

Communication

Introducing a Marine Biorefinery System for the Integrated Production of Biofuels, High-Value-Chemicals, and Co-Products: A Path Forward to a Sustainable Future

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Abstract: Biofuels have many environmental and practical benefits as a transportation fuel. They are among the best alternatives to fossil fuels- thanks to their capacity for negative carbon emissions, which is vital for archiving the global ambition of a net-zero economy. However, conventional biofuel production takes place on inland sites and relies on freshwater and edible crops (or land suitable for edible crop production), which has led to the food versus fuel debate. It also suffers technical and economical barriers owing to the energy balance and the cost of production compared with fossil fuels. Establishing a coastal integrated marine biorefinery (CIMB) system for the simultaneous production of biofuels, high-value chemicals, and other co-products could be the ultimate solution. The proposed system is based on coastal sites and relies entirely on marine resources including seawater, marine biomass (seaweed), and marine microorganisms (marine yeasts and marine microalgae). The system does not require the use of arable land and freshwater in any part of the production chain and should be linked to offshore renewable energy sources to increase its economic feasibility and environmental value. This article aims to introduce the CIMB system as a potential vehicle for addressing the global warming issue and speeding the global effort on climate change mitigation as well as supporting the world's water, food and energy security. I hope these perspectives serve to draw attention into research funding for this approach.

Keywords: bioenergy; marine fermentation; seawater; marine yeast; microalgae; seaweed; circular economy; high value chemicals



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1. Introduction

Global warming has reached an alarming level of nearly 1.3 °C above pre-industrial levels and is increasing yearly [1]. This is largely due to carbon emissions from the fossil fuels that we rely on for energy, especially for transportation [2]. If we do not act quickly and collectively, global warming could exceed an increase of 4 °C by 2100 [3]. This will lead to catastrophic and irreversible climate change, including severe drought and rising sea levels, resulting in severe shortages of water and food supplies, as well as the disappearance of cities and extinction of many species of organisms. Hence, global carbon emissions must rapidly decrease to net-zero by 2050, then further decrease to a negative value to stay within the safe limits (1.5 °C) established by the Paris Agreement in 2016 [4]. This requires us to replace fossil fuels with clean energy sources. Among many alternatives, biofuels are an attractive option because their production process has a great capacity for carbon capture and storage (CCS). Biofuels store energy in different forms including liquid and gas, which are easy to store in tanks and transport, and are compatible with the established technologies in the transportation sector [5,6]. However, we do not have enough arable land and freshwater to grow enough biomass for biofuel production to satisfy the likely demand and to capture the carbon already released into the atmosphere using the current approach for bioenergy production. On the other hand, seas and oceans cover more than 70% of the Earth's surface and contain more than 97% of the Earth's water as well as the

minerals needed for biomass production and subsequent conversion to bioenergy [7,8]. Therefore, a biorefinery system based on the marine environment and resources could be a practical solution and a vehicle for sustainable climate mitigation as well as energy, food, and water security.

This article aims to propose a coastal integrated marine biorefinery (CIMB) system for the simultaneous production of biofuels, high value chemicals (HVCs), and other valuable products as a viable and sustainable approach for global warming mitigation and green economy. The proposed system relies solely on marine resources including seawater, marine biomass (seaweed), and marine microorganisms (yeast and marine microalgae). The system refrains from using any arable land and freshwater throughout the production chain. This will increase the economic and environmental value of the system, potentially achieving a negative water footprint (WF) and negative carbon footprint (CF) for the products. In order to clearly present the CIMB system, the article briefly discusses the limitations associated with the current approach (the inland-freshwater-biorefinery (IFB) system) for biofuel production. In addition, the article proposes the coastal seawater biorefinery (CSB) system and the coastal marine biorefinery (CMB) system as the base for the CIMB system. The article also briefly introduces the idea of integrating the CIMB system with other renewable inshore and offshore energy systems for maximum efficiency and productivity of the renewable energy sources. If this proposal attracts the necessary funding, it could play a prime role in addressing global warming in a sustainable way that supports food, water, and energy security. The following sections explain the current standard biorefinery system (IFB) and the development of marine-based systems (CSB, CMB, and CIMB).

