A Preliminary Life Cycle Analysis of Bioethanol Production Using Seawater in a Coastal Biorefinery Setting

Abdelrahman S. Zaky [1,*], Claudia E. Carter [1], Fanran Meng [2] and Christopher E. French [1,3]

[1] School of Biological Sciences, University of Edinburgh, King's Buildings, Edinburgh EH9 3FF, UK; A.Zaky@ed.ac.uk (A.S.Z); A.Zaky@cu.edu.eg (A.S.Z); cloudycarter@gmail.com (C.E.C); c.french@ed.ac.uk (C.E.F)

[2] Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB2 1PZ, UK; fm392@cam.ac.uk

[3] Zhejiang University-University of Edinburgh Joint Research Centre for Engineering Biology, International Campus, Zhejiang University, Haining, Zhejiang, 314400, China; c.french@ed.ac.uk

[*] Correspondence: A.Zaky@ed.ac.uk; A.Zaky@cu.edu.eg; Tel.: 00447474440333

Abstract: Bioethanol has many environmental and practical benefits as a transportation fuel. It is one of the best alternatives to replace fossil fuels due to its liquid nature which is similar to petrol and diesel fuels traditionally used in transportation. In addition, bioethanol production technology has the capacity for negative carbon emissions which is vital for solving the current global warming dilemma. However, conventional bioethanol production takes place based on an inland site and relies on freshwater and edible crops (or land suitable for edible crop production) for production, which has led to the food vs fuel debate. Establishing a coastal marine biorefinery (CMB) system for bioethanol production that is based on coastal sites and relies on marine resources (seawater, marine biomass and marine yeast) could be the ultimate solution. In this paper, we aim to evaluate the environmental impact of using seawater for bioethanol production at coastal locations as a step towards the evaluation of a CMB system. Hence, a life cycle assessment for bioethanol production was conducted using the proposed scenario named Coastal-Seawater and compared to the conventional scenario, named Inland-Freshwater (IF). The impact of each scenario in relation to climate change, water depletion, land use and fossil depletion was studied for comparison. The coastal-seawater scenario demonstrated an improvement upon the conventional scenario in all the selected impact categories. In particular, the use of seawater in the process had a significant effect on water depletion showing an impact reduction of 31.2%. Furthermore, reductions are demonstrated in natural land transformation, climate change and fossil depletion of 5.5%, 3.5% and 4.2% respectively. This indicates the positive impact of using seawater and coastal locations for bioethanol production and encourages research to investigate the CMB system.

Keywords: Bioethanol; LCA; marine fermentation; seawater; *Saccharomyces cerevisiae*; water footprint; bioenergy; biofuel; marine yeast; GHG

1. Introduction

Growing concern regarding the effect of anthropogenic activity on climate change has given impetus to research greener energy sources. Governments worldwide, including the UK, are committed to reaching climate change goals detailed in the Paris Agreement [1]. To reach these goals it is essential to base infrastructure on a framework of sustainable technology, not only to reduce emissions but also to mitigate environmental changes already generated such as long-lived carbon dioxide (CO_2) emissions.

Transportation is a major contributor to climate change, accounting for 20.45% of global CO_2 emissions in 2014 [2]. These emissions, along with other greenhouse gases

(GHGs), are released from the production and combustion of fossil fuels, mainly coal, petrol, and diesel. In addition, fossil fuels are also a dwindling finite resource. Efforts to reduce GHG emissions are looking at green energy sources as a sustainable alternative to fossil fuels for powering vehicles. The prominent candidates are hydrogen and renewable electricity as well as biofuels including bioethanol, biodiesel and biogas [3]. Implementation of hydrogen in vehicles is hindered by logistical issues in its storage and cost [4, 5] while electric power is not yet feasible in many vehicles including watercraft , aircraft , long distance commuter vehicles, and heavy duty vehicles. This is mainly because of challenges in practical range due to limited battery energy density [6], payload and total cost. In contrast, biofuels are both promising and immediately applicable alternative fuels. Biofuels can offset the carbon released upon combustion during their production.

Bioethanol is a liquid renewable biofuel that is widely used in blends with gasoline to improve the octane rating of the vehicle's engine and reduce carbon footprint. It is produced by microbial fermentation of sugars, and these sugars are sourced from biological materials such as sugary and starchy crops (1st generation bioethanol), lignocellulosic biomass (2nd generation bioethanol) and seaweed (3rd generation bioethanol). During cultivation, these biological materials absorb CO_2 from the atmosphere by photosynthetic growth. Furthermore, fermentation of the derived sugars   produces a highly pure stream of CO_2 and can thus be integrated with carbon capture and storage (CCS) technology [7]. Together with CCS, bioethanol production can achieve negative emissions necessary to help in reaching the UN's climate goals. In addition, there are many pathways for carbon capture, storage and utilisation (CCSU) (**Error! Reference source not found.**), each coming with their own environmental footprints [8]. It has been demonstrated that when linked with carbon sequestration, bioethanol production can be carbon negative. However, it is important that the CCS and carbon utilisation pathways are selected with high regard to the environmental impact. For example, if the captured carbon were to be used in enhanced oil recovery, the carbon captured during the bioethanol production process would be brought to zero or even surpassed by the carbon release in combustion of the mined oil.

Although bioethanol is regarded as a promising alternative fuel, there are some economic, policy and environmental issues associated with the current production processes. For example, a lack of policy to support ethanol-petrol blending in many countries results in a lack of demand as well as high production costs. Whilst the US government mandates supply of E10 at a minimum, the petrol served in the UK is not regulated and is generally only E5. A production process incurring lesser cost or one that offsets costs with greater earning potential would encourage bioethanol production. This lack of policy support is mainly due to the food security vs biofuel feedstock supply debate which regards bioethanol production as a threat to the food supply as it consumes the arable land and freshwater that are vital for producing food crops. A new pathway for bioethanol production that reduces freshwater consumption and arable land use would achieve social acceptance and encourage policymakers to legislate policies that support bioethanol production and utilisation.

Weak ethanol-petrol blends such as E10 and E15 (10 and 15% ethanol) can be safely and readily introduced into supply [9]. It has shown that blending petrol with ethanol lowers emissions during combustion [10, 11]. The UK government estimated that using the E10 ethanol blend in the UK could cut CO_2 from road transport by 750,000 tonnes per year which   is equivalent to removing 350,000 cars off roads [12]. Ethanol use in combustion engines offers reductions in emissions and improvements in power and energy efficiency compared to fossil fuels such as diesel and petrol [13]. Additionally, ethanol is biodegradable and evaporates in open spaces [14]. This means it is unlikely to cause significant damage, environmental or otherwise, upon spillage.

Transforming land for biofuel feedstock cultivation in addition to that necessary for food production, a phenomenon known as land use change (LUC), comes with a severe environmental impact [15] and prompts concerns over food security. For this reason, the Renewable Energy Directive (EU) imposed a 7% ceiling on the use of bioenergy for

transportation where derived from food crops in 2018 [16]. This has prompted a transition from the first-generation biofuels derived from food-based feedstocks such as corn (used in the USA), sugarcane (used in Brazil), wheat and sugar beet (used in the UK), to the second-generation biofuels which are derived from non-food lignocellulosic biomass such as wheat straw, switchgrass, willow and miscanthus. Currently in-development are third-generation biofuels produced using algal and waste feedstocks requiring no land.

Biofuels can have greater water footprint (WF) than fossil fuels [17], highlighting the importance of considering a fuel product's impact across its entire life cycle rather than only in combustion. The WF of first-generation bioethanol ranges from 1,400 to 9,800 litre (L) of freshwater per L of ethanol [18, 19], hence it presents an environmental concern. With much of the world facing water scarcity, there is understandable resistance to bioethanol at the cost of water supply. Although second-generation bioethanol from crop residues demonstrate much lower WF [20], the WF can be reduced further by focusing on the entire process rather than feedstock only. One way to do that is to utilise seawater instead of freshwater for preparing the fermentation medium for bioethanol production. This suggests the construction of biorefinery facilities in a coastal location and using marine yeast strains for fermentation.

