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Novel macroalgae (seaweed) biorefinery systems for integrated chemical, protein, salt, nutrient and mineral extractions and environmental protection by green synthesis and life cycle sustainability assessments

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Abstract

Highly efficient macroalgae based chemical factories and environmental protection have been comprehensively studied for the first time to displace fossil resources to mitigate climate change impact. Wild macroalgae by (bio)phytoremediation and residual macroalgae by biosorption can be used to treat wastewaters, marine environment, soil and sludge. Cultured macroalgae can be processed through drying, milling, grinding, suspension in deionised water and filtration extracting sap of heavy metals; centrifugation of solids recovering nutrients; ion exchange resins of supernatants separating protein and polysaccharides; dialysis purifying protein from salts and pretreatment of polysaccharides producing a sugar platform. Protein profiling shows the presence of the essential amino acids as well as others as food additive, flavour enhancer and pharmaceutical ingredient. Sugars can be converted into a chemical: levulinic acid by controlled acid hydrolysis; 2,5-furandicarboxylic acid by heterogeneous catalytic reaction; succinic acid by tricarboxylic acid cycle; lactic acid by fermentation, with

3-5 times market value than bioethanol. Protein, sugar based chemical and inorganics give the highest to the lowest climate change impact savings of 12, 3 and 1 kg CO_2 equivalent kg^{-1} product. Their cost of production is estimated at \$2010 t^{-1}, significantly lower than their market prices, making the integrated marine biorefinery system economically more attractive than lignocellulosic terrestrial biorefinery systems. Social life cycle assessment indicates that the highest to the lowest avoided social impacts will be from the displacements of animal based protein, sugars and minerals, in Indonesia, China and Philippines (producing 27 million tonnes per annum, 93% of global production), respectively.

Keywords: bioseparation, techno-economic analysis, life cycle assessment, resource efficiency and resource recovery, green chemicals and protein profiling, simulation modelling.

Introduction

The current pace of utilising fossil resources, coal, crude oil, natural gas and shale gas, to produce commodity products to meet increasing societal demands leads to the rise in average global temperature this century exceeding 2 ^{o}C above pre-industrial levels and consequently ecosystem damages[1,2]. To mitigate climate change impacts, highly efficient multi-faceted multi-product biorefinery systems must be developed to replace and dominate over fossil based systems. A biorefinery is an integrated system with efficient and flexible conversion of biomass feedstocks, through a combination of physical, chemical, biochemical and thermochemical processes, into multiple products[1]. The concept was developed by an analogy to the complex crude oil refineries adopting the process engineering principles applied in their designs, such as feedstock fractionation, multiple value-added productions, process flexibility, integration and efficiency[1]. Integrated biorefinery system is thus needed to replace crude oil refinery system and displace petroleum derived products.

Traditionally, starchy crops were enzymatically hydrolysed and fermented to produce so-called first-generation bioethanol, oily crops and microalgae to biodiesel via transesterification and

solid organic waste to biogas and digested matter via anaerobic digestion[3,4,5,6]. More recently, lignocelluloses in plant cell walls are used as the feedstock for the production of second generation biofuels and residues as biochar with complete in-process integration for zero waste added value productions[4,5,6]. Current advances in heterogeneous catalysts for transesterification of oily wastes and residues, while not as dramatic as those in biochemical pathways, are providing new ways to replace middle distillate aviation fuels[1]. There are policy supports, such as, tax incentives, guaranteed prices and direct support for investment and production in one hand, blending requirements and mandates for public fleets on the other hand, and broadly, fuel standards, public research and trade measures and various cross-sectorial policies for biofuel or bioenergy production system. Many of these developments are thus being driven by strong public support inevitably resulting in higher risks of externalities and more volatile market prices and hindering translational self-sustainable systems development[3,7]. Biofuel or bioenergy production system alone is far from being optimal, because functionalities in processing steps and molecules are not comprehensively mapped to maximise performance from added value productions. Amidst of all the current research and development efforts, there is an unmet need to bring together the critical areas of process integration and life cycle sustainability assessment with techno-economic, social and environmental aspects, for overall sustainability[7]. Adopting and adapting these tools would provide a means of establishing a baseline, against which new integrated multi-product biorefinery systems can be benchmarked for green investment.

Terrestrial resources such as lignocelluloses have been concentrated to develop the science needed to manage human uses of ecosystem services, with a few recent exceptions, such as algal biorefineries as a strategic solution for the food, energy and water nexus issues of biofuel production[8]. However, their environmental performance in terms of land use and land use change (LULUC) shows them in negative lights in some studies[9]. Algae are proving to alleviate

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LULUC impacts through a marine algae biorefinery approach. However, microalgae have been of research focus[4,5,6,8] than macroalgae. Macroalgae integrated biorefinery systems are thus a nascent field of clean technology and sustainable developments.

Figure 1 depicts a map of global macroalgae also known as seaweed production (in tonnes) by country in 2015[10]. Its worldwide production was estimated to be 30 million tonnes, with culture and wild seaweed accounting for 29 million and 1 million tonnes, respectively. About 50 countries engage in seaweed cultivation globally, with the top five producers that constitute 98% of total production concentrated in East Asia: China, Indonesia, Philippines, South Korea and Japan[10]. Seaweed has been used as a source of sustenance by coastal human communities in these countries. Low capital investment, low crop/harvest cycle and ease of cultivation make it very attractive to these coastal communities. Its ability to blossom in low-tide areas makes it particularly safe for women and children to maintain seaweed plots, thereby providing an extra source of income for their families, who predominately engage in fishing for subsistence[10].

Figure 1

In addition to its use in rural coastal areas, there is a growing interest in the use of seaweed as raw material for other industrial sectors. This interest emanates from the unique chemical composition of seaweed: its high carbohydrate, protein and salt concentrations[11]. Thus, it is envisaged that seaweed can be used as a feedstock for biorefineries, where its carbohydrate contents can be converted into high-value organic chemicals[11] and salts salvaged for mineral production. Sugars are also a source of lipids via oleaginous yeast[12] and the lipids can be converted into biodiesel by transesterification[13]. Of particular interest is the extraction of high value biologically-active oligosaccharides alongside protein with essential amino acids from macroalgae[14,15]. However, no literature is available on macroalgae integrated biorefineries, linking (bio)phytoremediation of soil and water for environmental protection, and post-life, recovery of inorganic resources (salts and minerals) and valorisation of organics into added

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value products (commodity products from sugars, food, feed and pharmaceutical products from protein and nutrients as soil conditioner). This paper thus conducts the first comprehensive study on macroalgae based green chemical synthesis and environmental protection. In addition, there is a significant gap in terms of a robust study encompassing triple bottom sustainability assessment of marine biorefinery systems. Thus, herein, the potential integrated biorefinery systems along the supply chains in the above-mentioned seaweed-producing countries are presented. Therefore, this study sets a precedence through a rigorous analysis of economic, environmental and social aspects of macroalgal biorefinery systems for the recovery of all possible products and resources. This paper is situated to develop integrated macroalgae biorefineries to confront the United Nations Sustainable Development Goals 2, 6, 7, 8, 9, 12 and 13.

Macroalgae or seaweed as a feedstock to biorefinery

Table 1 shows a comparison of compositions between selected macroalgae, hardwood and softwood species[16]. Compositions of macroalgae suggest that the sugar, protein and extractive and ash platforms extracted from macroalage have medium to very high potentials in co-producing added value products[16]. Macroalgae in contrast to terrestrial biomass do not need the rigidity provided by lignin in marine environment. Absence or low quantity of lignin helps in microbial degradation of marcoalagae to produce biofuels and chemicals.

Table 1

Figure 2 shows the guidelines developed for potential economic production and utilisation of the various platforms, i.e. sugar, protein, lignin and inorganic in chronological decreasing order of market values, respectively, that can be extracted from biomass. Following the guidelines, thus, macroalagae can be effectively utilised to produce sugar, protein and inorganic platforms, while hardwood and softwood can be effectively utilised to produce sugar and lignin platforms, respectively. The added value product options from lignin utilisation is illustrated elsewhere[1].

As the focus of this work is macroalgae biorefinery, the acquisition and utilisation of inorganic, protein and sugar platforms are discussed in this paper as follows.

Figure 2

Inorganic platform

Macroalgae can be used to treat wastewaters, marine environment, soil and sludge by (bio)phytoremediation during growth phase by removing and detoxifying metals, minerals and salts from the environment. Residual or waste macroalgae can also be used for biosorption of environmental contaminants.

(Bio)phytoremediation during growth phase. Aquatic system contamination with heavy metals has become a critical problem in regions with rapid industrialization and economic growth. In agricultural regions where airborne pollution precipitates into the soil, the focus is especially on heavy metals that are readily absorbed by crops, creating a vector for their introduction into the food chain. Macroalgae can uptake and sequestrate heavy metals, minerals and salts from the environment during the growth phase. (Bio)phytoremediation is a term that makes use of biomass in this case macroalgae to remove heavy metals from aquatic system, due to positive concentration gradient between the aquatic system (at higher concentrations of metals) and cells of macroalgae (at lower concentrations of metals), thereby detoxify the aquatic system. The aquatic system often gets contaminated by heavy metals exceeding their permissible limits of discharge to the environment, due to anthropogenic activities. There are four different types of (bio)phytoremediation determine the mechanism of in-situ or ex-situ remediation of heavy metals. These are phytovolatilisation, phytostablisation, phytoaccumulation and phytoextraction. Phytovolatilisation involves the uptake of toxic metals, such as mercury, selenium and arsenic from the soil or sludge by plants and releasing them in less toxic forms (dimethyl selenide and mercuric oxide) to the atmosphere. Therefore, contamination control in aquatic systems and soil prevents the presence of many heavy and

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carcinogen metals in the food supply or in the environmental in general. However, the performance of macroalgae in terms of removal rate of toxic metals from soil or sludge is lower compared to terrestrial plants[17,18]. Figure 3 illustrates the mechanisms of (bio)phytoremediation by macroalgae during their growth phase[19]. Heavy metals that may undergo phytostablisation, phytoaccumulation or phytoextraction depending on the surrounding soil or aquatic system conditions and macroalgae strain. Phytostablisation is the only ex-situ remediation process, whereby the movements and bioavailability of pollutants are restricted by plant roots. The valences of the states of the metal pollutants do not change, but they accumulate around the roots and thereby have low concentrations in the environment.

Figure 3

Biosorption by residual and waste macroalgae. In addition to (bio)phytoremediation by wild macroalgae, many kinds of residual and waste marine algae, especially brown algae, have been found to be very effective biosorbents in capturing heavy metals (Pb, Cd, Cu, Zn, Cr, Co, etc.) from industrial effluents or wastewaters because of their high metal uptake capacities[20]. Contrary to bioaccumulation or biodegradation, metal removal mechanism in biosorption is not metabolically controlled[21,22]. Metal uptake in biosorption is mainly carried out through the interaction between metal ions and the cell walls of the biosorbents. Use of residual algal cells is more attractive as it generally offers higher metal binding capacity than live cells and allows multiple sorption-desorption cycles[23]. Desorption agents (HCl, NaOH, $CaCl_2$, etc.) and deionised water can be used to recover the adsorbed heavy metal ions on macroalgal biomass[24]. Maximum biosorption capacities of heavy metals by marine macroalgae vary between 0.39 and 1.66 mmol g^{-1} depending on the strain and are significantly higher than that reported for freshwater algae (0.5 to 1.0 mmol g^{-1}), bacteria (0.05 to 0.2 mmol g^{-1}) or fungi and yeast (0.2 to 0.5 mmol g^{-1})[24,25].

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The constituents of the biomass cell wall determine the biosorption capacity. In particular, the cell wall of brown algae is made of cellulose, which forms the fibrous skeleton, and alginate and fucoidan that constitute the amorphous embedding matrix[26]. The embedding matrix of red algae is made of sulphated galactans. Together the matrix and the skeleton of the cell wall determine the availability of the binding moieties, such as carboxyl, hydroxyl, phosphoryl, carbohydrate, imidazole, amine, phosphate, sulphuryl, sulfate, etc. and govern the metal binding capacities of the various strains of macroalgae[21]. A sequential or a cascading approach is thus necessary to develop simultaneous multiple extractions' protocol[27,28].

The chemical diversity of the cell wall constituents provides a number of different mechanisms for the biosorption of metals, such as ion exchange, complexation, physical adsorption, surface precipitation, electrostatic attraction, covalent binding, van der Waals attraction, etc.[21,29]. Amongst these, ion exchange is the most important and the principle mechanism of biosorption. The overall biosorption rate of heavy metal ions by macroalgae is determined by a number of factors including, concentration of metal ions and algae biomass, pH, contact time, temperature, amount of functional groups in the algae matrix, accessibility of these functional sites, the coordination number of the metal ion to be sorbed, etc.[23]. Also the metal uptake capacity of the different macroalgal strains will differ given the heterogeneity of the cell wall constituents in the different macroalgae species[26].

