EDBM	2.793	4.01	43.5
USA	HWW	REED/EDBM	2.858	3.83	34.0
China	HWW	REED/EDBM	1.536	3.28	113.5
HENS					
Location	Pretreatment	Downstream	Selling Price (\$/kg)	MVSP (\$/kg)	Difference (%)
Germany	ACTH	REED/EDBM	2.793	3.96	41.7
USA	ACTH	REED/EDBM	2.858	3.81	33.3
China	ACTH	REED/EDBM	1.536	3.22	109.6

Table 12 shows that the country which has a relatively closer value of the MVSP, and the current selling price, is the USA. Among all the three regions, China has the lowest location coefficient (as listed in Appendix 9, however, this is countered by low selling price in the region, making the difference (%) highest. Whereas, the USA presents a difference between the minimum selling price and the current price of ~40%, which is significantly lower, compared to the value obtained for Germany and China. Another possibility could be to import LA from China, provided that difference between the MSVP in USA and China (0.59 \$/kg for this case) is greater than the shipping cost. Substantiating this claim would require a detailed supply chain assessment (Including costs pertaining to shipping, loading, unloading, land transport and tariffs), which is outside the scope of analysis presented in the manuscript. Therefore, among the three regions, studied in this case, the USA would be a preferred place to locate the plant. However, it must be

acknowledged that none of the regions demonstrates a desirable payback, failing to recover the investment in 20 years of plant life.

5.2.2 Physical pretreatment

Configuring the process with or without dryer has more influence than just saving a dryer unit in the physical pretreatment. The drying process is a step that leads to an increase in the capital cost and the variable cost of production since it requires a high amount of energy to evaporate water present in the algae. Thus, since the process carried out is a fermentation, which requires water it seems logical that the drying step is not required.

However, not drying the biomass has some effects. Firstly, if the algae are not dried before entering the thermochemical pretreatment step, to produce the same amount of lactic acid, the equipment required is bigger. When drying the biomass, the solid content in the hydrolysis step is 20% while in this case is 12%. Thus, the reactor for hydrolysis and saccharification would have larger volumes which leads to an increase in the capital cost. Nevertheless, higher water content remains just until the fermentation step. At this point, the fermentation requirements set a sugar concentration of $\approx 150 \text{ g/l}^{48}$ homogenizing conditions until the end of the process.

Thus, both scenarios with hot water wash pretreatment are simulated and the techno-economic evaluation is performed to obtain the MVSP. As it is illustrated in Figure 16, the heat integration for hot water wash scenarios does not lead to the economic improvement of the process and therefore, in this case, the minimum selling price is just calculated in the base case. The results obtained are summarized in Table 13 were to see which scenario performs best, the minimum selling prices obtained without the dryer are compared with the lowest minimum selling price obtained with the dryer.

Table 13. Minimum selling price (\$/kg) comparison of the scenarios without dryer in the physical pretreatment and with hot water wash pretreatment

Scenario	SP (Market) of LA	MVSP ref. scenario of LA produced by Base Case	New MVSP of LA due to increased carbohydrate composition
d. hot water was pretreatment and REED/EDBM	2.86	3.83	3.80

Table 13 shows a similar picture as the one for the scenario with dryer in the physical pretreatment the lowest minimum lactic acid selling price is obtained in the scenario with the hot water wash and REED/EDBM downstream. However, the new MVSP is lower, leading to think that it is an advantageous option since the savings in the dryer purchase and utilities are higher than the extra cost of the equipment for handling the wet biomass.

As previously mentioned, the macroalgae carbohydrate composition strongly depends on the season. Therefore, the continuous production depends on efficient storage of the feedstock which conserves properly the biomass. Besides, when considering the transportation of the biomass, it is noticed that the shipping price would greatly increase when considering wet biomass instead of dried. Therefore, although the possibility of utilizing directly wet biomass is appealing, the dryer process turns more feasible (potentially near the harvesting location), and it is the one used currently. Nevertheless, since the techno-economic results show that the non-dryer scenario is better, a system in which not all the biomass were dried if it is going to be shortly used or it is going to be used close to the place it has been harvested should be investigated. The drying unit operation has a major impact of the economic operation of the suggested process. Hence, this operation must be designed based on the desired throughput and taking the logistics of the feedstock into consideration.