Seawater is non-potable and abundant, therefore its use in industrial scale fermentation reduces the WF of the product and would not detract from general water supply [21]. It is also freely available and thus offers a reduction in production cost. Halotolerant yeasts, sourced in the marine environment, would be applied in conjunction with seawater use. This is because they demonstrate improved function in seawater-based fermentation medium as compared to terrestrial yeasts [18, 22]. The marine yeast strain *S. cerevisiae* AZ65 produced bioethanol at a higher productivity rate and improved yield using freshwater-YPD medium and a similar productivity rate and improved yield using seawater-YPD medium compared to the industrial terrestrial strain *S. cerevisiae* NCYC2592. *S. cerevisiae* AZ65 was also able to produce bioethanol efficiently using seawater-molasses medium [18, 23].

The aim of this study is to quantify the environmental and cost impacts of bioethanol production using seawater fermentation at a coastal site. The preliminary life cycle and technoeconomic analysis of bioethanol explores three elements: coastal location, seawater medium and marine yeasts. A comparative study assesses the proposed coastal-seawater system as opposed to a conventional bioethanol production system from sugar beet.

.
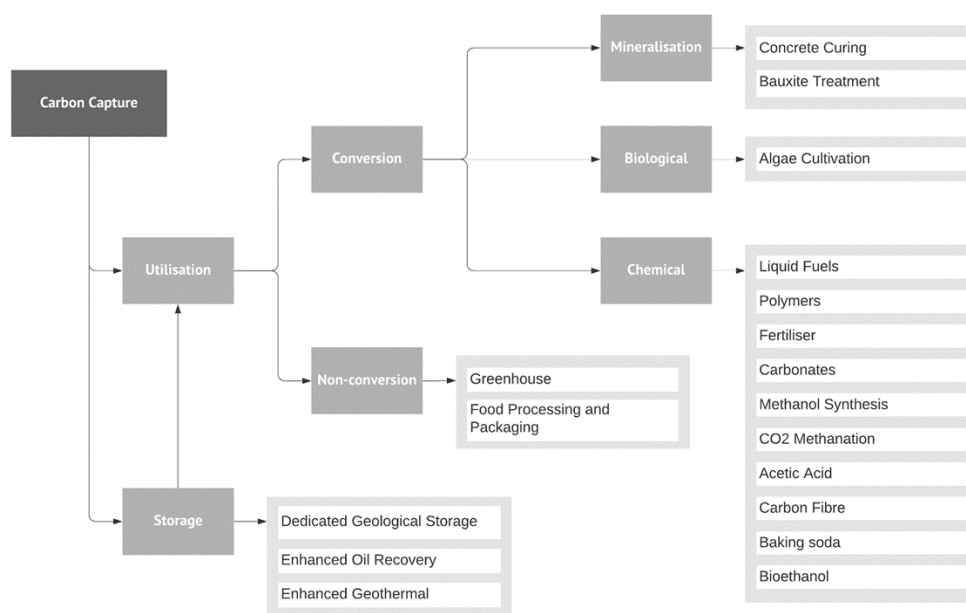
Figure 1. The diagram to illustrate the pathways of carbon utilisation and storage post-capture as described in the Global Status Report 2019 of the Global CCS Institute.

2. Materials and Methods

A comparative life cycle assessment (LCA) was conducted to evaluate the production of bioethanol from sugar beet using a standard fermentation and a seawater fermentation in accordance with standard methodology guidelines set out in ISO14040 [24]. Analyses were conducted with SimaPro v8 [25] and data were sourced from the Ecoinvent database v3.6 [26] and Agri-footprint database v4.0 [27]. The life cycle impact was assessed using ReCiPe Midpoint Hierarchist method with European normalisation. This considers 18 Environmental impact categories including Climate Change, Water Depletion, Land Use and Fossil Depletion. Water and land use were chosen for their pertinence to the current issues in production of bioethanol. Fossil depletion and climate change are areas in which bioethanol production has already reduced impact as compared to use of fossil fuels, and so are included to ascertain whether they can be further improved with the Coastal-Seawater scenario.

2.1. Goal and Scope

The goal of this study was to compare the environmental impacts of two approaches for bioethanol production from sugar beet on a cradle to gate basis. The study includes a) the conventional production approach using freshwater and inland locations, and b) the proposed approach using seawater at a coastal location.

The system boundary includes the feedstock preparation (i.e., sugar beet cultivation), bioethanol conversion, coproduct processing and all necessary transportation within that duration (**Error! Reference source not found.**). The construction of infrastructure and subsequent steps including use phase of the fuels are excluded in this study as the bioethanol products produced by different methods are assumed to be identical. The functional unit is 1 L bioethanol (95% bioethanol, 5% water).

2.2. Modelling and Input Data

Each production method was modelled, and system boundaries were defined for both scenarios. The conventional bioethanol production approach is designated the 'Inland-Freshwater' scenario. The system boundary for the Inland-Freshwater (**Error! Reference source not found.**A) includes sugar beet cultivation and harvesting, preparation of

the sugar beet syrup required for fermentation, wastewater treatment and processing required to produce bioethanol and coproducts.

The proposed model, known hereinafter as the 'Coastal-Seawater' scenario, retains identical feedstock and largely the same process as the Inland-Freshwater scenario with the notable differences being seawater use in fermentation, use of halotolerant yeasts and water processing to obtain additional coproducts. The Coastal-Seawater scenario system boundary (**Error! Reference source not found.**) includes the pre-treatment of the inlet seawater (
).

The life cycle inventory differed at various points to reflect the differences in efficiencies, processes and stages relating to the different resource use in each scenario (Tables 1, 2 and 3).

Electricity, sequestered CO_2, animal feed and LimeX - an agricultural product for soil pH correction - all have market value and are thus coproducts of the bioethanol production. Production of ethanol (black) along with the coproducts (shaded box) are considered the endpoint for this study. Distribution and use are indicated but not elaborated on as it is not part of the scope of this study. The wastewater treatment in this scenario is to reduce the environmental impact arising from its disposal.