Biosorption of heavy metals by macroalgae for wastewater treatment has been studied for Co(II), Cd(II), Cr(III) and Pb(II) ions on four species of red seaweeds *Corallina mediterranea*, *Galaxaura oblongata*, *Jania rubens* and *Pterocladia capillacea*[30], As(III) on green marine algae *Ulothrix cylindricum*[31], Cr(VI) on modified brown algae *Sargassum bevanom*[32], and Cu(II), Zn(II), Cd(II) and Pb(II) on green alga *Ulva lactuca*[33] (represented by Langmuir equilibrium isotherm model[34]); Cu(II) and Pb(II) ions on three brown algae namely, *Cystosiera compressa*, *Sargassum vulgare* and *Turbinaria*[35], Cd(II) and Ni(II) on modified brown algae[36],

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and Ni(II) on modified *Sargassum sp.* (brown algae)[37] (represented by Freundlich equilibrium isotherm model[34]); Co(II) on *Cystoseira indicia*[38], Cr(VI) and U(VI) on brown macroalga *Padina pavonia*[39] (represented by Temkin equilibrium isotherm model[34]); Ni(II) on *Oedogonium hatei*[40], Cr(VI) on *Gracilaria verrucosa*[41] and *Oedogonium hatei*[42], Cd(II) on *Hypnea valentiae*[43], and As(III), Ni(II), Cd(II), Cu(II), Pb(II) on *Nizmuddinia zanardini*[44], *Ceramium virgatum*[45] and *Laminaria japonica*[46] (represented by first order pseudo kinetic model); Ni, Cd, Pb, Cu, Fe, and Zn on *Sargassum muticum*[47], *Spirulina platensis*[48], and red seaweed *Kappaphycus sp.*[49] (represented by intraparticle diffusion model).

Protein platform

Macroalgae have significantly higher protein content in comparison to the terrestrial plant proteins sources[50]. Macroalgae proteins offer nutraceutical, pharmaceutical and cosmeceutical properties due to the presence of antioxidant, antihypertensive, immune-modulatory, anticoagulant and hepeto-protective substances[51,52,53]. Seaweed is also extensively utilised as ingredients in food additives (polysaccharide gels (hydrocolloids), polysaccharides and biologically active materials), pet food, feeds, human and animal food preparations owing to its high contents of polyunsaturated fatty acids, carbohydrates, vitamins, minerals, and dietary fibers[54]. Due to these reasons, the acquisition of proteins as well as carbohydrates from cultivated macroalgae in a controlled medium is an attractive value proposition. However, the key challenge is to retain the structure of the proteins intact, while also, maximising the yields of added value products from the sugar platform of the macroalgae. As discussed earlier, desorption agents and deionised water can be used to recover the adsorbed heavy metal ions on macroalgal biomass[19], protein extraction will need also simultaneous recovery of polysaccharides[51,52,53]. However, these studies lack a detailed process synthesis approach to develop conceptual integrated biorefinery systems. Figure 4 illustrates an integrated biorefinery configuration for the acquisition of the protein, sugar and inorganic platforms and

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nutrients, simultaneously. The synthesis steps are organised in a hierarchical order from high value low volume to low value high volume products. This process synthesis study is associated with Table 2 gives a comprehensive list of inventories in transferable units to enable commercial application as well as techno-economic and life cycle assessments.

Figure 4

Table 2

Biomass before and after oven drying, milling and grinding is suspended in deionised water, followed by filtration to extract the sap that contains minerals of heavy metal contents. The solid content is further centrifuged to recover the sediments containing nutrients (N, P, K) that can be applied as soil conditioner or compost. The suspension, filtration and centrifugation cycle with recycling from downstream to upstream unit operations can be repeated depending upon the recovery rate and purity of nutrient and heavy metals. The supernatants from centrifugation primarily contain polysaccharides and proteins that can be effectively separated by ion exchange resins. With the former being strongly negatively charged, is bound to the resins, which can be regenerated to extract the polysaccharides[52]. Proteins being weakly bound can be extracted as the eluent. The eluent after dialysis to get rid of the salts gives rise to the protein platform[52]. The polysaccharides separated by ion exchange resins need pretreatment to break down into constituent monosaccharides, discussed in the latter section.

As shown by protein profiling, glutamic acid, aspartic acid and arginine in high concentrations (5-25% by mass of protein), glycine, proline, serine, alanine, valine, threonine, phenylalanine, lysine and leucine in medium concentrations (4-9%) and histidine, isoleucine, methionine and tyrosine in low concentrations (<5%) can be extracted from protein depending on macroalgae strain and protein extraction protocol[52]. Amongst these, valine, threonine, phenylalanine, lysine, leucine, histidine, isoleucine and methionine have been classified as essential amino acids for human body. Moreover, macroalgae have the same amino acids as meat, egg, poultry,

soy and milk, thus, the protein extracted from macroalgae can displace meat, egg, poultry, soy and milk based proteins. Furthermore, glutamic acid salt is a food additive and flavour enhancer, aspartic acid is a building block for protein synthesis, and arginine helps in neurotransmission and blood flow, glycine in sleep and memory, proline in digestive health, serine in brain, muscle and skin health, and alanine in blood sugar level, respectively. Although currently lacking standard techniques for extraction of these amino acids, recognising their important roles in food and medicines, there will be further value generation propositions utilising the protein platform from cultivated macroalgae.

Sugar platform

Monosaccharides are held together by glycosidic bonds that can be broken down by hydrolysis liberating the constituent monosaccharides of the polysaccharides extracted alongside the proteins by ion exchange resin (Figure 4 and Table 2). The various methods of pretreatment broadly fall into two categories: addition of extraneous agent and application of energy[55]. The former incurs higher cost of chemical and downstream separation and purification and the latter incurs higher cost of energy and capital cost of pretreatment. Hydrolysis (acid or alkali or enzymatic), organosolv (extraction using organic solvent) and ionic liquid extraction use extraneous agents for biomass decomposition, while ultrasonication and microwave irradiation technologies make use of energy for biomass decomposition[55]. Steam explosion and supercritical water extraction technologies (also known as pulping as well as hydrothermal liquefaction, up to 450 ^{o}C and 250 bar) are a flexible method for biomass decomposition, because moisture is naturally present in biomass reducing the amount of steam requirement[55]. Pretreatment gives a sugar platform that upon valorisation gives platform chemicals or fuel as shown in Figure 4 and a solid cellulose phase, which can be conditioned to produce cellulose microfibrils with applications in healthcare sector or used as fuel to biomass boiler for energy production. The latter use of cellulose will be essential to meet on-site heat demand to produce

platform chemicals from the sugar platform. Any external fossil energy input to the system causes damage to the environment that should be eliminated by on-site bioenergy generation. Although lignin could be a potential fuel for on-site bioenergy generation, its absence or low concentration makes macroalgae an easier feedstock for chemical and biofuel production than terrestrial biomass.

Predominantly, cellulose and hemicellulose constitute the polysaccharides. Other complex polysaccharides are also available. The constituents of polysaccharides play two significant roles in macroalgae that also determine their application for human consumption. The two roles are energy storage and structural polysaccharides. The energy storing polysaccharides in brown, green and red algae are laminarin consisting of 20-25 glucose units, starch, and floridean starch and floridoside, with a structure similar to common starch, respectively[11]. The structural polysaccharides in these macroalgae types include alginate; ulvan and cellulose; and cellulose, agar and carrageenan, respectively[11]. By their obvious roles, structural polysaccharides are present in the cell walls of macroalgae.

The laminarin structure may vary in degree of branching, the degree of polymerization and the ratio of (1,3)- and (1,6)-glycosidic bonds. Extracted from brown algae, they offer biological activities such as antioxidant, antitumor, antimicrobial, immune modulation, drug delivery and anticoagulant properties[56] that determine their market applications such as functional foods and nutraceuticals and price as high as \$250 g^{-1}.

Starch consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin by weight[57]. Its main uses are as food conditioner, thickener and additive (~\$6 kg^{-1}).

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Alginate is made of uronic acids: mannuronic and guluronic acids. Alginates are used to increase viscosity, to form gels and jellies and to stabilise food and in textiles by giving a smooth texture[58] ($10 kg^{-1}).

Ulvans are acidic water-soluble sulphated heteropolysaccharides that contribute to the strength of the cell wall and give flexibility to the plant[56]. Their applications in the form of gels include chemical, pharmaceutical, biomedical and agricultural industries ($395 g^{-1}).

Celluloses are polymers of C6 sugars linked by β-(1–4)-glycosidic bonds. Celluloses could be a feedstock to applications ranging from energy, biofuel, through chemical to food ($4 kg^{-1})[55,59].

Agar is made of agarose and agaropectin, with agarose making up about 70% of the mixture. Agarose is a linear polymer, made up of repeating units of agarobiose, a disaccharide made up of D-galactose and 3,6-anhydro-L-galactopyranose. Agar can be used as a laxative, an appetite suppressant, a vegetarian substitute for gelatin, a thickener for soups, in fruit preserves, ice cream, and other desserts, as a clarifying agent in brewing, and for sizing paper and fabrics ($40 g^{-1}).

Carrageenan is a linear polysaccharide made up of a repeating dissacharide sequence of α-D-galactopyranose and β-D-galactopyranose. Carrageenan is used as a binder, thickening agent, and a stabiliser in medications, foods, and toothpaste. Carrageenan is also an ingredient in weight loss products ($30 kg^{-1}).

Green chemicals from sugar platform

The sugar platform has the greatest potential to generate a wide range of platform or building block chemicals to displace petrochemicals[1]. Chemicals derived from the sugar platform can be of two types, one that can directly displace a petrochemical, usually having the same chemical formula; the other offers the same functionality as a petrochemical (but with different chemical formula). The former usually would have an advantage of established market, while

the latter would have to find a niche market. Sugar platform is the most popular platform so far, giving rise to both types of chemicals.

Some chemicals offer many functionalities of petrochemicals and can be a precursor to numerous added value products with applications in pharmaceutical, specialty chemical, agricultural, solvent, platform chemical, fuel (additive) and energy sectors, detailed elsewhere[1]. These building block or platform bio-based chemicals are referred as 'sleeping giants'[55,59]. Sugars present in macroalgae are fermentable for production of bioethanol[60,61]. However, an added value proposition is the production of 'sleeping giant' chemicals with market price 3-5 times greater than bioethanol. Given the absence or low concentration of lignin in macroalgae, production of these chemicals is advantageous. Examples 'sleeping giant' priority chemicals include levulinic acid, 2,5-furandicarboxylic acid (FDCA), succinic acid and lactic acid from the sugar platform[1,11]. Their synthesis mechanisms are shown in Figures 5a-d, respectively.

Figure 5

Levulinic acid via controlled acid hydrolysis. There are various mechanisms concerned with the intermediate 5-hydroxymethyl (HMF) production from sugars. HMF is the intermediate of levulinic acid by one step hydrolysis mechanism. Thus, HMF production reaction mechanisms determine that of levulinic acid.

The conversion of sugars to HMF follow the pathways shown in Figure 5a. C5 sugars are directly dehydrated into HMF formation. C6 sugars can be decomposed into HMF by two reaction pathways: Lewis acid catalysed isomerization of C6 sugars into C5 sugars followed by dehydration into HMF formation; direct dehydration of C6 sugars into HMF formation. Between these two reaction pathways, the one passing through C5 sugars should be more selective towards HMF formation. On the basis of studies of the Lewis acid-catalysed isomerisation of hexoses, one can hypothesise that the combination of Lewis and Brønsted acidity could produce HMF by a combined isomerisation/dehydration reaction of C6 sugars.

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Through the addition of the hydroxyl group to position 5 in furanic ring, the opening of the ring takes place and subsequent rearrangement occurs as a result of electronic shift promoted by adding three hydroxyl ions.

The sugars factory to make levulinic acid has been recognised as early as 1930[62]. Researchers found that mineral acid hydrolysis of hexoses results in the formation of levulinic acid amongst other substances. Later, a patent was developed on the method of making levulinic acid by adding sodium chloride to the reaction mixture[63]. The presence of sodium chloride in the reaction mixture increased the activity of the mineral acid, thereby increasing its catalytic action. Levulinic acid was obtained by mixing equal quantities of starch and hydrochloric acid (specific gravity 1.1) and heating for twenty hours in a flask with a reflux condenser at 38^{o}C. The humus material was filtered out from the mixture and pressed. The resulting liquid mixture containing water, hydrochloric acid and formic acid among the main ones were distilled off and salt was filtered out from the residue stream containing levulinic acid under reduced pressure. Efforts in process optimisation since then have been devoted in lowering the reaction time and concentration of mineral acid, thereby increasing health and safety of the system being handled and decreasing the toxicity of the reaction mixture and at the same time increasing the productivity and selectivity. Consequently, the various other patents followed the trend. Efforts have also been in making the reaction process continuous. A controlled acid hydrolysis process has highest efficacy for eventually producing levulinic acid from sugars. Controlled hydrolysis of sugars in 2 weight% dilute H_2SO_4 catalyst produces levulinic acid, furfural, formic acid, in plug flow (210−230°C, 25 bar, 12 s) and continuous stirred tank (195−215°C, 14 bar, 20 mins) reactors[55,59]. Char is separated by filtration, and combusted and heat recovered into steam generation in a boiler to meet on-site heat/steam demand. Levulinic acid is extracted by methyl isobutyl ketone solvent and purified by distillation and a finishing step[55,59]. Both the acid

catalyst and solvent are recovered using distillation and solvent recovery unit, respectively and recycled, detailed elsewhere[55,59].