2. Inland-Freshwater-Biorefinery (IFB) System

Conventional biofuel production, for example, bioethanol, takes place based on an inland freshwater biorefinery (IFB) system model (Figure 1). This approach is associated with many drawbacks, including (a) high freshwater consumption, (b) high amounts of CO₂ released into the atmosphere, (c) high energy and high cost required for transportation of the substrates and the final products, and (d) difficulties and high cost associated with waste disposal [5]. Also, conventional biofuel production utilises terrestrial biomass that relies on freshwater and arable land; this has led to the food versus fuel debate. In addition, we do not have enough arable land and freshwater to grow enough biomass for biofuel production to satisfy the likely demand and to capture the excessive amounts of CO₂ that have been already released into the atmosphere.

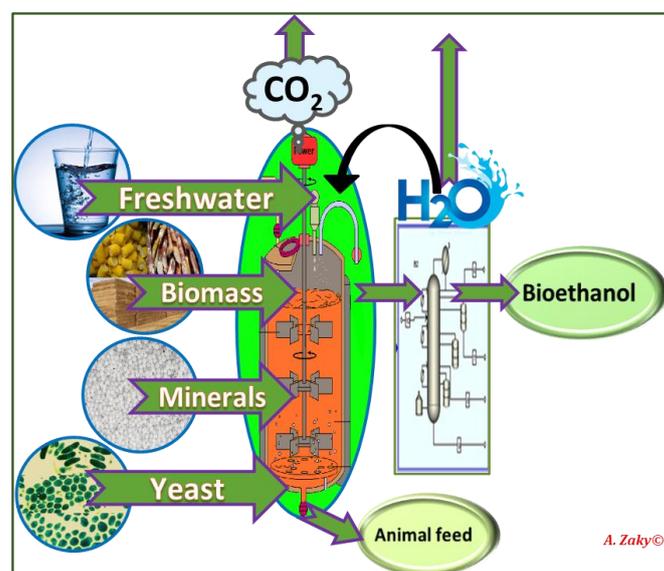


Figure 1. Inland-freshwater-biorefinery (IFB) system.

3. Coastal Seawater Biorefinery (CSB) System

The aim of proposing an assessment of the coastal seawater biorefinery (CSB) system (Figure 2) is to establish the environmental impact and economic value of moving the biorefinery industry to coastal sites and using seawater instead of freshwater in the fermentation process. This is the fundamental step required to accurately evaluate the CIMB system under investigation in this paper.

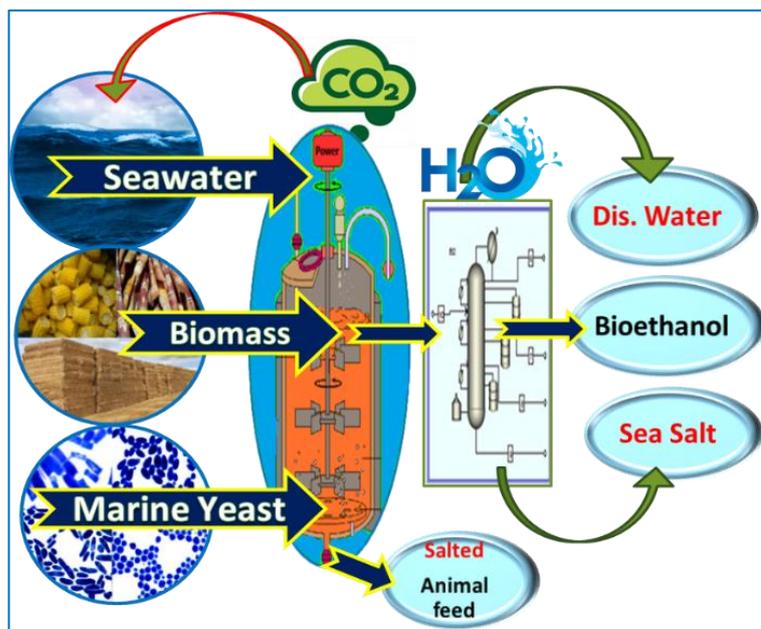


Figure 2. Coastal seawater biorefinery (CSB) system.