Figure 2b has been constructed using **Error! Reference source not found.**a as a basis with alterations that are specific to the Coastal-Seawater scenario. The seawater (SW) treatment stage particular to this scenario produces water that replaces tap water in the Inland-Freshwater scenario for the processes of washing and as fermentation medium. Furthermore, in this system the so-called wastewaters of the fermentation and drying stages are treated to become a coproduct with a market value rather than being treated for disposal. This also results in final water treatment being considered part of the 'Processing of Coproducts' subsystem rather than 'Ethanol Conversion'.
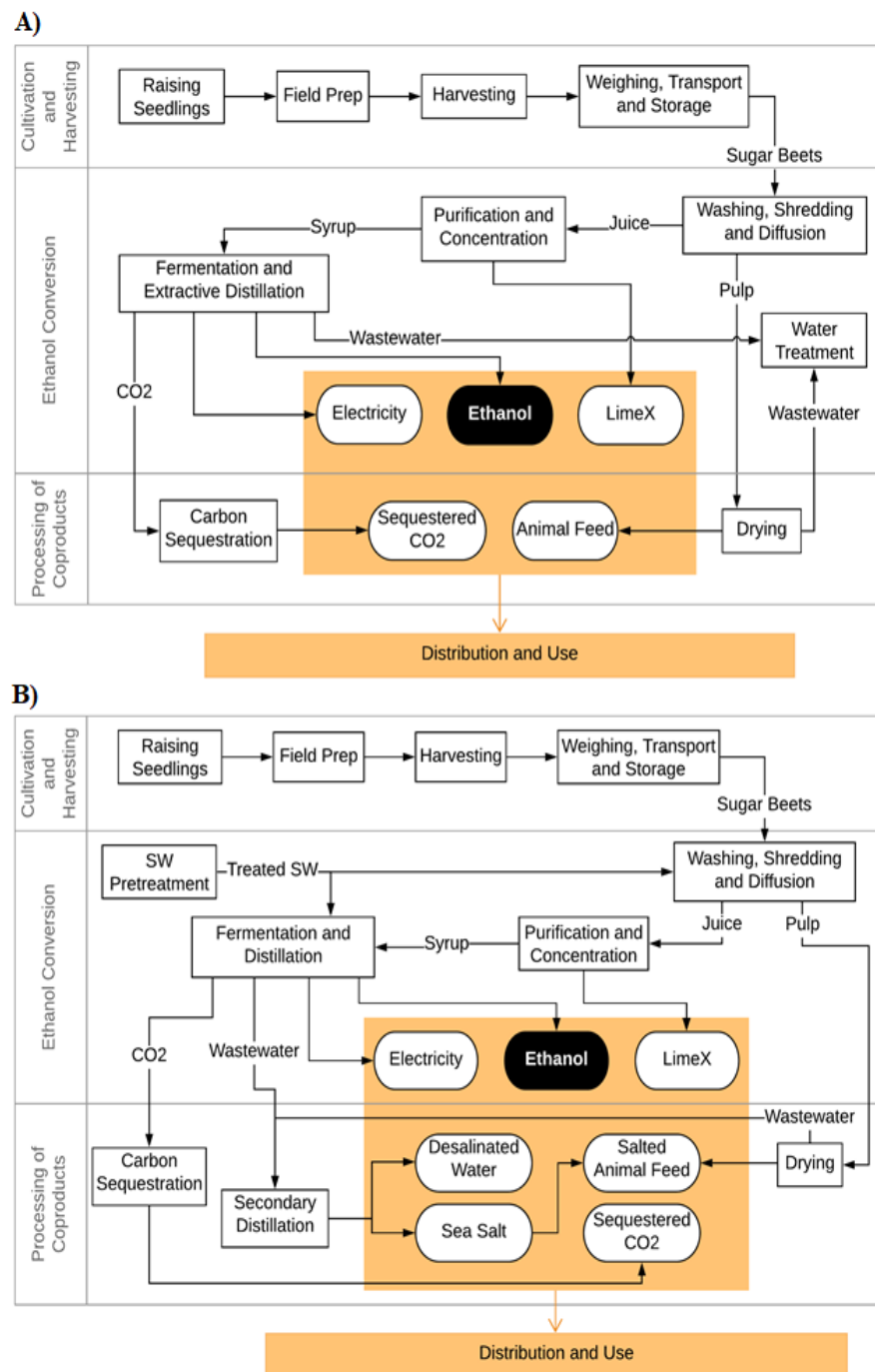
Figure 2: The diagram defining the system boundary of the study: A) Inland-Fresh-water Scenario. B) Coastal-Seawater Scenario. Inclusions are the intermediate stages (on arrows), processes (rectangle) and final products (rounded) in the production of bioethanol from sugar beet. The swimlanes of the diagram indicate subsystems. Production of ethanol (black) along with the coproducts (shaded box) are considered the endpoint for this study. Distribution and use are indicated but not elaborated on as it is not part of the scope of this study.

2.2.1. Sugar Beet Cultivation and Harvesting

Sugar beets are commonly grown in Europe for both food and energy. As a first-generation biofuel feedstock, their processing is well-established and practiced by many bioethanol manufacturers [28].

The input data for the cultivation and harvesting subsystem (Table 1) were identical in each scenario and were sourced from the Agri-footprint database [27]. The dataset describes a farm in Germany. This was not considered to significantly differ from UK practices due to congruent climates and stance on genetically modified crops, and thus presumably comparable soil management and application of agrichemicals.

2.2.2. Seawater Pre-treatment

It was determined that the seawater should be filtered to remove meso- and macro-plankton (i.e., larger than 20 mm in size) and sand prior to feeding into fermentors in the Coastal-Seawater scenario (Figure 3). Otherwise, these larger elements in the inlet water would be collected in the fermentation vessel and potentially hinder the downstream processing of the distillate and salt products. The flow of inlet water through a sedimentation tank removes sand, enabling its use for washing the sugar beet. For the portion used in the fermentation media this is followed by a basic filtration stage with 20 mm pore equivalence to remove large plankton. Any remaining microorganisms are neutralised by heat in preparation of the fermentation media.

The pre-treatment stage modelled has few inputs. Use of a sedimentation tank takes advantage of natural settling of sand at the base of the tank due to gravity – a passive process – and the sedimented sand is disposed of by return to the ocean. Filtration is achieved by flowing the water over a granular filtration bed through which it moves downward also by means of gravity. So, the only energy consumption is for pumping of the water from the ocean.
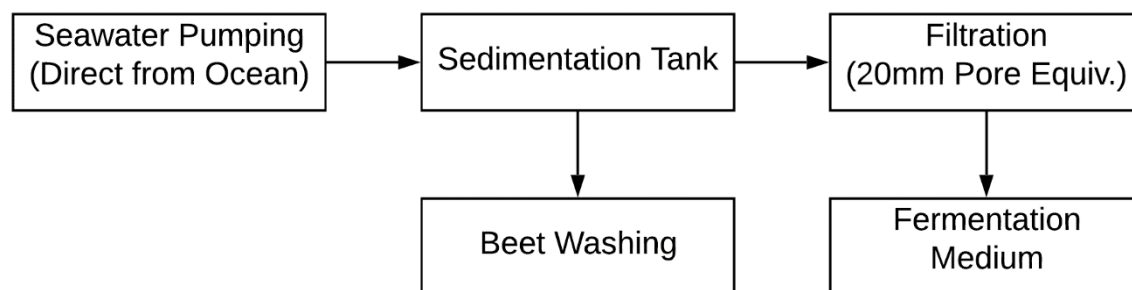
Figure 3: Sedimentation of sand achieves the purity required for sugar beet washing whilst a second stage of treatment by filtration prepares the water for use in the fermentation medium. Filtration is granular with an equivalent pore size of 20 mm to remove larger planktonic organisms

2.2.3. Sugar Beet Washing

The scenarios involve different resource use in sugar beet washing. The freshly harvested crop must be washed to remove soil and stones. Tap water is used in the Inland-Freshwater scenario while clarified seawater is assumed to be used in the Coastal-Seawater scenario.

2.2.4. Syrup Production

Next, the washed crop in each scenario is shredded, soaked, and pressed to release the sugars contained in the root into a juice. Subsequent concentration and purification yield a syrup with ~65-67% (w/w) fermentable sugars [29] which is appropriate for yeast fermentation. The solid portion, the pulp, is later processed to become animal feed.

2.2.5. Fermentation and Ethanol Recovery

The resultant syrup is fed into industrial scale bioreactors in which yeasts complete the conversion of sugar into bioethanol in anaerobic conditions. Terrestrial *Saccharomyces cerevisiae* yeasts complete the fermentation in the Inland-Freshwater scenario. The productivity of terrestrial *S. cerevisiae* is inhibited by the salinity of seawater, therefore the Coastal-Seawater scenario is modelled to involve marine yeast [18].

Both scenarios are modelled with ethanol recovery by distillation. In large industrial distillation columns, the product is separated from water resulting in ethanol of 95% purity with 5% water and trace amounts of solvent used in ethanol recovery.