FDCA via catalytic or biological conversion of HMF. To produce FDCA (Figure 5b), sugars are dehydrated to first form HMF using an acetone-water solution and acid catalyst (e.g. H_2SO_4). HMF is then reacted with an alcohol (R-OH) in the presence of a catalyst to produce an intermediate product called alkoxy-methyl furfural (RMF). Oxidation of the RMF yields the desired FDCA. The direct oxidation of HMF into FDCA production can also be done by using heterogeneous catalysts. The chemical catalytic routes have been thoroughly investigated[64]. The yield of FDCA product strongly depends on the catalyst used. Pt and Au nanoparticles are proven catalyst on various supports for HMF oxidation into FDCA. Cheaper and more abundant metal catalysts have been tried, but resulted in lower yield and selectivity. There are two main processes, crystallisation and distillation for FDCA separation and purification[66,66]. HMF is the primary precursor to FDCA and HMF in itself is a rather unstable molecule[67]. Increasingly, oxidation of HMF to obtain FDCA is becoming important, since its discovery[67], due to potential of replacement of terephthalic acid in the production of polyethylene terephthalate and polybutylene terephthalate[68,69,70]. Oxidation of HMF gives various products, diformyl furan, hydroxymethyl furan carboxylic acid, formylfuran carboxylic acid and FDCA[71]. All of them have various uses, but not limited to adhesives, sealants, composites, coatings, binders, foams, curatives, monomers and resins. Hence, all the products have market potentials and are important to recover. The reaction conditions are controlling factors of product selectivity. In the studied HMF oxidation processes, HMF is separated from the product mixture of sugar hydrolysis reactor by solvent extraction. A feedstock mixture of 0.828% Na_2CO_3 in 1% HMF is used to experiment the oxidation process. Air as oxidant is compressed to the oxidation reaction pressure. The product stream from the HMF oxidiser is flashed to separate air (mainly nitrogen) and solvent in the vapour phase from the FDCA

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product in the liquid phase. A second flash is needed to separate and recycle back the solvent to the HMF oxidiser. Nitrogen gas is purged. The liquid product from the first flash column is fed to a mixed-suspension, mixed-product-removal crystalliser to solidify FDCA at 25°C and 2.5 bar[65]. FDCA crystals of 98% purity are separated by filter. The filtrate primarily containing solvent is recycled back to HMF separator.

In the flowsheet producing liquid FDCA using a distillation column, the upstream process configuration is the same[65]. The solvent to be used for HMF extraction after sugar hydrolysis in this case can not be an aqueous solvent, because FDCA has high melting and boiling points, 342 and 420 °C, respectively. Therefore, a solvent must be selected, which also has a high boiling point. Literature shows high solubility of organic acids in trioctylamine, which can be used as the solvent to extract HMF prior to its oxidation step in the configuration with distillation as the main separation step to FDCA[65]. Liquid FDCA at a purity of 97% is obtained from the bottom of the distillation column.

Succinic acid via the tricarboxylic acid cycle (TCA). The citric acid cycle can be described through several stages and multiple steps, including numerous intermediates. Before entering the citric acid cycle, the D-Glucose is transformed into glucose-6-phosphate (glycolysis reaction), which through retro-aldol fragmentation produces two intermediates (triose phosphates), that subsequently are transformed into pyruvate. Then, the pyruvate is transformed into pyruvate dehydrogenase, through a set intermediate complexes, which subsequently by decarboxylation (oxidation), produce Acetyl-CoA. These steps are illustrated in Figure 5c(1). The combination of Acetyl-CoA with oxaloacetate promotes the formation of citrate by condensation (Figure 5c(2)). In this reaction, known as Claisen condensation, thioester is combined with ketone. The methyl carbon of Acetyl-CoA attacks the electron deficient ketone carbon of oxaloacetate, promoting the abstract of a proton and formation of a carbanion. So, carbanion will attack this oxaloacetate carbonyl carbon, catalysing the citrate

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formation (synthase reaction). The following step is the formation of isocitrate, by dehydration and hydration reactions, respectively. The following stage is the isocitrate dehydrogenase reaction, which consists of an oxidation coupled to a hydride transfer to $NAD(P)^+$ and the formation of an organometallic complex, that facilitates the direct decarboxylation to produce α-ketoglutarate. The α-ketoglutarate dehydrogenase splits the carbon-carbon bond and is related to pyruvate dehydrogenase and its decarboxylated product is the thioester (succinyl-CoA). Succinate is produce by succinyl-CoA synthetase reaction, which includes phosphoryl (Pi) reaction, followed by phosphoryl transfer to GDP (Figure 5c(3)). The next step is succinate dehydrogenase reaction. Starting from succinate and removing two hydrogen atoms leads to fumarate. FAD is reduced to form FADH2. The fumarate, is converted into a hydroxy-dicarboxylic acid, known as malate, generated by hydration of the double bond to generate a carbanion transition state. This carbanion leads to malate by protonic addition (Figure 5c(3)). Finally, the malate is oxidised into oxaloacetate, using NAD^+ and producing NADH as conjugate acid. This reaction completes the tricarboxylic acid cycle (TCA), by regenerating oxaloacetate.

Anaerobic fermentation for succinic acid production generally operates at pH values where the succinate salt rather than the free acid is produced at low concentrations[72]. The components of fermentation broth, depending on the microorganism, range from succinate, residual sugar or glycerol, by-products (e.g., ethanol, acetate, lactate, formate, malate, pyruvate, etc.), biomacromolecules (e.g., proteins, nucleic acids, polysaccharides, etc.), inorganic salts and water[73]. This complex composition of the resulting fermentation broth requires a series of treatment processes to obtain pure succinic acid. Downstream processing comprises: removal of cells mainly using membrane filtration or centrifugation; removal of impurities and primary separation of succinate from the fermentative broth using evaporation for removal of volatile impurities (e.g. water, acetic acid), precipitation, electrodialysis, solvent extraction, reactive

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extraction, and adsorption with ion exchange resin, active charcoal, molecular sieve, or zeolite; conversion of the succinic salt into free acid using hydrochloric or sulphuric acid, and refining to the required purity by vacuum evaporation or crystallisation[1].

Lactic acid via sugar fermentation. The conversion of sugars into lactic acid can be summarised into two main steps: i) retro-aldol fragmentation of fructose, producing two C3 intermediates or trioses and ii) isomerisation of these trioses into lactic acid (Figure 5d).

In the biochemical synthesis route, lactic acid is produced by fermentation of carbohydrates such as glucose, sucrose, or lactose using bacteria or fungi. Bacteria give high growth rate and product yield, but they require special nutrient supply. Fermentation is controlled by temperature and pH. The optimal conditions for lactic acid production are pH between 5.0 and 6.8 and temperature between 30 °C and 45 °C[74,75]. During fermentation, the accumulation of lactic acid decreases the pH. Low pH decreases the activity of bacteria. Thus, maintaining the pH of the fermentation mixture at the optimal value is critical. Furthermore, lactic acid must be kept in the lactate form to avoid product inhibition. An alkali is generally added to maintain lactic acid in the lactate form. Fermentation processes are also affected by the concentration of substrate, the product or the biomass produced by the microorganisms. If these concentrations are high, the yeast or bacterial growth can be inhibited.

CaOH can be added to the fermentation mixture as lactic acid neutraliser and to alleviate product inhibition[73]. The resulting lactate salt remains in the solution. After the fermentation broth is taken out of the fermenter, is acidulated with sulphuric acid to convert the salt back into lactic acid and insoluble calcium sulphate[76]. The broth is then filtered to remove cells and gypsum. The $CaSO_4$ is removed by filter press. The clarified broth can be treated with activated carbon and ion exchange resins and concentrated by water evaporation to produce technical and food-grade lactic acid[77,78]. However, the quality of the product is not suitable for lactylates, polymers and other derivatives.

To produce a polymer grade product, the lactic acid in the clarified broth is concentrated by evaporation and then esterified with methanol or ethanol[79]. The resulting ester is recovered and purified by distillation. The purified ester is hydrolysed to return to the lactic acid form, now with a higher purity. Then, lactic acid is evaporated and the recovered alcohol is recycled. This process produces a product as pure as the petrochemical based product and is suitable for polymer production.

Techno-economic, life cycle and social life cycle assessments

The methodologies for techno-economic analysis (TEA)[1], life cycle assessment (LCA)[1] and social life cycle assessment (SLCA)[80] are shown in Figure 6a-c, respectively.

Figure 6

TEA methodology. TEA involves data collections on delivered cost of equipment, scaling factors and Chemical Engineering Plant Cost Index (CEPCI) for the delivered cost of equipment, discount rate and annual capital charge for capital cost estimation and personnel cost and costs of feedstock, utilities and chemical reagents for operating cost estimation[1,55,59]. The revenues are generated from selling the marketable products. Furthermore, any credits on products are to be added to the revenues and taxations and landfill and emission charges are to be subtracted from the revenues. The discounted cash flow calculation is then applied to estimate the net present value with respect to a chemical plant's life, as shown in Figure 6a. The stages of TEA as shown in Figure 6a are interactive helpful to analyse sensitivity of output due to input variables.

TEA Results. Table 3 gives the input variables[1] to estimate the delivered cost of equipment of the integrated biorefinery system producing protein, sugar and inorganic platforms. The throughput of the system is assumed at 5 tpd (t day^{-1}) dry macroalgae. Based on 8000 operating hours per year, the hourly dry tonnage is 0.23. Based on 80% moisture content, the wet biomass mass flowrate is 1.14 tph (t $hour^{-1}$). The oven dry tonnage (odt)

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biomass (30% moisture w/w) flowrate is 0.33 tph. The product yields from the integrated biorefinery system utilising brown macroalgae are sugars: 0.16 tph, proteins: 0.023 tph, salts: 0.034 tph, nutrients: 0.01 tph and minerals at ppm level, respectively. The total delivered costs of equipment for levulinic acid, FDCA, succinic acid and lactic acid production systems from the sugar platform are estimated from literature[55,59,81,82,83,84]. The total capital investment, i.e. five times the delivered cost of equipment, is annualised at 13% for each system[1]. The utility consumptions are given in Table 2. Electricity and steam prices are \$0.046[85] and \$0.005[1] MJ^{-1}, respectively. Based on a cost[86] of \$50 t^{-1} of dry macroalgae (0.23 tph) and the correlations given in Figure 6a and Tables 2-3, the annual cost of production from the integrated biorefinery system is 3.7 million \$ y^{-1}. This gives the cost of production of each product from the system at \$2010 t^{-1}, significantly lower than the market price of the polysaccharides, i.e. upto \$395 g^{-1} (ulvans) as well as the market price of essential amino acids \$58 kg^{-1}, making the integrated biorefinery system economically feasible. The cost of production is also lower than the market price of salts (\$7 kg^{-1}), but higher than the market price of nutrients (\$5.4 t^{-1})[55,59]. As the production rate of nutrients is insignificant, an overall profitable economic performance of the macroalgae integrated biorefinery system is forecasted.

The prices (\$ t^{-1}) of levulinic acid, FDCA, succinic acid and lactic acid are 4500, 2450, 1800 and 1300, respectively. Their yields (tph) from the sugar platform are 0.021, 0.1, 0.12 and 0.15, respectively. For the given cost of \$50 t^{-1} of dry macroalgae and the correlations given in Figure 6a and Tables 2-3, the annual cost of production (in million \$ y^{-1}) of levulinic acid, FDCA, succinic acid and lactic acid from the sugar platform (without the cost of production of the sugar platform) is 2.7, 2.2, 2.2 and 3, respectively. However, when the cost of production of the sugar platform of \$2010 t^{-1} is added, their annual cost of production (in million \$ y^{-1}) becomes 3.7, 5.3, 4.8, 8.4 and 5.6, respectively. These costs of production in \$ t^{-1} of the chemical product are equal to 2895, 2620, 4620 and 3055, respectively, indicating decreasing

economic feasibility in the order of: levulinic acid > FDCA > lactic acid > succinic acid, respectively. Furthermore, when the chemical production from the sugar platform is combined with the protein extraction in an overall integrated biorefinery system (Figure 4), the production of any building block or platform or "sleeping giant" chemical utilising the sugar platform becomes economically feasible. Based on the revenues generated from the extracted protein and chemical alone, a discounted cash flow of 4-8 million \$ y^{-1} (\$440-880 t^{-1} wet seaweed) is estimated, with decreasing order of profitability from FDCA through lactic acid and levulinic acid to succinic acid, respectively. Thus, FDCA is the target green chemical from the sugar platform extracted from macroalgae, co-producing protein and inorganic platforms, from the economic perspective.

Table 3

LCA methodology. The true feasibility of any proposed biorefinery system must be carried out using environmental impact assessment[87]. LCA is a holistic and systematic environmental impact assessment tool in a standardised way[1]. The LCA methodology shown in Figure 6b follows the guidelines of the International Organisation for Standards (ISO) 14040[88], 14041[89] and 14044[90], practical implementation of which has been discussed for sustainable biorefinery developments[1]. The system boundary includes the direct, indirect and embedded inputs and outputs. For each biorefinery unit operation inventory given in Table 2, resource and emission inventory data are extracted from Ecoinvent 3.3[91] and characterised and aggregated for life cycle impact assessments (LCIA) using the CML method[92] in SimaPro 8.2.3.0[93]. Although the CML method generates two primary resource depletion potentials, i.e. abiotic and fossil fuel depletion potentials, and nine primary to mid chain emission impact potentials, i.e. global warming, ozone layer depletion, human toxicity, freshwater aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidation, acidification and eutrophication potentials, only a few life cycle impact categories are relevant

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for sustainable biorefinery design and decision making[1]. With this respect, fossil fuel depletion, global warming and freshwater aquatic ecotoxicity (a measure of water pollution) potentials are the key ones control the decision making realised in the food and healthcare sector[94,95].