The potential advantages of moving the biorefineries to coastal sites include the following: (a) easy and direct access to an abundant source of water and minerals; (b) potential for safe storage of the excess CO_2 produced; (c) direct access to a safe site for biological waste disposal after appropriate treatment procedures; (d) easy access to low cost and low carbon footprint transportation by sea freight; (e) easy access to marine biomass; and (f) promoting the use of biofuels in the shipping transport sector [5]. In addition, the potential advantages of using seawater in the biorefineries include the following: (a) reducing WF of the product, (b) reducing the requirement for addition of minerals, (c) reducing airborne contamination, (d) producing distilled water and sea salt as additional co-products, (e) enhancing the distillation process, and (f) enhancing the quality of the residual solids for use as animal feed [5]. Hence, adopting the CSB approach could significantly enhance the efficiency of biofuel production. It could also encourage the development of research on third generation biomass (seaweed and marine microalgae) for efficient and economically viable biofuels and HVC production.

Recent research showed that seawater could replace freshwater for the production of bioethanol without compromising productivity. This was achieved using the novel marine yeast strain *S. cerevisiae* AZ65 and using YPD medium and sugarcane molasses made up using seawater [5,9]. A specific HPLC method was developed to determine sugars, salts, organic acids, ethanol, and other alcohols in seawater-based samples [10]. In addition, a preliminary life cycle analysis (LCA) of the production of bioethanol using seawater in a coastal setting showed the potential for significant improvement on 15 out of 18 ReCiPe midpoint impact categories including climate change, water depletion, land use, and fossil fuel depletion compared with those of conventional inland-freshwater bioethanol production [11]. Building upon these findings, intensive investigation of bioethanol production from the conventional first- and second-generation biomass using the CBS system (seawater, marine yeast, and terrestrial biomass) is required to confirm the positive role of

replacing freshwater with seawater in the fermentation process. The study should include the following research areas:

1. Optimisation of bioethanol production from conventional first-generation biomass—such as animal feed grade wheat, sugar beet, corn, and sugarcane—using seawater and marine yeast (such as the novel *S. cerevisiae* AZ65). Freshwater and industrial yeast strains (such as *S. cerevisiae* NCYC2952) should be used as a control. The experimental work for optimisation should include as many parameters as possible. The most important parameters for optimisation include substrate pre-treatment and sugar generation (varying depending on the substrate), yeast strain selection, fermentation conditions (anaerobic, microaerobic, and aerobic), fermentation mode (batch, fed-batch, and continuous), solid loading of the substrate (10–25%), and yeast inoculum (1–5 OD). Other parameters for optimisation include the fermentation temperature (28–35 °C), agitation speed (50–200 rpm), pH (4–7), and starch saccharification enzymes (type and concentration). These conditions are proposed based on the previous seawater-based bioethanol production from pure sugar and sugarcane molasses [5,9,12].
2. Optimising bioethanol production from crop and fruit waste (broken or rejected fruits and crops) using seawater and marine yeast. The source of these wastes can be farms, the food and beverages industries, and many others. Freshwater and industrial yeast should be used for comparison. The optimisation parameters are similar to those described above.
3. Optimising bioethanol production from conventional second-generation biomass such as lignocellulosic biomass (miscanthus and switchgrass), lignocellulosic agricultural residues (rice and wheat straws), and forestry waste. The optimisation parameters for the fermentation process can be similar to those discussed above, but the pre-treatment and hydrolysis of the biomass are more complicated and require more experimentation. For example, optimisation of the pre-treatment using different techniques such as acid, alkaline, or other methods should be conducted using seawater as a reaction medium. Optimisation of hydrolysis conditions using different enzymes and enzyme cocktails, especially halotolerant enzymes, should also be performed in seawater-based mixtures.
4. Investigating the effect of sea salts on the distillation process. Seawater contains about 35 g/L of salts, which is expected to have a positive impact on distillation owing to entrainment effects and reduced solubility of ethanol in salty water.
5. Assessment of the water footprint (WF) and carbon footprint (CF) of bioethanol and HVC of the CSB system and comparison of the results with the conventional system.
6. A comprehensive life cycle analysis (LCA) of bioethanol production using the CSB system in comparison with the conventional production system (IFB). This should focus on examining the greenhouse gas emission, water depletion, land use, and fossil fuel depletion of the different process configurations.
7. Techno-economic analysis (TEA) of mass and energy balance model using data from the literature and experimental measurements for capital cost and operating cost estimation. The economic metrics including the minimum selling price of bioethanol, net present value, and internal rate of return will be compared for investment analysis against the conventional production approach. LCA and TEA should consider the co-products and the impact of the possibility of CO₂ storage in the sea and of the additional co-products generated in the CSB system.