2.2.6. Processing of Coproducts

The coproducts in the Inland-Freshwater scenario include CO_2 and animal feed only while in the Coastal-Seawater scenario, additional coproducts including sea salt and distilled water are also obtained, and the produced animal feed is supplemented with sea salt. The inventory data for this subsystem are summarised in Table 3. Certain coproducts in the outlined systems are produced via additional processing which is not directly contributory to ethanol production. Processes solely associated with coproducts are in a distinct subsystem. The biogenic CO_2 released is considered as a coproduct with many potential commercial uses as illustrated in Figure 1. The CO_2 released as an output of fermentation is assumed to be 100% pure for the purposes of this study. This reflects an ideal anaerobic fermentation, where one mole of glucose provided corresponds to a yield of two moles ethanol and two moles CO_2 only. Consequently, the CO_2 stream from the fermentation vessel only requires treatment by compression for storage.

As a part of the CCS process, the CO_2 stream is compressed, necessitating electricity supply, in preparation as a coproduct. However, the full pathway of the CO_2 capture, storage and utilisation (CCSU) is not modelled as the distribution and use phase of product and coproducts' life cycles are not within the scope of this study.

Table 1: Life Cycle Inventory: Cultivation and Harvesting of Sugar Beet (SB) which is identical to inland-freshwater and coastal-seawater scenario.

Input Data	Unit	Inland-Freshwater / Coastal-Seawater [a]
Occupation, arable	m²a/ kg SB	10000
Water, unspecified natural origin, DE	m³/ kg SB	186.1
Energy, from diesel burned in machinery/RER Energy	MJ/ kg SB	7367.25
Manure, from pigs, at pig farm/RER Energy	kg/ kg SB	8732.39
Potassium chloride (NPK 0-0-60), at regional storehouse/RER Energy	kg/ kg SB	162.38
NPK compound (NPK 15-15-15), at regional storehouse/RER Energy	kg/ kg SB	213.41
PK compound (NPK 0-22-22), at regional storehouse/RER Energy	kg/ kg SB	91.55
Potassium sulphate (NPK 0-0-50), at regional storehouse/RER Energy	kg/ kg SB	20.84
Triple superphosphate, as 80% $Ca(H_2PO_4)_2$ (NPK 0-48-0), at regional storehouse/RER Energy	kg/ kg SB	16.35
Ammonium sulphate, as 100% $(NH_4)_2SO_4$ (NPK 21-0-0), at regional storehouse/RER Energy	kg/ kg SB	28.55
Calcium ammonium nitrate (CAN), (NPK 26.5-0-0), at regional storehouse/RER Energy	kg/ kg SB	242.87
Liquid urea-ammonium nitrate solution (NPK 30-0-0), at regional storehouse/RER Energy	kg/ kg SB	56.34
Urea, as 100% $CO(NH_2)_2$ (NPK 46.6-0-0), at regional storehouse/RER Energy	kg/ kg SB	65.94

Lime fertilizer, at regional storehouse/RER Energy	kg/ kg SB	290.74

(a) Data for Inland-Freshwater scenario was obtained from Durlinger et al (2014) [27] which was assumed to be the same for Coastal-Seawater scenario .

Table 2: Life Cycle Inventory: Sugar Beet to Ethanol Conversion

Input Data	Unit	Inland-Freshwater	Seawater-Coastal	Source (a)
Washing and Syrup Production				
Tap Water	L/kg SB	5.000	0	[30]
Seawater	L/ kg SB	0	5.000	
Electricity (washing)	kWh/ kg SB	4.000	4.000	[31]
Hydrochloric Acid	g/ kg SB	0.025	0.025	
Formaldehyde	g/ kg SB	0.150	0.150	[32]
LimeX Recovered	g/ kg SB	45.000	45.000	
Water Inlet/Treatment				
Wastewater Treatment (for disposal)	m3 H2O / kg Et	3.140	0	[29]
Electricity (Seawater Pumping)	kWh/ m3 H2O	0	0.004	[33]
Fermentation				
Clean Sugar Beet	kg/ kg Et	8.535	8.535	
Sulphuric Acid	kg/ kg Et	0.026	0.026	
Sodium sulphate	kg/ kg Et	0.003	0.003	[26]
Fresh Water for Medium	L/ kg Et	0.814	0	
Seawater for Medium	L/ kg Et	0	0.814	
Water for cooling	kg/ kg Et	0.3	0.3	[34]
Anti-Scalant	g/ kg SB	0.040	0.040	
Coke	g/ kg SB	1.800	1.800	
Anti-Foam	g/ kg SB	0.200	0.200	[32]
Electricity (Surplus)	kWh/ kg SB	0.694	0.694	

(a) The sources are references for the Inland-Freshwater scenario while the Seawater-Coastal scenario data was assumed as appropriate.

Table 3: Life Cycle Inventory: Processing of Coproducts

Input Data	Unit	Inland-Freshwater	Coastal- Seawater	Source (a)
Carbon Sequestration				
CO_2 from fermentation	kg/ kg Et	0.713	0.713	[26]
Electricity	kWh/ kg CO_2	0.105 (b)	0.105(b)	[35]
Animal Feed Production				
Wet Sugar Beet Pulp	kg/ kg Et	1.392	1.392	[26]
Process Steam	MJ/ kg wet pulp	1.413	1.413	
Electricity for drying	MJ/ kg wet pulp	0.043	0.043	[27]
Dried Sugar Beet Pulp	kg/ kg wet pulp	0.243	0.243	
Distillate Water Treatment				
Water from distillation	kg/ L Et	0	7.000	
Sea Salt from distillation	kg/ L Et	0	0.208	[36]

(a)   The sources are references for the Inland-Freshwater scenario while the Seawater-Coastal scenario data was from assumptions/calculations in this study.

(b)   average taken of range 90-120kWh stated in the source

2.3. Allocation

There are several coproducts associated with each scenario. Energy-based allocation method as adopted by the European Parliament [37] was applied to allocate the environmental impacts between main products and coproducts

3. Results

The life cycle impact assessment used the ReCiPe Midpoint Hierachist method in SimaPro with 18 impact categories by default. The Coastal-Seawater scenario demonstrated reductions in 15 of these impact categories and was the same in the remaining three impact categories relative to the Inland-Freshwater scenario. The environmental impact reduction was primarily in the water depletion category with a decrease of 31.2%. Climate change, natural land transformation, urban land occupation and fossil depletion were all reduced by 3.5-5.5%. Agricultural land occupation showed no change as the modelled first-generation feedstock production relies on arable land in both scenarios (Figure 4 and Table 4).
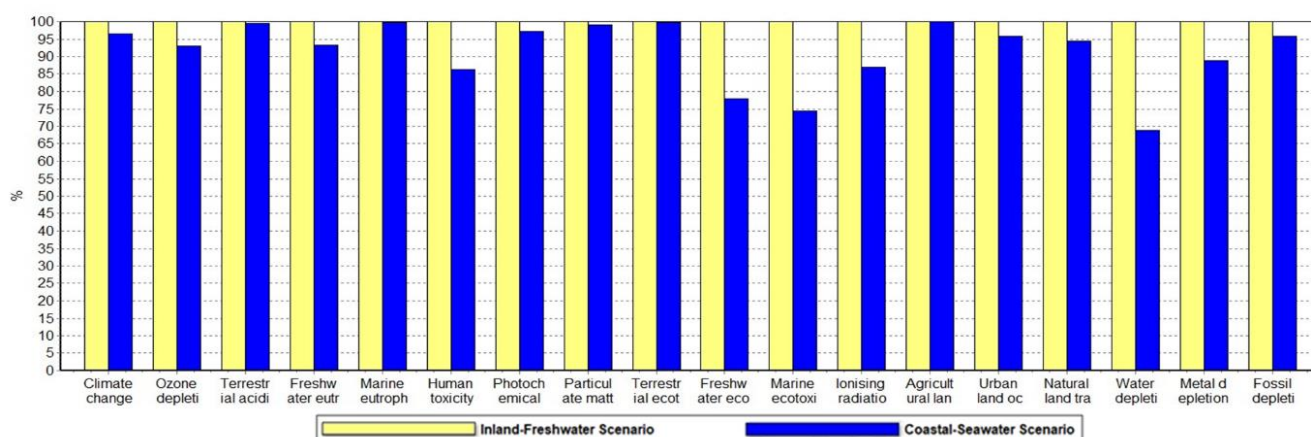
Figure 4: Complete life cycle environmental impacts of the two scenarios of bioethanol production. The data has been characterised for direct comparison of the scenarios in each impact category based on ethanol (95% in solution state) from sugar beet. Alloc Def. U.