The environmental benefits are due to the displacement of petroleum derived equivalent products (attributional LCA). Future environmental benefits can be realised by improving and optimising the energy mix that is the hotspot in the supply chains (consequential LCA). Both the attributional and consequential LCA studies are thus important for sustainability of the integrated biorefinery system[1]. The net saving is estimated by environmental savings subtracted by environmental costs estimated over the lifetime of the biorefinery system.

The main products that can give environmental savings due to displacements of equivalent petroleum derived products are chemical (levulinic acid / FDCA / succinic acid / lactic acid), protein, salts, nutrients and minerals, offsetting fossil resources currently being used to produce these products. Chemical product from biorefinery can displace equivalent petrochemical. The protein extracted from macroalgae can displace meat, egg, poultry, soy and milk based proteins. Nutrients produced in the system can displace inorganic fertiliser derived from primary fossil resources. Salts can displace equivalent petroleum derived reagents. Excess electricity if generated can displace grid electricity and thereby offset equivalent amount of fossil needed to generate the same amount of electricity. Self-sufficiency by on-site energy supply and recycling water is essential for sustainability of the integrated biorefinery system. Table 4 gives Ecoinvent 3.3 datasets[91] assimilated for the various integrated biorefinery process inventories.

Table 4

LCA results. Table 2 shows the bases of data collection from Ecoinvent 3.3[91]. The data are generated for cultivated 1 kg dry brown macroalgae. Macroalgae contain moisture by 60-90% (w) that needs to be driven off by oven drying at 60 ^{o}C for 2-3 days. Based on the latent heat of vaporisation of water to superheated low pressure steam of 2.8[1] MJ kg^{-1}, the heat

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requirement for oven drying is 10 MJ kg^{-1} dry macrolage. The first and second stages of milling and grinding cost 10-50 kWh t^{-1} dry biomass[96]. The quantity of deionised water to recover minerals, nutrients and salts from the oven dry macroalgae can range from twice to as much as twenty times depending on their mineral content and type, cultivated or wild. Cultivated macroalgae are more suited for integrated biorefinery system because protein and sugar platforms can be recovered under controlled environment. Filtration power to move 1 kg of water is 0.4 kWh to separate minerals[97]. A decanter centrifuge with high removal efficiency of fine particles (0.1-100 μm) consumes 0.53 to 5.5[98] kWh m^{-3}, with an average power consumption of 3 kWh m^{-3}. Dialysis and ion exchange resins have a negligible resource use due to efficient regeneration process[99]. Pretreatment of polysaccharides is required to break the linkages between monosaccharides to produce the sugar platform. The sugar platform extracted from algae has been explored mainly for biofuel production and very little for other value added productions[100]. The heat of pretreatmet[101] is proportional to glycisidic bond energy (90 kJ mol^{-1}) and inversely proportional to molar mass (130 g mol^{-1}). The sugar platform (30% moisture w/w) is further analysed for the production of levulinic acid or FDCA or succinic acid or lactic acid. Levulinic acid yield is 46% of cellulose content in biomass[55,59]. 18% of cellulose and 40% of hemicellulose give rise to formic acid and furfural. The balance of hemicellulose and the entire lignin result in char formation[55,59]. The organic rich effluent gives a biogas stream 30% (w/w)[102] and a residual organic stream 8% (w/w dry biomass). The resultant biogas and char have a calorific value of 23 and 16 MJ kg^{-1} and are combusted in a boiler to produce steam at 80% efficiency[55,59]. Excess steam after fulfilling on-site demand can be expanded through a back pressure steam turbine to generate power at 35% efficiency[55,59]. The steam demand by the levulinic acid production process is 12 MJ kg^{-1} sugar platform[55,59]. The biogas and char combustion only fulfils 50% of the onsite heat demand, thus requiring external supply of the balance of heat. The sugar content of dry macroalgae is assumed at 70% (w/w). FDCA yield is

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64% (w/w) of sugar[103] and requires 5 MJ kg^{-1} FDCA and 3.9 MJ kg^{-1} fructose for fructose to FDCA and sugar to fructose conversions, respectively[104]. Succinic acid yield is 75% (w/w) of sugar[105] and requires electricity: 1.672 kWh kg^{-1} succinic acid and 3.114 kg steam with enthalpy 2.8[1] MJ kg^{-1} subtracted by heat supplied by biogas (0.606 MJ kg^{-1} succinic acid)[106]. Lactic acid yield is 93% (w/w) of sugar[107] and energy of 9.5 MJ kg^{-1} lactic acid[108].

The LCIA results are generated in the three significant categories, i.e. fossil fuel depletion, global warming and freshwater aquatic ecotoxicity potentials, for five individual systems, i.e. integrated biorefinery producing protein, sugar and inorganic platforms and levulinic acid, FDCA, succinic acid and lactic acid productions from the sugar platform. Individual systems' impacts are sensitive to the fuel mix to meet their onsite electricity and heat demands shown in Table 2. Thus, the sensitivity of electricity and heat supplies on the individual systems' impacts must be analysed consequentially. The electricity grid mix of Switzerland (CH) and the global (GLO) natural gas based heat generation well match the results reported for succinic acid production from sugars, 0.88 kg CO_2 equivalent per kg succinic acid[106] or 0.42 kg CO_2 equivalent per kg dry macroalgae. Two other scenarios selected for consequential analysis are electricity grid mix of Great Britain (GB) and the global (GLO) natural gas based heat generation and electricity and heat generation from locally resourced biogas (Biogas). The improvements in the LCIA results of the systems due to increasing renewable bioenergy supply are illustrated in Figure 7. It is obvious that in all three categories, the systems show improvements from the GB to Biogas energy mix scenarios due to the increased renewable energy mix in the system. For example, the global warming potential (in kg CO_2 equivalent per kg dry macroalgae) decreases from 2.87 to 0.05 for integrated biorefinery producing protein, sugar and inorganic platforms, and from 0.31, 0.82, 0.87 and 0.99 to none for levulinic acid, FDCA, succinic acid and lactic acid productions from the sugar platform, respectively. A

biogas based energy system can thus eliminate any environmental impact due to the processing of macroalgae through an integrated biorefinery system.

Figure 7

At the product level, environmental impacts and savings due to displacement of fossil derived equivalent products can be calculated using an allocation approach. Based on the mass distributions between the various products, the sugar and protein platforms, salts, nutrients and minerals are allocated 0.7, 0.1, 0.15 and 0.05 proportions and none of the total burdens of the integrated biorefinery system producing protein, sugar and inorganic platforms. For the Switzerland scenario, the fossil fuel depletion (in MJ per kg dry macroalgae), global warming (in kg CO_2 equivalent per kg dry macroalgae) and freshwater aquatic ecotoxicity (in 1,4-Dichlorobenzene (DCB) equivalent per kg dry macroalgae) potentials of the sugar platform are 11.75, 0.76 and 0.15, respectively. The global warming potential of protein from macroalgae is thus estimated at 0.11 kg CO_2 equivalent per kg dry macroalgae, which is 1.1 kg CO_2 equivalent per kg protein – this is insignificant compared to the meat protein results in 13 kg CO_2 equivalent per kg protein. Thus, macroalgae protein has a realistic chance to mitigate the climate change or global warming potential impacts (12 kg kg^{-1} protein resourced from seaweed).

The LCIA of chemical productions from macroalgae can be estimated by the summation of the impacts of the sugar platform from macroalgae and the impacts of the chemical productions from the sugar platform. In the Biogas based energy mix scenario, the global warming potential of levulinic acid, FDCA, succinic acid and lactic acid productions from macroalgae is estimated at 0.34, 0.15, 0.45 and 0.18 kg CO_2 equivalent per kg dry macroalgae, which is 3.75, 0.34, 0.86 and 0.27 kg CO_2 equivalent per kg of the chemical product, respectively. As a reference point for comparison, lactic acid production in Europe from petrochemical, via the reaction between acetaldehyde and hydrogen cyanide, causes 3.47 kg CO_2 equivalent per kg lactic acid[91]. Due

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to the low cellulose concentration in macroalgae, the production of levulinic acid from macroalgae via the sugar platform is not environmentally viable, while the other three target chemicals from macroalgae have comparable impacts as their productions from first generation feedstocks such as corn[106,108]. The increase in environmental burden due to low yields can be easily offset by bioenergy provision within the macroalgae integrated biorefinery system. The target "sleeping giant" building block or platform chemicals from macroalgae via the sugar platform in decreasing order are lactic acid > FDCA > succinic acid from the environmental perspective. Thus, from the perspectives of both the economic and environmental feasibilities, the choice of target chemical from the sugar platform from macroalgae is FDCA. The salts and nutrients have global warming potential of 0.16 and 0.05 kg CO_2 equivalent per kg dry macroalgae, respectively, in the Switzerland scenario.

SLCA methodology. For the adoption of innovative, integrated, flexible biorefinery systems, SLCA must also be conducted to avoid unintended side effects on the society. The SLCA methodology shown in Figure 6c in accordance with the UNEP/SETAC[109], has now become more practicable with the emergence of the social hotspot database (SHDB)[110]. In the SHDB, for each country, inventory data (in terms of US$ in 2002) has been assimilated for each product type or sector. As inevitable, each product type or sector is dependent on every other product type or sector due to interconnected supply chains[80]. The inventory data for each product type or sector for each country was then translated into social life cycle impact assessments (SLCIA), in five main themes: labour rights & decent work; health & safety; human rights; governance; and community infrastructure and underneath twenty two sub-themes[1,80]. While intertwined supply chain data assimilation from the global trade analysis project (GTAP)[111] provides a strong foundation, the present SHDB platform does not allow changing of inventory data and hence, adaptation for a bespoke study. This prevents a dynamic SLCA using the SHDB[91]. In terms of SLCIA results, the SHDB platform gives comparisons

between medium-risk hours-equivalent (mrh eq.) between given product types or sectors and between given countries in each theme[80].

Given the static nature of the SHDB platform, potential avoided social risks from the displacement of equivalent products can be assessed to focus research and development efforts. The basis of comparison between products and between countries can be one US$ (in 2002: the base year in the SHDB platform) of worth of product or the total US$ of worth of product based on its country-specific current production rate.

SLCA results. The potential commodities that can be displaced by macroalgae protein, sugars and salts are food products, sugar and mineral products identified in the SHDB platform. Their potential production rates of 10%, 70% and 15% are applied to the current production rates of macroalgae in the three leading producing countries, China, Indonesia and Philippines, respectively, for comparison. Their current prices (in $ kg^{-1}) of 58, 4, 7 are then applied to obtain the total US$ of worth of the products based on their country-specific current production rates. The current market prices are converted to 2002 US$ values as par the input requirements in the SHDB platform.

Figure 8 illustrates the five social impact categories per commodity / country. Following a general trend, Indonesia exhibits the highest avoided social impacts, followed by China that is closely followed by Philippines, respectively, by the displacement of conventional commodities by macroalgae based equivalent commodities. Amongst the commodities, sugars display the highest avoided social impacts, followed by protein and salts, from macroalgae, on the basis of one US$ (in 2002: the base year in the SHDB platform) of worth of the commodities. However, taking their potential production rates from the current production rates of macroalgae in the three countries as the bases, protein shows the highest avoided social impacts, followed by sugars and salts. The latter bases are more reliable as these take account of potential production rates. The priority products from macroalage in decreasing order would

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thus be protein, sugars and salts, respectively. The countries exhibiting higher avoided social impacts should seriously explore macroalgae based alternative for the greatest impactful commodity for social sustainability.

Figure 8

Furthermore, how integrated macroalgae biorefineries can confront the United Nations Sustainable Development Goals (SDGs)[112]: 2, 6, 7, 8, 9, 12 and 13, is discussed here.

SDG 2: Zero Hunger (by alternative cheapest way of protein sourcing including essential amino acids from seaweed for developing countries);

SDG 6: Clean Water and Sanitation (by in-situ bioremediation of heavy metals by macroalgae that helps restoration and management of water-ecosystem);

SDG 7: Affordable & Clean Energy (by affordable clean energy access from macroalgae, via the extraction of energy storage polysaccharides);

SDG 8: Decent Work and Economic Growth (by "economic productivity through diversification and technological upgrading and innovation");

SDG 9: Industry, Innovation and Infrastructure (by "increased resource-use efficiency and greater adoption of clean and environmentally sound technologies and industrial processes");

SDG 12: Responsible Consumption and Production (by less meat consumption a more sustainable lifestyle in developed countries by alternative seaweed protein and products and maximising resource efficiency and infrastructure sustainability);

SDG 13: Climate Action (by underwriting national policies, strategies and planning for eliminating climate change impact culprit, meat and fossil derived products, by seaweed or similar alternatives, in developed countries).

Overall, seaweed can provide a holistic sustainable solution to environmental damages, climate change impact, water pollution and deforestation due to meat consumption. More benefits can be shown by integrating seaweed biorefinery process synthesis model as shown here, with its

cultivation model, for circular economy closing the loop[1,113]. About a third of global population is expected to be undernourished by 2050[112]. Seaweed should be globally exploited to provide a cheap source of protein including essential amino acids for undernourished populations and replace meat in developed countries supporting equity. This paper should form the basis of sustainable development of seaweed biorefineries for reliable access to foundational goods.