This sensitivity analysis also shows the effect of the solids dilution rate in the economics of the plant. When using the biomass without the drying step, it is using the biomass with 12% solids dilution. It shows that the higher solids dilution, the higher capital costs implies since bigger equipment is required and higher is the utility demand for cooling/heating.

5.2.3 Variations in carbohydrates present in the feedstock

As previously mentioned, the feedstock composition is very susceptible to the type of macroalgae, the season when it is harvested and to the location of growth. In the initial calculations, the carbohydrates used are laminaria, mannitol and cellulose and their percentage in the biomass are calculated as an average of these carbohydrates in different *Laminaria* sp. (Table 1. Chemical composition of the brown algae laminaria sp., adjusted from Table 1). However, if the brown algae considered is *Laminaria Latissima*, whose amount of laminaria and mannitol is higher (comparison is shown in Table 14 a.) when harvested in the proper period of the year the process gives a different picture and the results are outlined in Table 14 a.

Table 14 a. shows that increasing the carbohydrates, results in an increase in the yield of the process. In order to gain insights on its effect on the MVSP, the minimum selling prices of the best obtained scenario is presented in Table 14 b, together with the lowest minimum selling price of the initial scenarios.

Table 14. a) Results from increasing the carbohydrate composition in the feedstock for scenario hot water wash pretreatment and REED/EDBM (d). b) Minimum selling price (\$/kg) comparison of the hot water wash pretreatment scenarios with maximum percentage in composition of mannitol and laminaria.

a. Sensitivity	Base case	Sensitivity
Laminaria (%)	16.5	18
Mannitol (%)	12	15

Biomass (kg/h)	353555.3	321826.0
Yield (%) kg LA/kg solids	25.9	29.5
Yield (%) kg LA/kg carbohydrates	45.1	47.6
Lactic acid (kg/h)	11005.1	11391.2
b. Minimum selling price (\$/kg) comparison		
SP (Market) of LA	MVSP ref. scenario of LA produced by Base Case	New MVSP of LA due to increased carbohydrate composition
2.86	3.83	3.67

In Table 14. b one can see that the project becomes more financially attractive due to the higher yield of the process. As in the case of the average *Laminaria* sp. composition, the best design is the hot water wash pretreatment and REED/EDBM, with a minimum selling price of 3.89 \$/kg. However, it must be acknowledged that this option is challenging to achieve, since, to maintain the continuous processing capacity, it would be required to harvest, dry and store the feedstock for the whole year. This would lead to a peak of energy in this period to dry the huge amount of biomass and enormous storage tanks which would increase notably the variable cost of production and capital cost.

5.3.4 Fermentation of alginate

Alginate is a carbohydrate present in high percentages in most brown algae species. However, in previous calculations, it has not been taken into account for the production of lactic acid, due to inability of microbial strains to convert alginate into lactic acid together with the sugars from *laminaria*, mannitol and cellulose.

Thus, a sensitivity analysis is conducted to predict, how the economy of the plant would change, if the assimilation of the alginate would be possible. It is assumed that the hypothetical microbial strain would perform in a similar way to the modified *E. coli* which has been recently found and

can directly produce ethanol from alginate without the requirement of a pretreatment⁸. The results obtained from this scenario are shown in Table 15.

Table 15. Results from increasing the carbohydrate composition in the feedstock for scenario hot water wash pretreatment and REED/EDBM (d).

	Base case	Sensitivity
Laminaria (%)	16.5	16.5
Mannitol (%)	12	12
Alginate (%)	Not utilized	23
Biomass (kg/h)	353555	213040
Yield (%) kg LA/kg biomass	31.12	52.16
Yield (%) kg LA/kg carbohydrates	45.1	75.6
Lactic acid (kg/h)	11005	11112

As foreseen, the yield of the process greatly improved since the big percentage of carbohydrates that alginate represents. The yields for this case almost double the base case that was previously utilized.

To see how this enhanced utilization of feedstock affects the economy of the project, techno-economic simulations are performed. The resulting cumulative cash flow obtained for the suggested designs for the best scenario (hot water wash pretreatment and REED/EDBM) is shown in Figure 18.