Table 4 Complete life cycle environmental impacts of the two scenarios of bioethanol production.

Impact category	Unit	Inland-Freshwater	Coastal Seawater
Climate change	kg CO_2 eq	1.30E+00	1.26E+00
Ozone depletion	kg CFC-11 eq	4.37E-08	4.06E-08
Terrestrial acidification	kg SO_2 eq	4.13E-02	4.11E-02
Freshwater eutrophication	kg P eq	3.96E-04	3.69E-04
Marine eutrophication	kg N eq	2.44E-02	2.44E-02
Human toxicity	kg 1,4-DB eq	1.33E-01	1.15E-01
Photochemical oxidant formation	kg NMVOC	3.30E-03	3.21E-03
Particulate matter formation	kg PM10 eq	6.05E-03	5.99E-03
Terrestrial ecotoxicity	kg 1,4-DB eq	1.82E-03	1.81E-03
Freshwater ecotoxicity	kg 1,4-DB eq	2.30E-03	1.79E-03
Marine ecotoxicity	kg 1,4-DB eq	1.66E-03	1.23E-03
Ionising radiation	kBq U235 eq	1.38E-01	1.20E-01
Agricultural land occupation	m^2a	1.47E+00	1.47E+00
Urban land occupation	m^2a	3.14E-03	3.01E-03
Natural land transformation	m^2	1.48E-05	1.40E-05
Water depletion	m^3	9.13E-01	6.28E-01

| Metal depletion | kg Fe eq | 3.84E-03 | 3.41E-03 |
| Fossil depletion | kg oil eq | 2.43E-01 | 2.32E-01 |

The Climate Change impact category describes the effect of the system on global temperature reported in 'year per kilogram CO_2 equivalent' (kg CO_2eq) based on the most recent IPCC 100-year global warming potential [38]. The overall Coastal-Seawater scenario demonstrated a 3.5% reduction in climate change impact (Figure 4). Figure 5 shows that climate change is a relatively impactful category with European normalisation factors applied. This represents a significant improvement upon the Inland-Freshwater scenario. It worth noting that the use of seawater in washing the sugar beets alone enabled a 1.5% reduction in the climate change impact. The complete impact assessment results for beet washing only in both scenarios are indicated in Figure 6 and Table 5.

The water depletion describes the freshwater consumption in cubic metres (m^3) of the system. Only groundwater and surface waters – i.e., freshwater sources – are considered. Seawater use in the Coastal-Seawater scenario displaces tap water and therefore does not contribute to water depletion. The impact assessment showed that the Coastal-Seawater scenario has 31.2% less impact on water depletion than the Inland-Freshwater scenario (Figure 3). In the beet washing stage, the use of seawater instead of freshwater reduced water depletion impact of the clean sugar beet by 70% (Figure 6 & Table 5).

The land use category factors in the type of land occupied by the process and inputs to the process. The units for occupation are in area and time occupied (m^2*annum) whilst for transformation it is area (m^2). Agricultural land occupation remained identical in the production of clean sugar beet and the endpoint production of bioethanol and its coproducts. The normalised graph (Figure 5) shows that this is by far the most impactful of the selected categories for bioethanol production in Europe. Urban occupation was reduced in the Coastal-Seawater scenario by 34.2% for sugar beet washing (Figure 6 & Table 5) and 4.1% in the overall process (Figure 4). Natural land transformation was the most significantly reduced land use category with reductions in the beet washing and overall process of 41.9% (Figure 6 & Table 5) and 5.5% (Figure 5) respectively.

The Coastal-Seawater scenario showed a reduction of 4.2% in the fossil depletion impact category in both the washing stage and the overall process (Figure 4). The normalised chart indicates that this is a significant category when results are calculated using European normalisation factors (Figure 5).
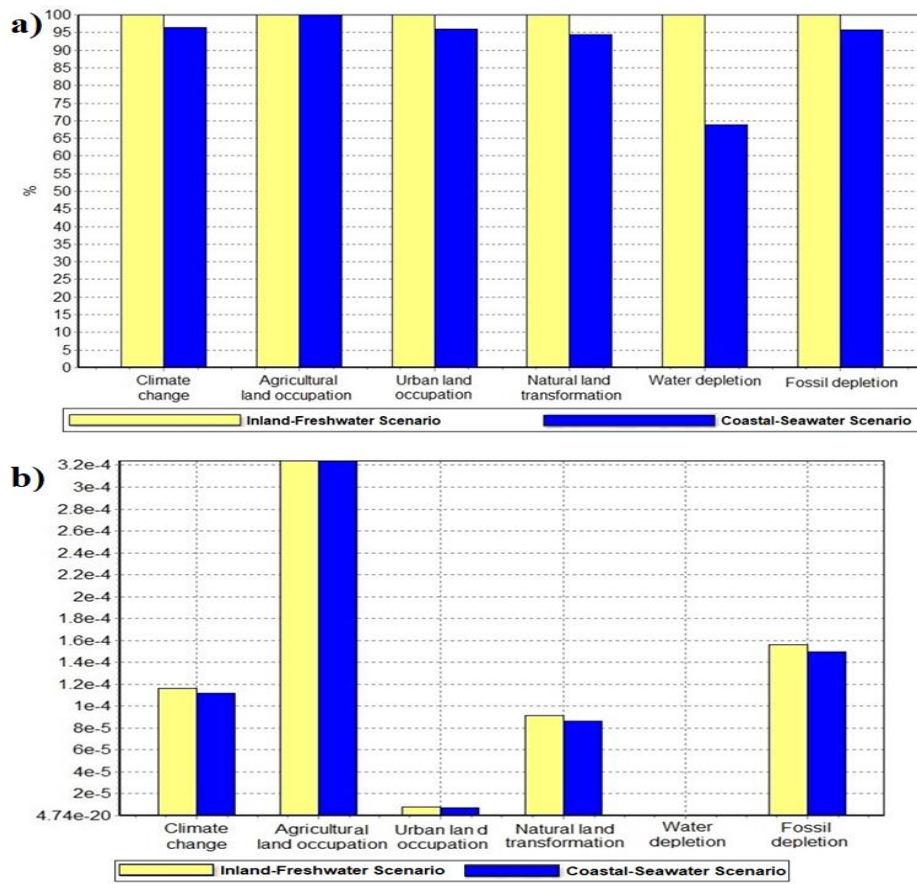
Figure 6: Comparative life cycle environmental impacts of the two scenarios of bioethanol production. a) The data has been characterised for direct comparison of the scenarios in six impact categories based on ethanol (95% in solution state) from sugar beet, Alloc Def, U. b) The values have been normalised for their relative significance using ReCiPe European normalisation method on SimaPro.
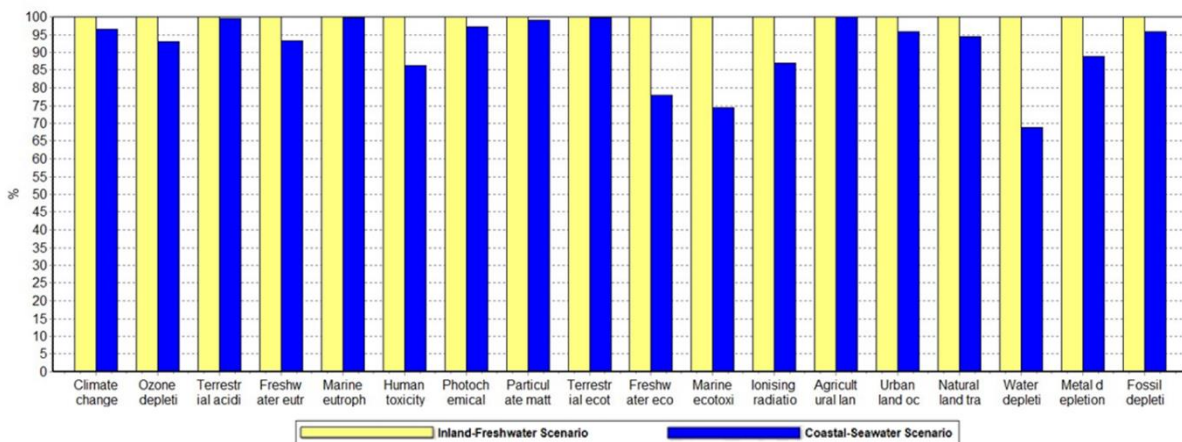
Figure 5: Complete Impact Assessment Results for Beet Washing Only in Each Scenario – Graph Characterised for Direct Comparison in 18 Impact Categories.