Conclusions

Macroalgae have been studied for environmental protection and as a feedstock for chemical factories employing integrated biorefinery concept. Wild type macroalgae by (bio)phytoremediation and residual and waste macroalgae by biosorption can be used for environmental protection by removing and detoxifying metals, minerals and salt from the environment. Seaweed is also a source of essential amino acids for human body as well as other amino acids that are used as food additive, flavour enhancer, a building block for protein synthesis, and that help in neurotransmission, blood flow, sleep, memory, digestive health, brain, muscle and skin health, and blood sugar level, etc. However, currently there is no standard technique to retain the structure of the proteins intact, while also, maximising the yields of added value products from the sugar platform derived from macroalgae. In an attempt to fill this gap, novel biorefinery systems have been developed to coproduce sugar, protein, inorganic (salts, minerals and metals) and nutrient platforms from macroalgae by holistic rigorous systematic process modelling, synthesis and integration analyses applying green chemistry principles. The design activity provides the process inventories as the basis for the estimation of the capital and operation costs, costs of production of individual products, discounted cash flows, (environmental) life cycle assessments of overall systems as well as individual products and avoided environmental and social impacts due to displacement of individual fossil derived products. Important insights have been generated into target products from synthesis, integration and life cycle sustainability assessments comprising economic,

environmental and social aspects. The target platform or building block chemical is 2,5-furandicarboxylic acid, followed by lactic acid, from the sugar platform from macroalgae based biorefinery system, from both economic and environmental feasibility perspectives. Succinic acid and levulinic acid are ranked next due to their lower yields. They exhibit a win-win situation, with environmental feasibility for the former and economic feasibility for the latter. Sustainability of sugar derived platform chemical strongly depends on how energy is resourced. With increasing self-generation in terms of on-site combined heat and power or bioenergy generation and decreasing fossil based external energy supply, feasibility of sugar derived platform chemical increases. Thus, with increasing renewability in energy mix in future, levulinic acid as the sugar derived target platform chemical would be seen in a more positive light giving the highest return on investment and cash flows. Seaweed is a food in many parts of the world, with the top five producers that constitute 98% of total production concentrated in East Asia: China, Indonesia, Philippines, South Korea and Japan. Social life cycle assessment validates that producing protein, sugars and minerals from macroalgae to displace food, sugar and mineral products in the leading producing countries, China, Indonesia and Philippines, makes an attractive value proposition for investing in marine integrated biorefinery systems. Further, its investigation to provide a cheap source of protein including essential amino acids for undernourished populations and replace meat in developed countries has been justified to support the UN SDGs and circular economy.

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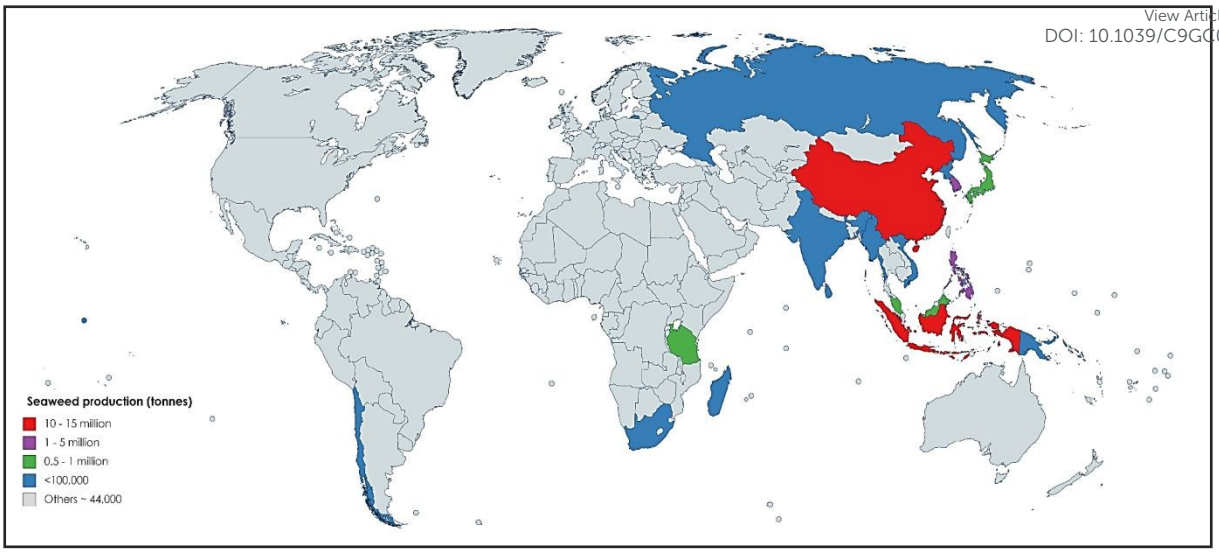

Figure 1. 2015 Seaweed production, by country[9].

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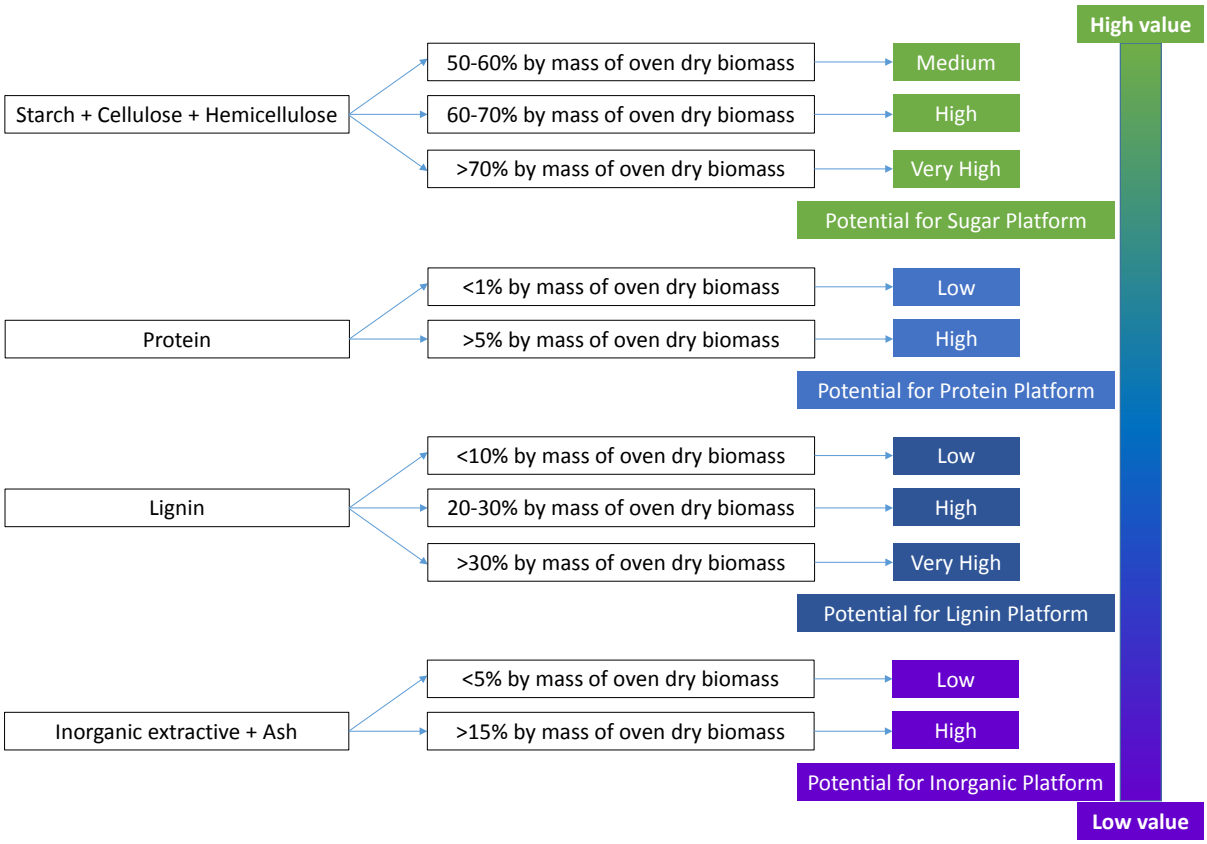

Figure 2. Guidelines for potential economic production and utilisation of the various platforms, i.e. sugar, protein, lignin and (from inorganic extractive and ash) inorganic that can be extracted from an oven dry biomass.

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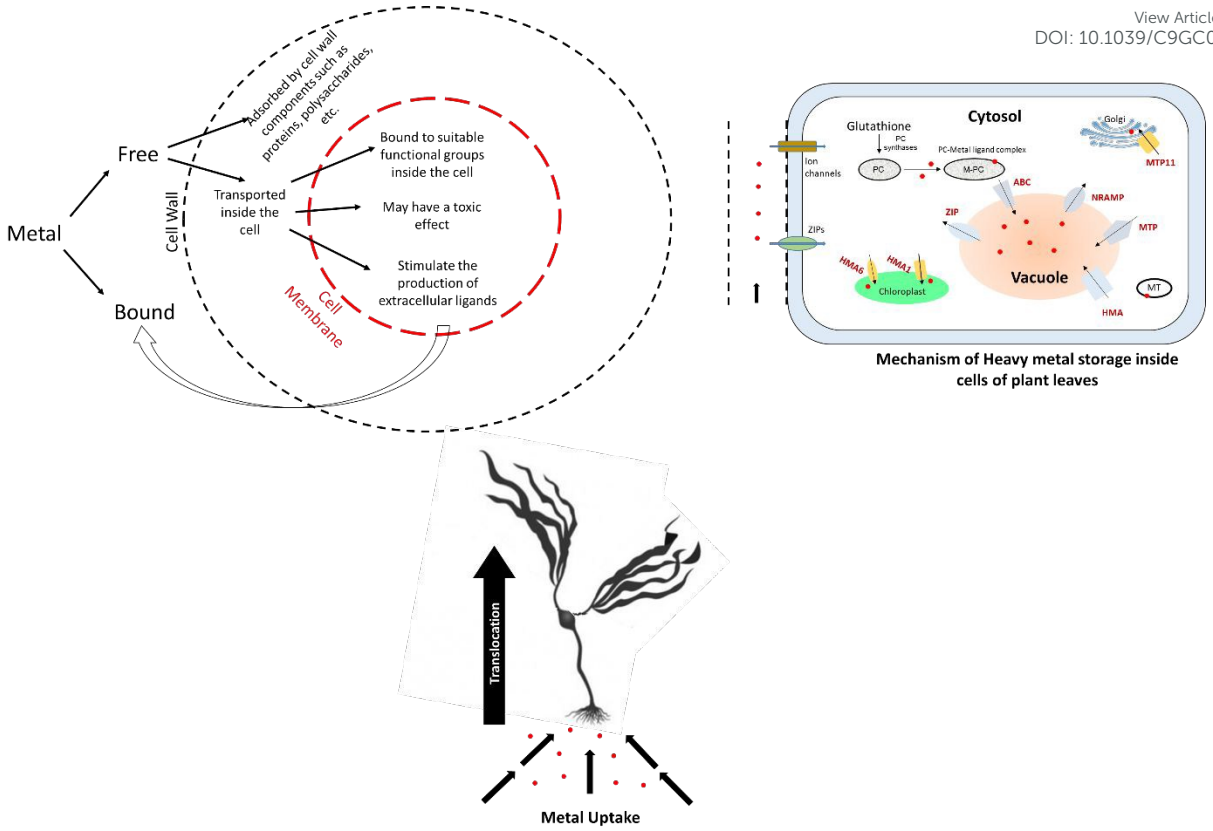


Figure 3. Routes involved in the uptake and sequestration of heavy metals in macroalgae[14]. Heavy metals in the (waste)water/sludge are absorbed in the rhizoids or holdfasts (root-like growths that anchor macroalgae to a substrate). From here they can be translocated further and can either be adsorbed by cell wall components such as proteins, polysaccharides, etc. or enter the cytosol of cells through transporters (ZIP) or ion channels and bind to suitable functional groups. Also shown is the generic mechanism of heavy metal storage inside cells of plant leaves.

M: Metal ion, PC: Polychelatin, ZIP: ZRT/IRT-like Protein, also known as Zinc-iron permease, MTP: Metal tolerance protein, ABC: ATP-binding Cassette, HMA: Heavy metal ATPase, NRAMP: Natural resistance-associated macrophage protein, MT: Metallothioneins (chelator).