Figure 18 illustrates the cumulative cash flow analysis for the scenario with REED/EDBM downstream. It shows how including the fermentation of alginate, the economics of the plant change radically. The scenario which does not utilize the alginate does not recover the initial

investment in the twenty years represented. On the other hand, when fermenting the alginate, the plot shows positive results having the break-even point in the 11th year (starting production).

Figure 18. Cumulative cash flow analysis for the scenario with hot water wash and REED/EDBM downstream.

Consistent with the previous finding, the best scenario is the one with Reverse Electro Enhanced Dialysis and Electrodialysis with Bipolar Membrane. Hence, it is demonstrated that investing in a strain which could metabolize alginate would be feasible since it leads to making the process of production of lactic acid from brown algae viable.

The inputs used in the techno-economic model are subject to uncertainties. MVSP is a parameter that accounts for all the costs incurred during the process. In reality, crude oil prices, consumer demand, feed supply and several other external events may have some impact on the MVSP as well. Having such a framework at disposal equips stakeholders with an option to zoom-in to a specific time point in future or choose to play with a broader range of parameters to foresee

pitfalls. As economics happens to be one of the three pillars (along with the environment and social), based on which long term sustainability of technology is claimed, such techno-economic frameworks should be appraised and adapted to specific cases before any research and development activity is performed. It is acknowledged that for a true sustainability assessment, the environmental impact must also be calculated. While this is out of the scope of this manuscript, the results generated are complementary and hence, is used for populating Life Cycle Assessment (LCA) inventories⁵⁹ and combined in an economic single score to be able to find the trade-offs between economic and environmental sustainability⁶⁰.

6. Conclusions

The manuscript investigates process configurations and subsequent economic evaluations of the production process of polymer-grade lactic acid. Four major design configurations are simulated to be able to assess which model-based scenario has better feasibility. Techno-economic evaluation is performed on the optimized configurations and the new MVSP (Minimum Viable Selling Price) is compared with the base case values.

Considering the set of initial considerations, the scenario which performs the best is the hot water wash pretreatment and REED/EDBM (Reverse Electro Enhanced Dialysis / Electrodialysis with Bipolar Membrane) as a downstream purification method. Thus, although the acid pretreatment results in better yields, the techno-economic analysis shows that the extra cost in variable cost and capital cost (extra equipment required for conditioning after the acidification) is not justified. Thus, the MVSP is 3.83 \$/kg for the optimal process design.

When changing the initial considerations such as location and feedstock composition, the model displays its sensitivity. The location of the plant is observed to be a very sensitive parameter

since it affects both fixed and variable cost and capital cost as well. Nevertheless, hot water wash pretreatment and REED/EDBM downstream stands out as the process with least MVSP in the USA, Germany and China. In this way, the USA emerges as the best location to construct a LA plant since the difference is the lowest, 34%.

Finally, the effect of the feedstock composition is assessed. This is observed by two different simulations:

- varying biomass composition (*Laminaria Latissima*) with higher laminaria and mannitol content as feedstock.
- including a scenario with the fermentation of alginate.

In both cases, the feasibility of the plant is improved. While using *Laminaria Latissima*, resulted in an increase in the percentage of laminaria from 16.5 to 18 %, and mannitol from 12 to 15 %, the MVSP decreases from 3.83 \$/kg to 3.67 \$/kg. In a hypothetical scenario, when considering the utilization of alginate, the results completely changed and the investment is recovered in 11 years with the SP kept at its current value, 2.86 \$/kg. While many of the previous results have implied towards unfeasible economics, this outcome has revealed some potential, warranting scientific exploration for utilizing alginate fraction in macroalgae. Hence, it could be concluded that unless entire carbohydrates present in the macroalgae are exhausted towards products, the production of LA would likely lead to unfavorable economic results. Moreover, the annual production of this algae is acknowledged to be a key practical constraint as at-times the availability is not enough for constructing a LA plant with the current capacity set. The capacity was set to construct a plant comparable with real LA plant supplied by other feedstocks.

In conclusion, this manuscript demonstrates that the realization of detailed optimization potential can be achieved, by applying the documented framework at the conceptual stage of research. The output of such an assessment can be used as a yardstick to find and implement necessary scientific exploration, leading to an economically viable production of bio-based chemicals.

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