4. Discussion

4.1. Water Depletion Impact and Other Benefits of Seawater Fermentation

Water in the Coastal-Seawater scenario is directly piped from the sea, a source that does not factor into WF as freshwater does. In the initial stage of water use in the process, sugar beet washing, use of seawater had 70% less water depletion impact of the clean sugar beet than the Inland-Freshwater scenario. Overall, the Coastal-Seawater scenario achieved a 31.2% net reduction in the water depletion impact compared to the Inland-Freshwater scenario. This demonstrates the potential of seawater usage in industrial scale bioethanol production to achieve a significant reduction in water depletion impact.

The normalisation chart (Figure 5) reveals that water depletion is a relatively low impact category when European normalisation factors are applied. Water scarcity does not rank among the main environmental issues in most of Europe and so whilst the water depletion impact is significantly reduced in the Coastal-Seawater scenario, other impacts have more relative importance to the overall environmental impact of European bioethanol.

There is a high likelihood that through use of a seawater fermentation medium a high purity (97-99%) ethanol can be obtained for a fraction of the energetic cost associated with freshwater-based ethanol purification. Pure ethanol production would usually be done by a three-step extractive distillation of the fermentation broth: first distillation to 95% pure ethanol with 5% water, followed by extractive distillation requiring a solvent to increase the purity by water removal and finally distillation to remove the solvent. This process is highly energy intensive, as estimated by Lee and Pahl [39], where 50-80% of the overall process energy is required for producing highly pure ethanol. Addition of salts to the fermentation broth prior to extractive distillation has been suggested as a means to enhance ethanol recovery, reducing the number of stages to a single distillation [40]. In the coastal case, sodium chloride salt from the seawater medium is already dissolved in solution and thus may improve extraction efficiency and energy balance, which will be the focus of future research.

The scenarios were modelled with a single distillation stage yielding 95% pure bioethanol in the Inland-Freshwater scenario. The Coastal-Seawater scenario may have yielded a higher purity, due to the salt's effect, and so produce higher value bioethanol. However, this requires support with practical data. The purity of the bioethanol produced has a direct link with economic value. Anhydrous ethanol is necessary for fuel use as water can induce corrosion and rust in engines.

4.2. Climate Change and CCS Technology

Bioenergy production has been suggested as an ideal industry for coupling with CCS technology [41], enabling a potential overall carbon negative process. The high purity stream of CO_2 exiting the fermentation vessel can be easily collected for compression and storage, as compared to crude oil refineries which emit a range of gases and require a capture technology to filter emissions, far more processing and thus higher costs [7].

The CCS technology that is incorporated into conventional production, on which the Inland-Freshwater scenario in this study was modelled, tends to be short-term. Sequestration in products such as carbonated beverages delays CO_2 release for the shelf life of the product. On the other hand, sequestration in the deep sea, such as geological injection, is a long term storage solution [42]. Offshore storage has been proposed as offshore continental shelves offer significant capacity which is necessary to meet 2050 climate goals [43]. Owing to the location of the Coastal-Seawater scenario, offshore oceanic injection is likely to be a feasible solution to store the CO_2.

In this study the climate change impact was reduced by 3.5%. Normalisation factors for Europe revealed that this category is of relatively high importance which amplifies the reduction in the overall impact of the product by implementation of the Coastal-Seawater scenario.

4.3. Coproduct Profiles and Economic Discussion

The investigated scenarios for bioethanol production yielded different coproduct profiles. Utilisation of waste streams (i.e., beet pulp and sea salt) adds value to the overall process and can thus improve the economic viability of biofuels. Both scenarios generate biogenic CO_2 through fermentation that could be stored to increase the CCS ability of the bioethanol. However, there is a potential for more efficient CO_2 storage in case of the Coastal-Seawater scenario. The CO_2 generated during the fermentation at coastal locations can be stored safely and permanently in the deep sea (at 3000 m depth or more) as the CO_2 becomes a heavy liquid that sinks to the ocean floor [44, 45].

Also, both scenarios produce beet pulp as animal feed but in case of the Coastal-Seawater scenario, beet pup is salted as a result of washing with seawater or by adding sea salt to the pulp following the juicing stage. In addition, if the process does not recycle the yeast for the next fermentation cycles, the salted yeast will be added to the pulp to produce a high value sea-salted animal feed. Salts are usually added to the feed, either by the retailer or by the consumer, as animals require the nutrients. Production of sea-salted animal feed in the coastal scenario comes without the expense of additive sea salt and can be presumably marketed at a greater value than unsalted feed.

In addition, the use of seawater in the Coastal-Seawater scenario enabled the additional production of distilled water and sea salt, neither of which are present in the Inland-Freshwater scenario. Sodium chloride, other minerals and trace elements are naturally contained in seawater. These remain dissolved through to the distillation stage at which point they are precipitated out, resulting in water and sea salt.

Also, addition of sea salt and distilled water to the coproduct profile further improves the economic situation in the Coastal-Seawater scenario. Originating from the sea, the water is desalinated in the process of distillation and so is converted from a free and abundant resource to a valuable product. By contrast the Inland-Freshwater scenario, which reflects current practices, treats the spent freshwater as waste and thus without value. Added revenue streams without significant additional costs make this the economically preferred scenario.

The value of water as a product dictates whether this element of the proposed coastal biorefinery balances the economic system. As a product of extractive distillation, the produced desalinated water would be non-potable. This is due to trace amounts of the solvent applied for ethanol recovery. Water utility companies identify a demand for non-potable water which lends a market value to this product. The purity of the water resulting from this process is not yet known. The water treatment required to achieve a potable product may be worth the cost.

Implementation of a biorefinery operating a seawater fermentation would be more beneficial to countries facing extreme water scarcity that have access to seawater. The value of desalinated water in these countries would be more economically favourable than in countries with plentiful freshwater resources. Desalination is an expensive method to produce water alone, but as part of the coproduct profile of bioethanol fuel production the economics may be more balanced.