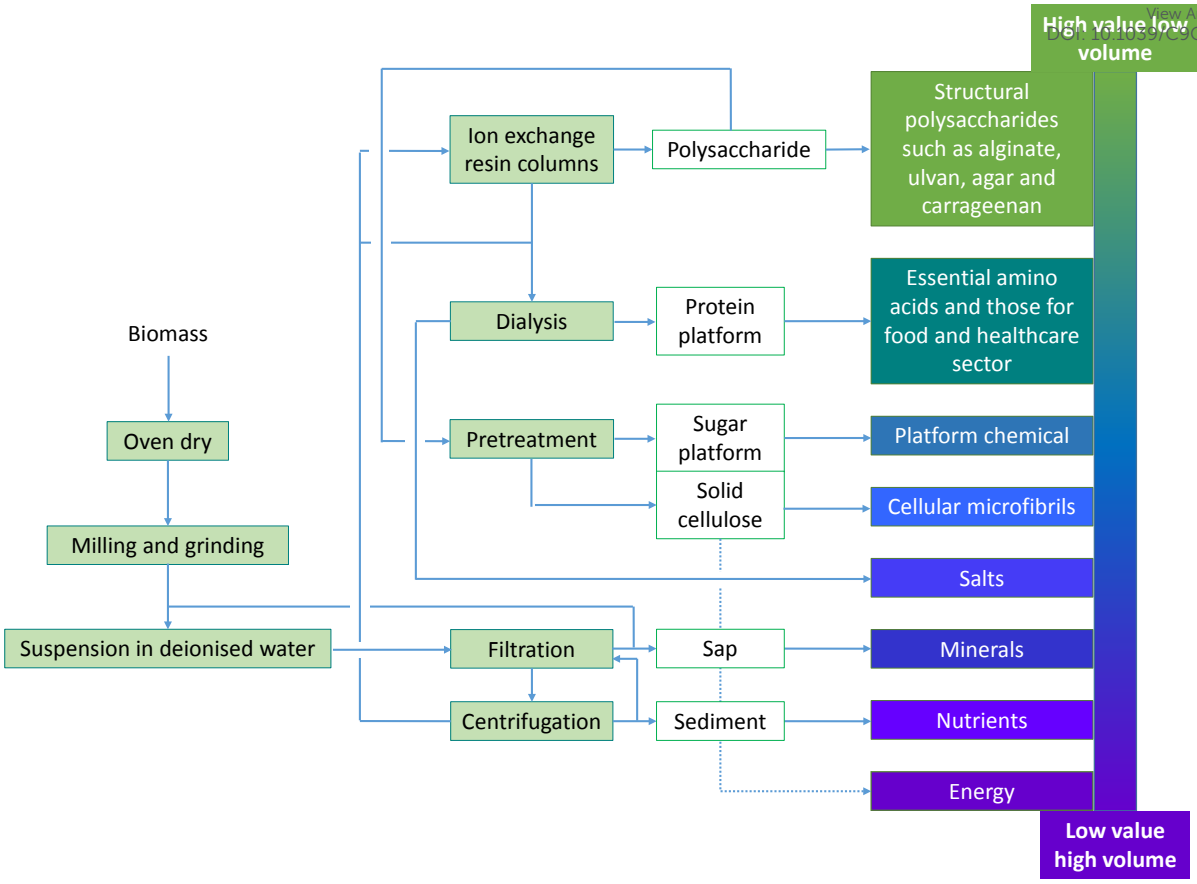


Figure 4. Integrated biorefinery configuration for the acquisition of the protein, sugar platform, nutrient, minerals and salts for industrial scale application.

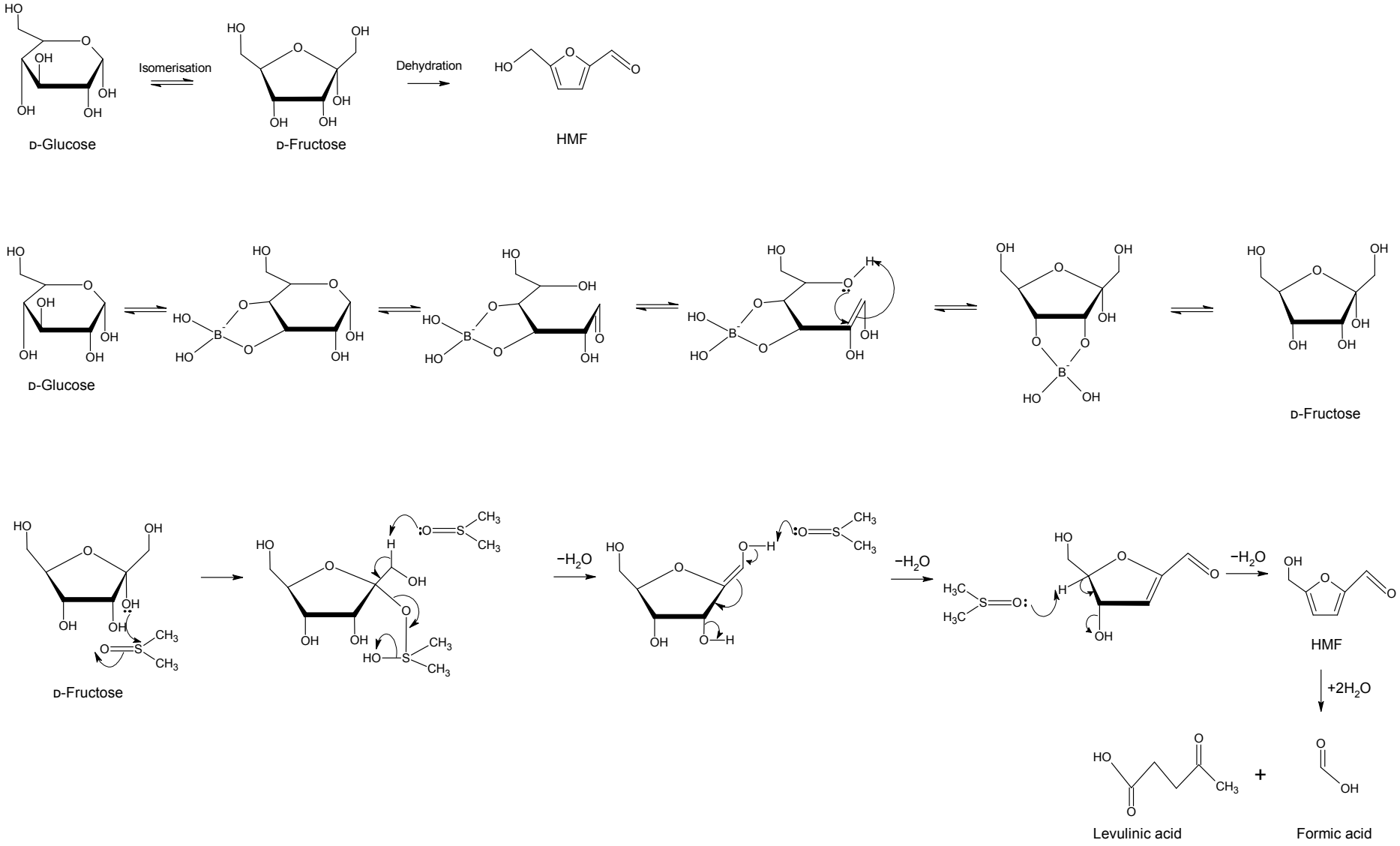


Figure 5a. Conversion of glucose to HMF, isomerisation of glucose to fructose and fructose to levulinic acid via HMF formation.

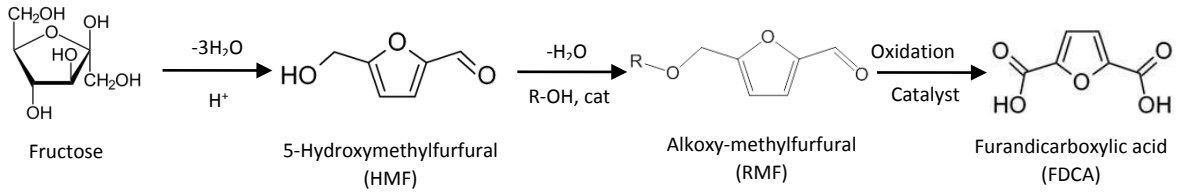
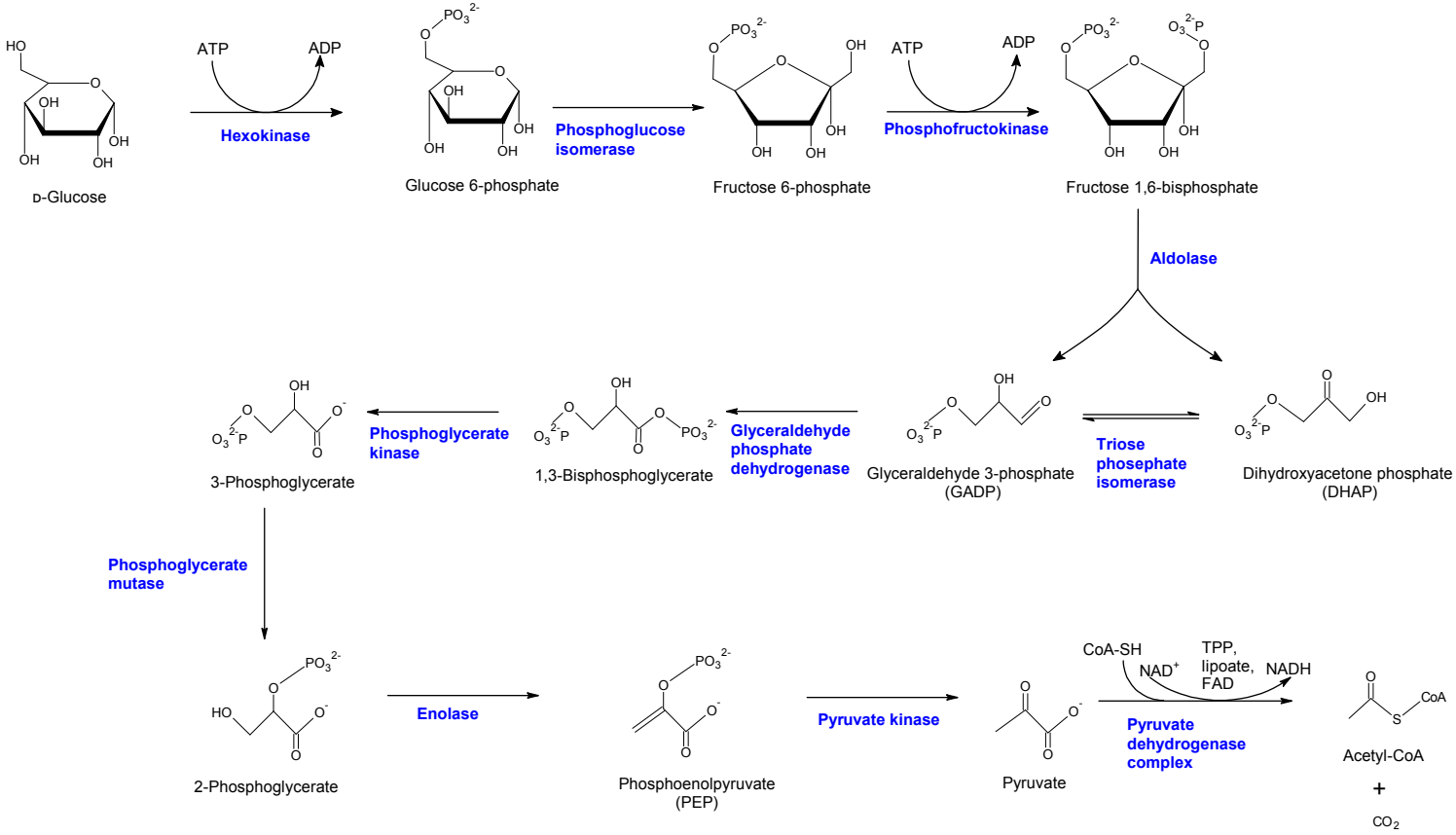


Figure 5b. FDCA via catalytic or biological conversion of HMF.



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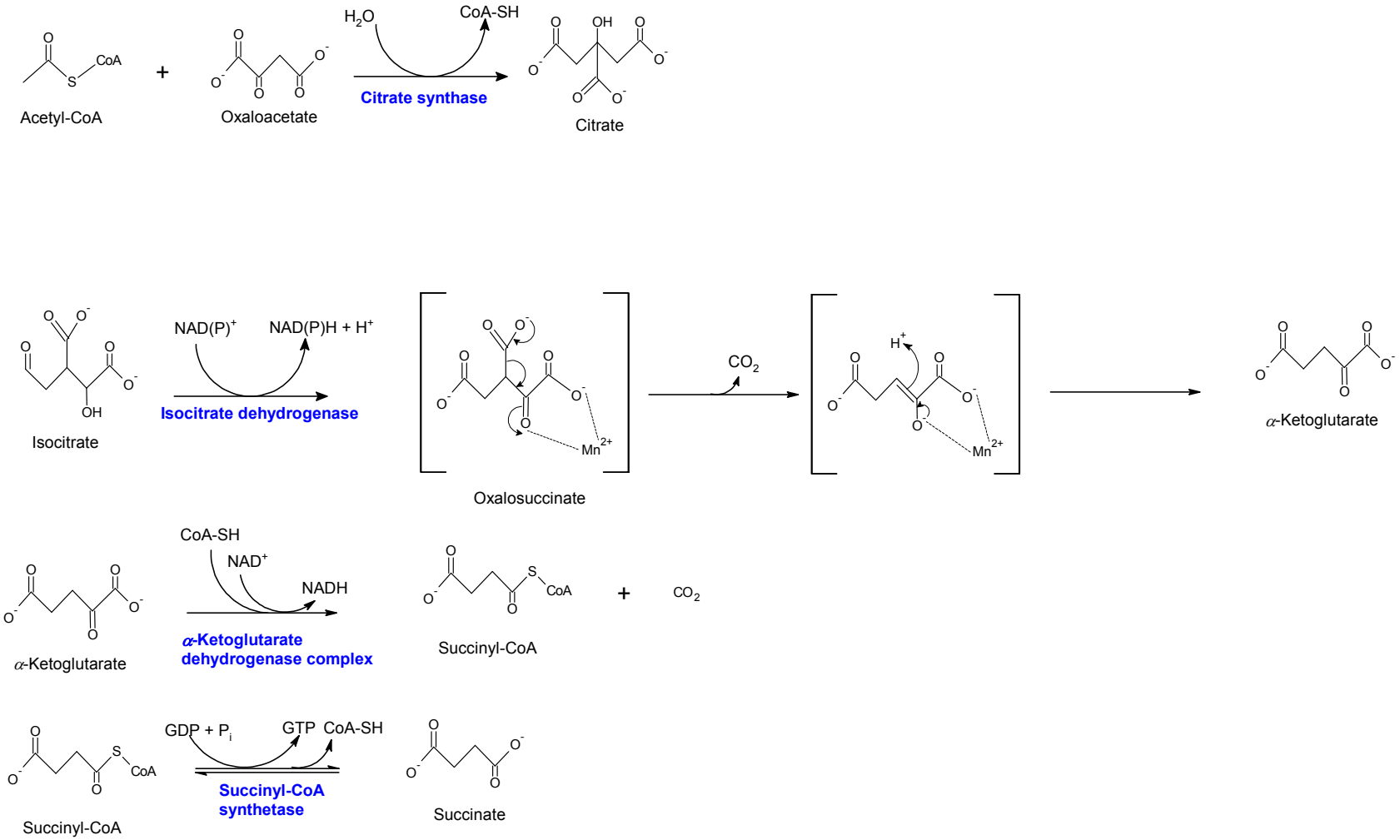