4.4. Assumptions and Limitations

This study has been done under the assumption that the Coastal-Seawater scenario utilises a similar amount of electricity as in the Inland-Freshwater scenario. However, experimental investigation may indicate that the Coastal-Seawater scenario consumes less overall electricity compared to the Inland-Freshwater scenario especially in beet washing and ethanol distillation steps and therefore, it may produce more surplus electricity. Also, this study assumed that both scenarios require the addition of similar amounts of sodium sulphate in the fermentation media, however, typical seawater contains enough sodium (10.556 mg/L) and sulphate (2.649 mg/L) and therefore addition of sodium sulphate could be eliminated in the Coastal-Seawater scenario [46]. Anti-foam could be also eliminated or at least reduced in the Coastal-Seawater scenario because the high concentration of salt in seawater could work as   an anti-foam [47]. In addition, unlike the Inland-Freshwater

scenario, part of the distilled water produced in the Coastal-Seawater scenario can be re-used in the system eliminating the need for external distilled water for cooling. Taking all these points into consideration for re-modelling the Coastal-Seawater scenario would lead to improved environmental and economic results.

Furthermore, bioethanol production rate and productivity were assumed to be equivalent in both scenarios. This is because the Coastal-Seawater model would ideally involve the use of marine yeast strain for fermentation in seawater-based medium. Marine yeast can produce bioethanol using seawater at almost similar rate that industrial terrestrial yeast using freshwater. The marine *S. cerevisiae* strain AZ65 recorded ethanol production at a rate of 1.62 g/L/h using seawater as compared to 1.65g/L/h by terrestrial strain NCYC2592 using freshwater [18] and reached maximum ethanol productivity of 4.15 g/L/h using YPD-seawater medium and 2.46 g/L/h using Molasses-seawater medium [23]. The production rate and productivity of seawater-bioethanol can be improved by further optimisation of the fermentation parameters and improving the marine yeast strain.

On the other hand, the cost of construction of both the bioethanol plant and the oceanic CO_2 injection site were not included in this study. This improved the comparability between the scenarios, if these structures have long enough lifetime that these capital costs can be paid back quickly. However, the capital investment in the two scenarios is likely to differ which can be addressed in future work.

4.5. Future Perspectives: Towards a Coastal Integrated Marine Biorefinery (CIMB) System

In this analysis the cultivation and harvesting of the feedstock subsystem produces identical results between the coastal and Inland-Freshwater scenarios. This has resulted in no change in agricultural land use between the two scenarios (Figure 4). The European normalisation factors, however, show that this is by far the most important of the selected categories (Figure 5).

Also, although the Coastal-Seawater scenario produces freshwater, its water depletion impact is not negative. This shows that the volume of freshwater produced does not offset that used in the production process. In the Coastal-Seawater scenario, seawater was applied to beet washing and the fermentation medium. However, the majority of water depletion takes place in the cultivation and harvesting.

This work was conducted to evaluate the environmental feasibility of the coastal setting and seawater use, with a view to then incorporate marine biomass (such as seaweed and marine microalgae) in the Coastal-Seawater system to reach a fully marine based biorefinery. This is predicted to greatly reduce environmental impact of water depletion and land use – agricultural land occupation to be specific. Further practical work will determine the processing requirements needed for marine biomass feedstock in a coastal biorefinery using seawater medium, and this new scenario should be again analysed via comprehensive LCA to obtain comparable results.

Marine biomass sources including macro- and microalgae have potential for use as feedstock. They do not require freshwater or land for cultivation and are therefore a desirable feedstock. A coastal location puts the production process in close proximity to marine resources. In addition to the access to seawater and marine biomass, the coastal location offers other potential benefits that have not been included in this study due to lack of data availability and research time. As the concept gains traction further integration with other technology systems could be explored. Another benefit of a coastal location is the ease of transportation by sea. The fuel product as well as the coproducts (water, salt, animal feed and LimeX) could be exported by freight shipping widening access to the fuel beyond its immediate area. Thus, a marine-based biorefinery in a coastal location is likely to improve both the sustainability and feasibility of bioethanol production [36, 48, 49] contributing to the global effort to achieve environmental targets.

Furthermore, coastal location improves accessibility to renewable power sources. In this analysis where electricity was necessary, such as in CO_2 compression and beet pulp drying, the source of the electricity was from the grid which includes non-renewable sources. Direct connection to renewable sources, such as offshore windfarms and wave

energy sites, could be integrated into the process to further improve the environmental impact towards net zero targets. This translates to reduced transport costs – both monetary and environmental – and may have further benefits.

5. Conclusions

The LCA presented in this study demonstrated the value of a coastal biorefinery using marine yeasts and seawater medium in reducing the environmental impact of bioethanol production. Environmental impact reduction was primarily in the water depletion category with a decrease of 31.2%. Climate change, natural land transformation, urban land occupation and fossil depletion were all reduced by 3.5-5.5%. Agricultural land occupation saw no change due to the modelled first-generation feedstock which relies on arable land for feedstock production. Coupling with CCS and water desalination show environmental improvements upon current bioethanol production. Further opportunities for environmental impact reduction owing to the coastal location are also discussed, particularly regarding climate change and land use. Further work is suggested to integrate marine biomass (seaweed and marine microalgae) for a complete integrated marine biorefinery system based on coastal sites. This would immensely reduce the water and carbon footprint for bioethanol, likely to net negative values, and increase the economic feasibility of the process. Utilisation of the marine resources in a marine biorefinery system based on coastal locations for the intensive production of biofuels and biobased products has the potential for speeding up the global effort on climate change mitigation as well as water, food, and energy security.

Author Contributions: Conceptualization, A.S.Z.; methodology, C.E.C.; software, C.E.C.; validation, C.E.C., A.S.Z. and F.M.; formal analysis, C.E.C.; investigation, C.E.C., and A.S.Z.; resources, C.E.F. and A.S.Z.; data C.E.C. and F.M.; writing—original draft preparation, C.E.C. and A.S.Z.; writing—review and editing, F.M. and C.E.F.; visualization, A.S.Z. and C.E.F.; supervision, A.S.Z. project administration, A.S.Z. and C.E.F; funding acquisition, A.S.Z. and C.E.F. All authors have read and agreed to the published version of the manuscript.

Funding: Please add: This research received no external funding

Data Availability Statement: In this section, please provide details regarding where data supporting reported results can be found, including links to publicly archived datasets analyzed or generated during the study. Please refer to suggested Data Availability Statements in section "MDPI Research Data Policies" at https://www.mdpi.com/ethics. You might choose to exclude this statement if the study did not report any data.

Acknowledgments: The authors would like to thank Dr R. Camilla Thompson from the School of Engineering at the University of Edinburgh for her great assistance and guidance with SimaPro software.

Conflicts of Interest: The authors declare no conflict of interest.

References

1.   United Nations, *Paris Agreement*, U. Nations, Editor. 2016, United Nations: Paris. p. 1-27.

2.   Ritchie, H. and M. Rosner. *CO2 and Greenhouse Gas Emissions*. 2020   [cited 2020 20/04/20]; Available from: https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions.

3.   Fulton, L.M., et al., *The need for biofuels as part of a low carbon energy future.* Biofuels, Bioproducts and Biorefining, 2015. **9**(5): p. 476-483.

4.   Zhang, J., et al., *A review of heat transfer issues in hydrogen storage technologies.* 2005.

5.   Felderhoff, M., et al., *Hydrogen storage: the remaining scientific and technological challenges.* Physical Chemistry Chemical Physics, 2007. **9**(21): p. 2643-2653.

6.   Den Boer, E., et al., *Zero emissions trucks: An overview of state-of-the-art technologies and their potential.* 2013.