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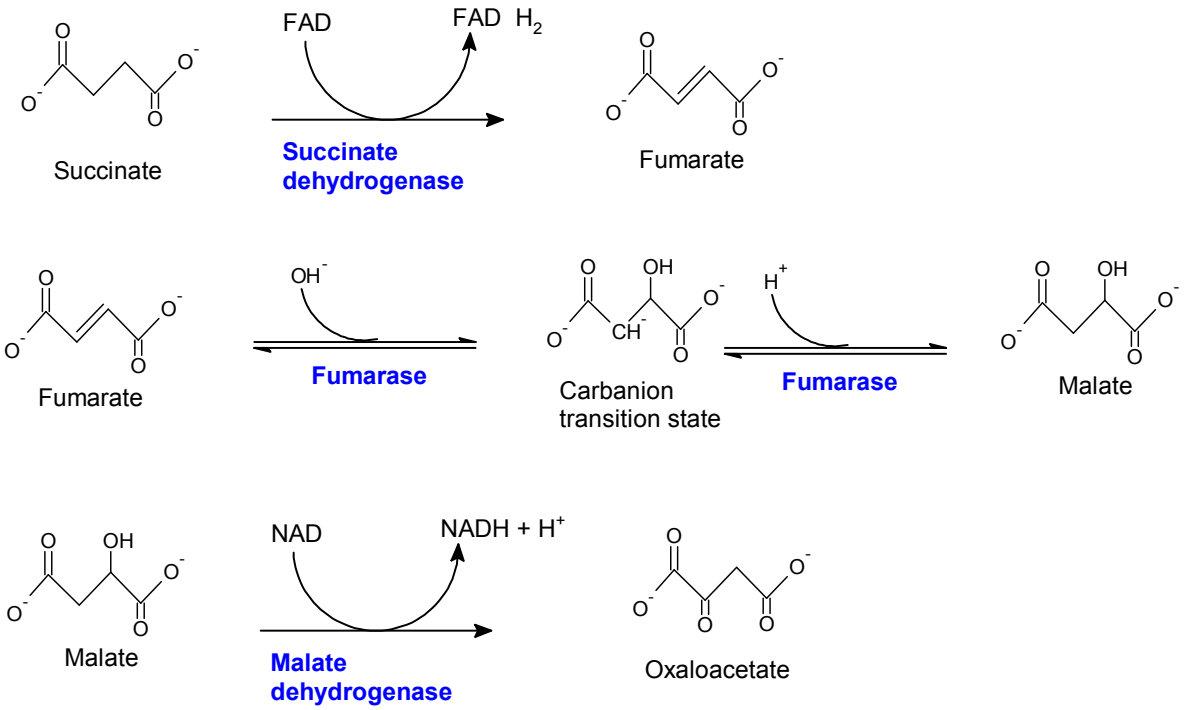

(3)

Figure 5c. Succinic acid via the tricarboxylic acid (TCA) cycle.

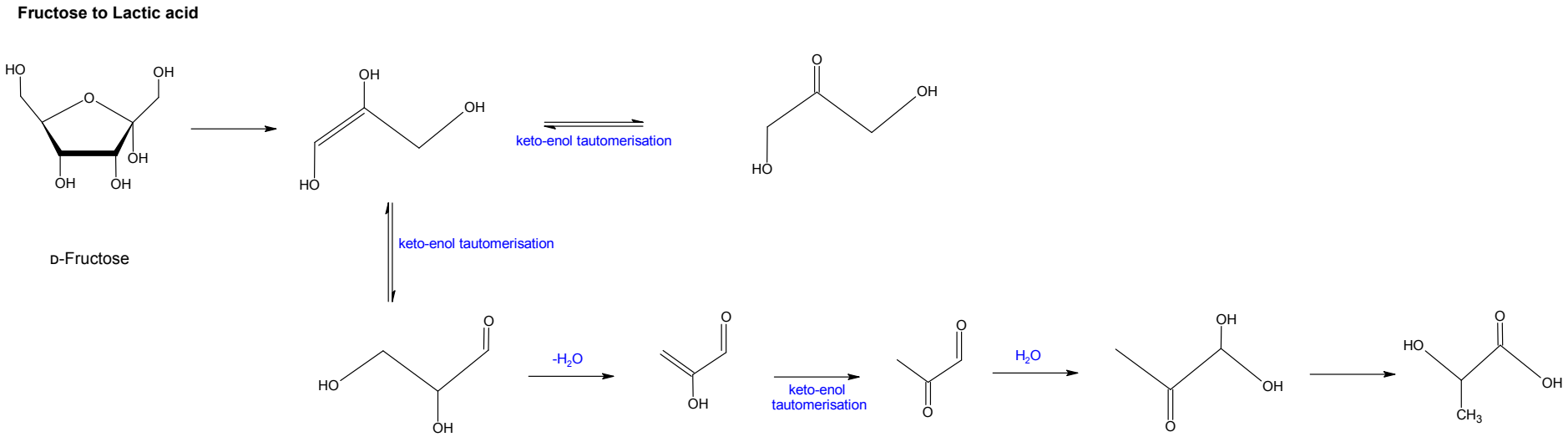

Figure 5d. Lactic acid via sugar fermentation.

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$$\text{Net Present Value} = \sum_{\text{plant life in years}} \frac{\text{Net Cash Flow}}{(1 + \text{Discount rate})^{\text{year}}}$$

$$= \sum_{\text{plant life in years}} \frac{(\text{Revenues} - \text{Annual capital cost} - \text{Total OPEX})}{(1 + \text{Discount rate})^{\text{year}}}$$

Annual capital cost = Annual Capital Charge × Total capital cost

Desired payback time = f(Annual Capital Charge, Discount rate)

Total capital cost = 5 × Delivered cost of equipment
Delivered cost of equipment:
Apply scaling factor for economy of scale and levelise the cost

Total OPEX = 1.3 × (fixed operating cost + variable operating cost)

fixed operating cost = 0.55 × Delivered cost of equipment + 2 × personnel cost

variable operating cost = total cost of feedstock, utilities and reagents

Figure 6a. Techno-economic assessment framework.

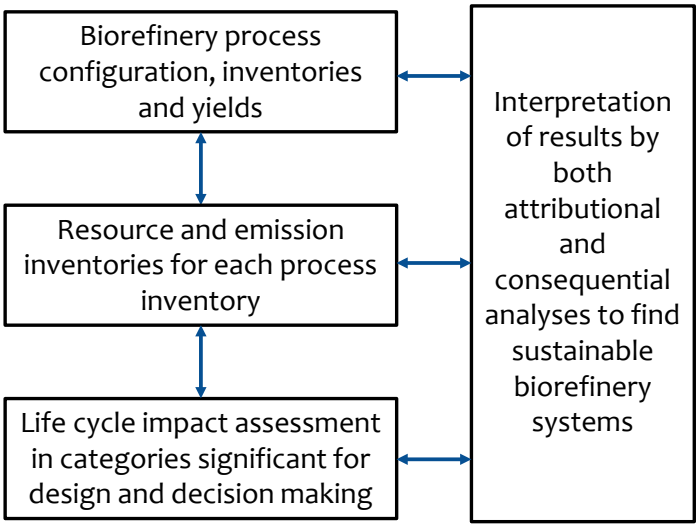

Figure 6b. Life cycle assessment framework.

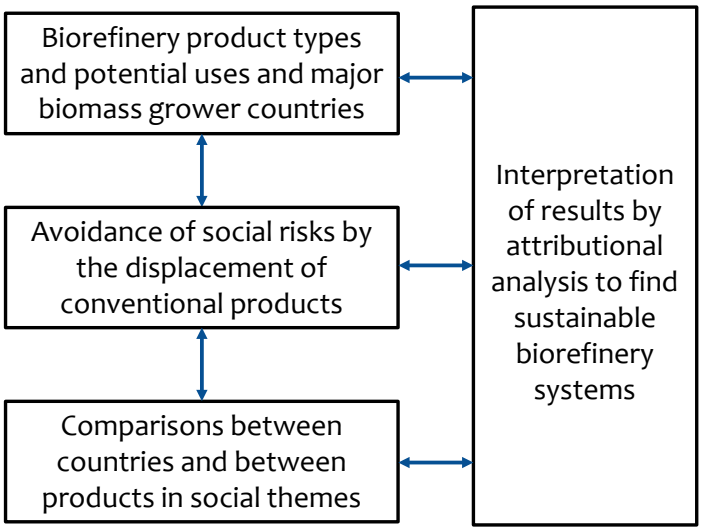

Figure 6c. Social life cycle assessment framework.

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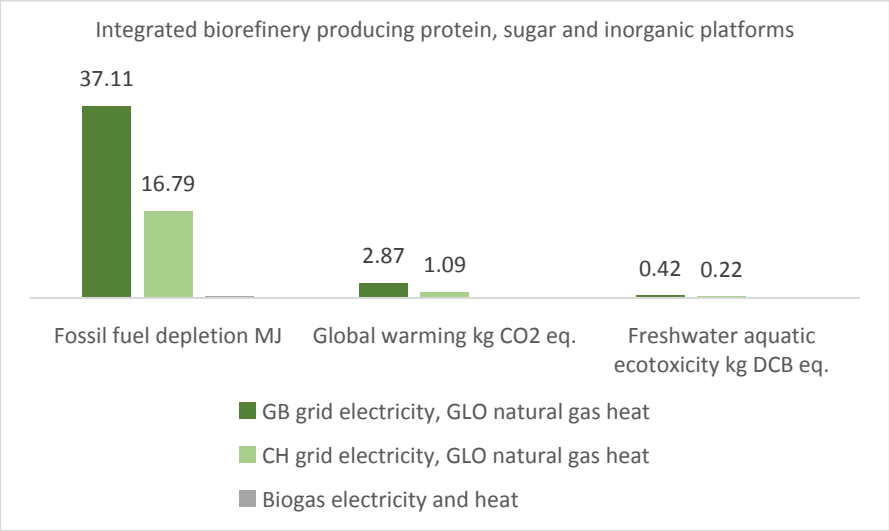

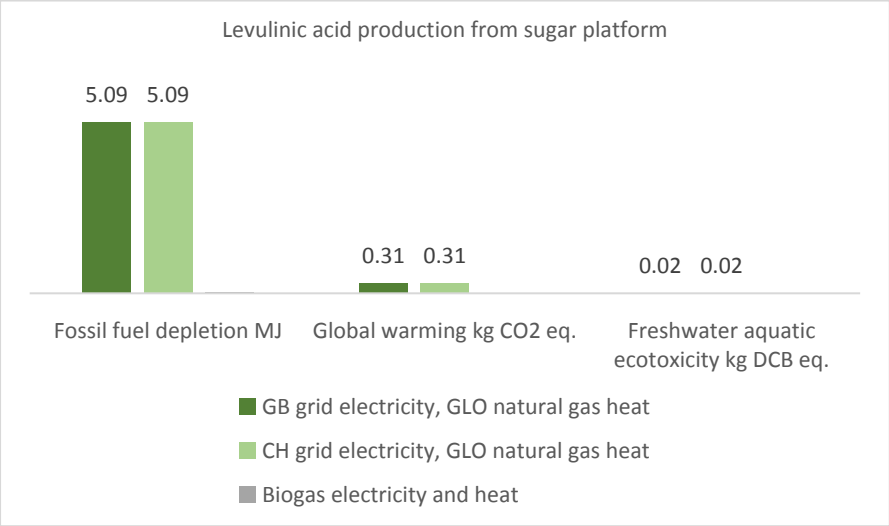

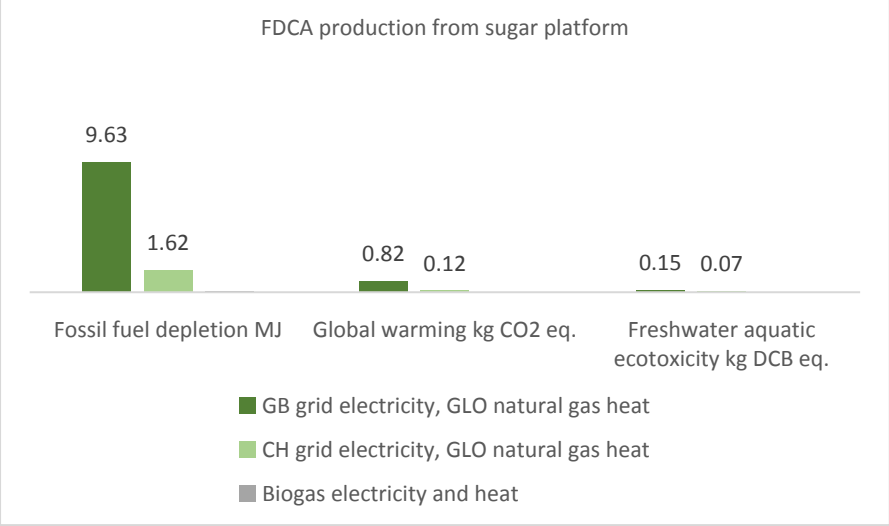

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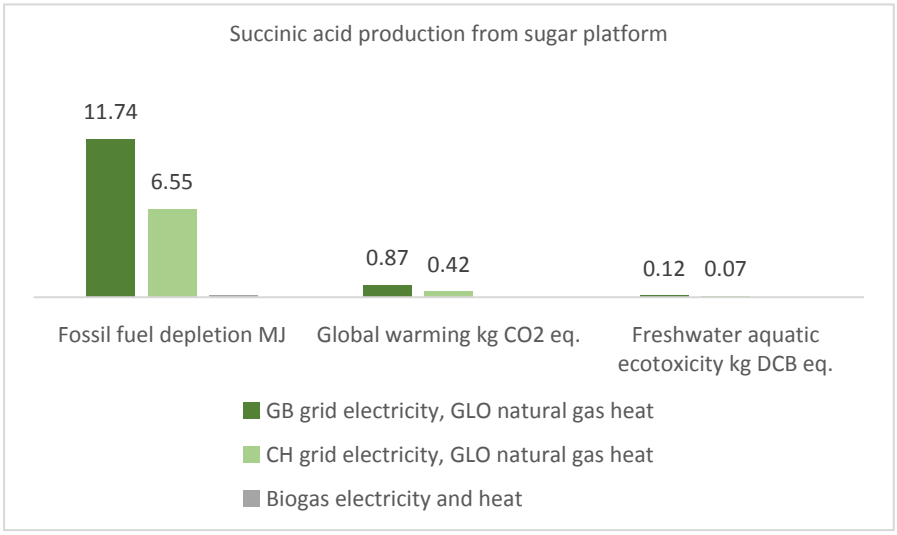

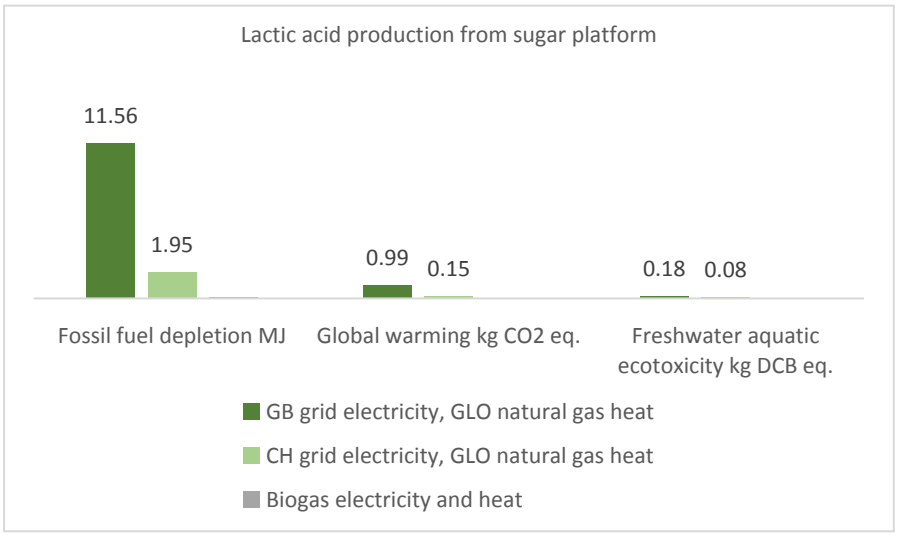

Figure 7. Life cycle impact assessment results of integrated biorefinery producing protein, sugar and inorganic platforms and levulinic acid, FDCA, succinic acid and lactic acid productions from the sugar platform for three scenarios: electricity grid mix of Great Britain (GB) and the global (GLO) natural gas based heat generation; electricity grid mix of Switzerland (CH) and the global (GLO) natural gas based heat generation; electricity and heat generation from locally resourced biogas.

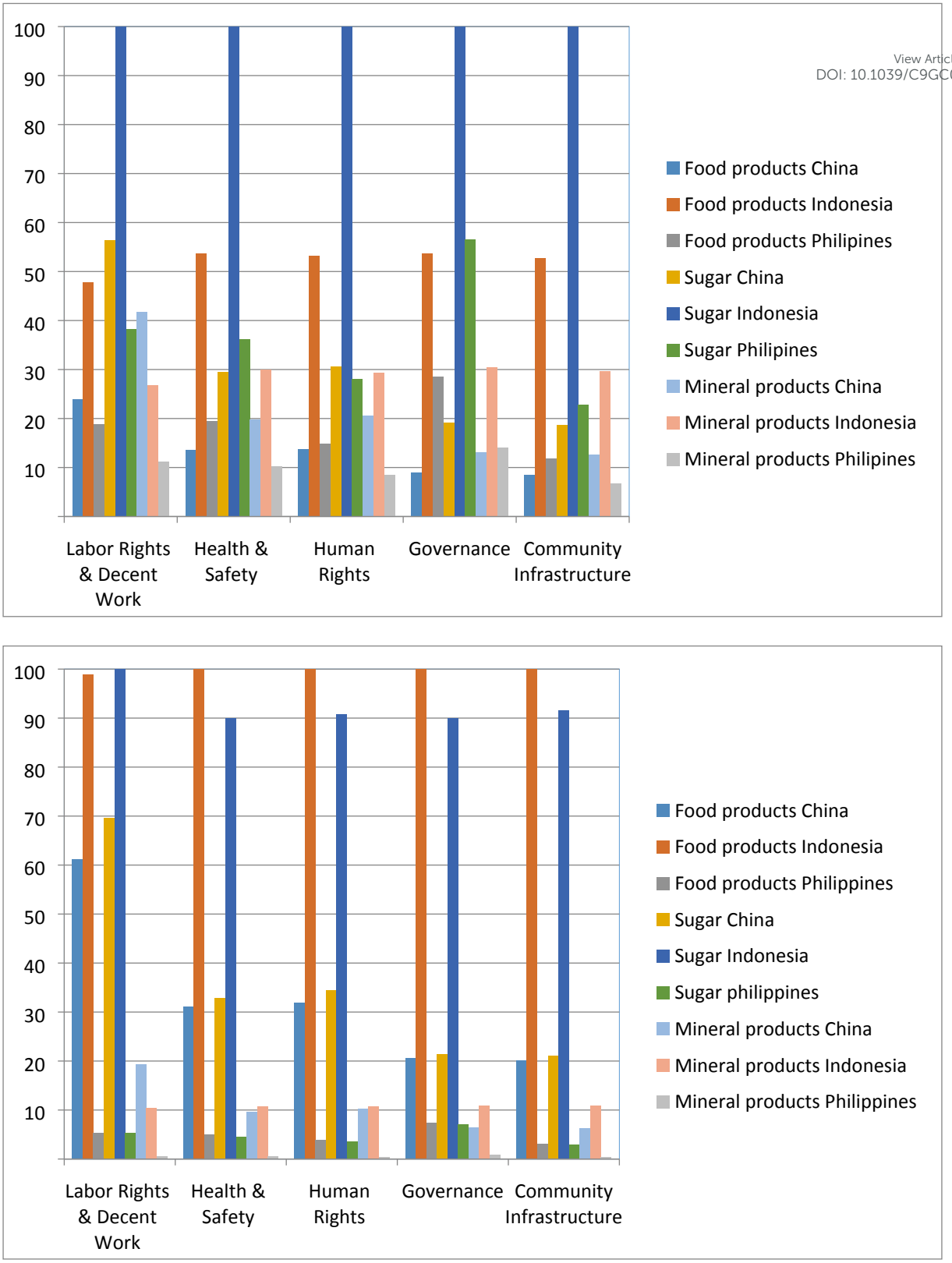

Figure 8. Avoided social impacts in five main themes in % scale for individual commodities and top three macroalgae producing countries: taking 1 US$ worth of individual product values as the basis (top); taking individual products potential production rates from the current production rates of macroalgae in the three countries as the basis (bottom).

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Table 1. Compositions of selected macroalgae, hardwood and softwood species[16].

% mass of dry biomass	Brown	Green	Red	Hardwood	Softwood
	(Sargassum)	(Sea lettuce)	(Euchemia)		
Starch	0.1	0.7	1	0.5	0.1
Cellulose	20.3	8	6	43.9	37.9
Hemicellulose	42.8	42.1	66	28.4	22.7
Lignin	7.3	3.3	1.8	24	33.1
Protein	9.6	12	7.5	0.6	0.5
Extractives	1.9	4.1	1	1.9	3.4
Ash	17.1	25.7	15	0.6	0.3
Total	99.1	95.9	98.3	99.9	98
Calorific value (MJ kg^{-1})	14.02	15.88	12.5	20.62	19.35
Potential for extraction of platform:					
Sugar	High	Medium	Very high	Very high	High
Protein	High	High	High	Low	Low
Lignin	Low	Low	Low	High	Very high
Extractives and ash	High	High	High	Low	Low

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Table 2. Biorefinery process inventories per kg dry macroalgae.

Processing step	**Inventory**
Oven dry	60-90% moisture content by mass of wet macroalgae; oven dry at 60°C for 2-3 days. 10 MJ heat.
Milling and grinding	0.05 kWh power
Suspension in deionised water	2 kg deionised water proportional to the mineral / nutrient / salt contents
Filtration	0.4 kWh power
Centrifugation	3 kWh power
Dialysis	0.075 kWh on the basis of salt removal
Pretreatment	0.5 kJ for polysaccharides decomposition into sugar platform. Could vary between 0.05-5 kJ depending on g mol^{-1} of polysaccharides
Levulinic acid production from sugar platform	Yield: 0.46 (w levulinic acid / w cellulose). 0.5% (w make up sulphuric acid / w sugar). 4 MJ heat. Residual organic stream 8%
FDCA production from sugar platform	Yield: 0.64 (w FDCA / w sugar). Energy use for electricity, heat and reagent supplies: 5 MJ
Succinic acid production from sugar platform (crystalisation)	Yield: 0.75 (w succinic acid / w sugar). 0.5% (w make up hydrochloric acid / w sugar). 4.3 MJ heat and 0.9 kWh power
Lactic acid production from sugar platform	Yield: 0.93 (w lactic acid / w sugar). Energy use for electricity, heat and reagent supplies: 6 MJ

Table 3. Input variables for capital cost estimations.

	Base cost million $	Scale factor	Base capacity	Current capacity	Unit	CEPCI at base year	Current levelised delivered cost of equipment million $	Recent CEPCI
Drying	7.6	0.8	33.5	1.14	t h^{-1} wet biomass	394.3	0.73	567.5
Milling	0.37	0.7	50	0.33	t h^{-1} biomass (30% moisture w/w)	402	0.02	567.5
Grinding	0.41	0.6	33.5	0.33	t h^{-1} biomass (30% moisture w/w)	394.3	0.04	567.5
Filtration	2.92	0.7	18.5	0.23	t h^{-1} deionised water	402	0.19	567.5
Centrifugation	1.05	0.65	10.1	0.01	t h^{-1} dry solid	402	0.02	567.5
Ion exchange resin column	2.39	0.33	83.3	0.22	t h^{-1} dry feed	402	0.47	567.5
Dialysis	1.05	0.65	10.1	0.03	t h^{-1} dry solid	402	0.04	567.5
Pretreatment	1.41	0.78	83.3	0.16	t h^{-1} dry feed	402	0.02	567.5
Integrated biorefinery producing protein, sugar and inorganic platforms							1.52	
Levulinic acid production from sugar platform							1.95	
FDCA production from sugar platform							1.22	
Succinic acid production from sugar platform (crystallisation)							3.99	
Lactic acid production from sugar platform							1.73	

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Table 4. Ecoinvent 3.3 databases selected for the integrated biorefinery system. CH: Switzerland; GB: Great Britain; GLO: Global; RER: EU.

Electricity, high voltage {**CH**}| market for | Ecoinvent 3 - allocation, default - unit
Electricity, high voltage {**GB**}| production mix | Ecoinvent 3 - allocation, recycled content - unit
Heat, central or small-scale, natural gas {**GLO**}| market group for | Ecoinvent 3 - allocation, default – unit
Biogas {**GLO**}| market for | Ecoinvent 3 - allocation, default – unit
Sulfuric acid {**GLO**}| market for | Ecoinvent 3 - allocation, default – unit
Hydrochloric acid, without water, in 30% solution state {**RER**}| hydrochloric acid production, from the reaction of hydrogen with chlorine | Ecoinvent 3 - allocation, default - unit
Lactic acid {**RER**}| production | Alloc Def, U Ecoinvent 3 - allocation, default - unit