7.   IPCC, *Special report on carbon dioxide capture and storage.* 2005, Cambridge University Press, Cambridge.

8.   GlobalCCSInstitute, *Global Status of CCS Targeting Climate Change.* 2019.

9.   Pal, A., *Blending of ethanol in gasoline: Impact on SI engine performance and emissions.* International Journal of Thermal Technologies, 2014. **4**(1): p. 1-5.

10.   Al-Hasan, M., *Effect of ethanol–unleaded gasoline blends on engine performance and exhaust emission.* energy conversion and management, 2003. **44**(9): p. 1547-1561.

11.   Muñoz, M., et al., *Bioethanol blending reduces nanoparticle, PAH, and alkyl-and nitro-PAH emissions and the genotoxic potential of exhaust from a gasoline direct injection flex-fuel vehicle.* Environmental science & technology, 2016. **50**(21): p. 11853-11861.

12.   Transport, D.f. *Fuelling a greener future: E10 petrol set for September 2021 launch*. 2021   [cited 2021 04/03/2021]; Available from: https://www.gov.uk/government/news/fuelling-a-greener-future-e10-petrol-set-for-september-2021-launch.

13.   Bailey, B.K., *Performance of ethanol as a transportation fuel*, in *Handbook on Bioethanol*. 2018, Routledge. p. 37-60.

14.   Speidel, H.K. and I. Ahmed, *Biodegradability characteristics of current and newly-developed alternative fuels*. 1999, SAE Technical Paper.

15.   Dias De Oliveira, M.E., B.E. Vaughan, and E.J. Rykiel, *Ethanol as fuel: energy, carbon dioxide balances, and ecological footprint.* BioScience, 2005. **55**(7): p. 593-602.

16.   European Union, *Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources (Text with EEA relevance.).* Official Journal of the European Union, 2018. **328**: p. 82-209.

17.   Liu, X.V., S.K. Hoekman, and A. Broch, *Potential water requirements of increased ethanol fuel in the USA.* Energy, Sustainability and Society, 2017. **7**(1): p. 18.

18.   Zaky, A., et al., *The establishment of a marine focused biorefinery for bioethanol production using seawater and a novel marine yeast strain.* Scientific Reports, 2018. **8**.

19.   Gerbens-Leenes, W., A.Y. Hoekstra, and T.H. van der Meer, *The water footprint of bioenergy.* Proceedings of the National Academy of Sciences, 2009. **106**(25): p. 10219.

20.   Gerbens-Leenes, P., *Green, blue and grey bioenergy water footprints, a comparison of feedstocks for bioenergy supply in 2040.* Environmental Processes, 2018. **5**(1): p. 167-180.

21.   Domínguez de María, P., *On the use of seawater as reaction media for large-scale applications in biorefineries.* ChemCatChem, 2013. **5**(7): p. 1643-1648.

22.   Zaky, A., et al., *A New Isolation and Evaluation Method for Marine-Derived Yeast spp. with Potential Applications in Industrial Biotechnology.* Journal of Microbiology and Biotechnology, 2016. **26**(11): p. 1891-1907.

23.   Zaky, A.S., et al., *Improving the productivity of bioethanol production using marine yeast and seawater-based media.* Biomass and Bioenergy, 2020. **139**: p. 105615.

24.   International Organization for Standardization, *Environmental management: Life cycle assessment; requirements and guidelines*. 2006, ISO Geneva.

25.   Goedkoop, M., et al., *SimaPro Database Manual Methods Library.* PRé Consultants, The Netherlands, 2008: p. 22-25.

26.   Wernet, G., et al., *The ecoinvent database version 3 (part I): overview and methodology.* The International Journal of Life Cycle Assessment, 2016. **21**(9): p. 1218-1230.

27.   Durlinger, B., et al. *Agri-Footprint; a Life Cycle Inventory database covering food and feed production and processing*. in *Proceedings of the 9th International Conference on Life Cycle Assessment in the Agri-Food Sector*. 2014.

28.   Vierhout, R., *Renewable ethanol: driving jobs, growth and innovation throughout Europe.* State of the Industry Report, ePure European Renewable Ethanol Association, 2014.

29.   Šantek, B., et al., *Evaluation of energy demand and the sustainability of different bioethanol production processes from sugar beet.* Resources, Conservation and Recycling, 2010. **54**(11): p. 872-877.

30.   Mundi, G.S., R.G. Zytner, and K. Warriner, *Fruit and vegetable wash-water characterization, treatment feasibility study and decision matrices.* Canadian Journal of Civil Engineering, 2017. **44**(11): p. 971-983.

31.   Campiotti, C.A., et al., *Energy efficiency in Italian fruit and vegetables processing industries in the EU agro-food sector context.* RIVISTA DI STUDI SULLA SOSTENIBILITA', 2014.

32.   Mortimer, N., M. Elsayed, and R. Horne, *Energy and greenhouse gas emissions for bioethanol production from wheat grain and sugar beet.* Resources Research Unit School Of Environment And Development, Sheffield Hallam University, Sheffield, 2004.

33.   Rao, P., et al., *Energy considerations associated with increased adoption of seawater desalination in the United States.* Desalination, 2018. **445**: p. 213-224.

34.   Pfromm, P.H., *The minimum water consumption of ethanol production via biomass fermentation.* The Open Chemical Engineering Journal, 2008. **2**(1).

35.   Aspelund, A. and K. Jordal, *Gas conditioning—The interface between CO2 capture and transport.* International Journal of Greenhouse Gas Control, 2007. **1**(3): p. 343-354.

36.   Zaky, A.S., *Marine fermentation, the sustainable approach for bioethanol production.* EC Microbiology, 2017: p. 25-27.

37.   European Commission, *Directive of the European parliament and of the council on the promotion of the use of energy from renewable sources.* Brussels, 2008. **23**: p. 2008.

38.   Stocker, T., et al., *IPCC, 2013: climate change 2013: the physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change.* 2013.

39.   Lee, F.M. and R.H. Pahl, *Solvent screening study and conceptual extractive distillation process to produce anhydrous ethanol from fermentation broth.* Industrial & Engineering Chemistry Process Design and Development, 1985. **24**(1): p. 168-172.

40.   Pinto, R., M. Wolf-Maciel, and L. Lintomen, *Saline extractive distillation process for ethanol purification.* Computers & Chemical Engineering, 2000. **24**(2-7): p. 1689-1694.

41.   Budinis, S., et al., *An assessment of CCS costs, barriers and potential.* Energy strategy reviews, 2018. **22**: p. 61-81.

42.   Laude, A., et al., *CO2 capture and storage from a bioethanol plant: Carbon and energy footprint and economic assessment.* International Journal of Greenhouse Gas Control, 2011. **5**(5): p. 1220-1231.

43.   Schrag, D.P., *Storage of carbon dioxide in offshore sediments.* Science, 2009. **325**(5948): p. 1658-1659.

44.   Rackley, S.A., *Chapter 12 - Ocean Storage*, in *Carbon Capture and Storage*, S.A. Rackley, Editor. 2010, Butterworth-Heinemann: Boston. p. 267-286.

45.   Metz, B., et al., *IPCC special report on carbon dioxide capture and storage*. 2005: Cambridge: Cambridge University Press.

46.   Lenntech, *https://www.lenntech.com/composition-seawater.htm*. last accessed 14/07/2021.

47.   Behera, M.R., et al., *Foaming in Micellar Solutions: Effects of Surfactant, Salt, and Oil Concentrations.* Industrial & Engineering Chemistry Research, 2014. **53**(48): p. 18497-18507.

48.   Zaky, A.S., et al., *Marine yeast isolation and industrial application.* FEMS yeast research, 2014. **14**(6): p. 813-825.

49.   Greetham, D., et al., *A brief review on bioethanol production using marine biomass, marine microorganism and seawater.* Current Opinion in Green and Sustainable Chemistry, 2018. **14**: p. 53-59.