4. Coastal Marine Biorefinery (CMB) Systems for Biofuel Production

Marine fermentation refers to a fermentation process that utilises marine resources only (seawater, marine yeast, seaweed, and marine microalgae) throughout the production cycle [7]. Negative water and carbon emissions values, without using any freshwater, food crops, or arable land, can only be achieved when using marine biomass (seaweed and microalgae) as substrate. Seaweed and microalgae grow very fast and contain high levels

of carbohydrates and/or lipids and a wide variety of HVP. They do not require freshwater, fertilisers, or arable land for production. In addition, they have a high ability to absorb atmospheric CO₂ and convert it into carbohydrates and lipid—the two substrates for biofuel production. They also contain high value compounds that can be extracted to increase the feasibility of the biofuel production. Hence, marine biomass is regarded among the best feedstocks for bioenergy and HVC production, if its processing can be made efficient and economically viable.

4.1. The Main Items of the Marine Biorefinery Systems

4.1.1. Coastal Sites

Coastal sites are those with easy and direct access to seawater. The earth has around 620,000 km of coastline [13]. If we consider up to 1 km distance from the coastline to be economically viable for marine biorefinery systems, then we theoretically have about 620,000 km² of sea sites that are potentially suitable for marine biorefineries, provided that they are not already devoted to other human activities or disturbed by severe conditions. In addition, small islands, artificial islands, and areas around inshore and offshore wind farms can be ideal locations for establishing CMB systems.

4.1.2. Seawater

Seawater accounts for about 97% of the world's water and covers 360,663,099 km² (about 71%) of the Earth's surface, in the form of a connected network of aquatic ecosystems [14]. It is a renewable water source and readily accessible in most countries around the world, including those that already suffer severe freshwater shortages. Seawater is the main nutritional supplement for a large number of living organisms (biomass) such as seaweed, marine microalgae, marine yeast and bacteria, and other organisms that live in the marine environment. The salinity of the seawater of open seas and oceans is around 3.5% (*w/v*) salts, but it is influenced by the region and the season of the year. For example, the salinity of seawater in some parts of the Mediterranean Sea and the Red Sea can reach up to 3.9% and 4.1%, respectively, while it is only 2.8% in Wonthaggi, Australia [15,16]. Therefore, seawater can sustainably provide the water and minerals needed for bioenergy.

4.1.3. Seaweed

Seaweeds are multicellular macroalgae that grow in seawater. They grow rapidly in a wide range of sizes of different shapes and colours including more than 10,000 species of the fastest-growing plants on the planet, constituting one of the most important biomass resources in the marine environment [17,18]. Seaweeds are classified based on their pigmentation into three main groups: brown seaweeds (Phaeophyceae), red seaweeds (Rhodophyceae), and green seaweeds (members of the Chlorophyta) [19].

The chemical composition of seaweed varies greatly between species. Brown seaweed contains 12.2–56.4% carbohydrates, 4.3–24.0% protein, and 17.0–44.0% ash; while red seaweed contains 34.6–71.2% carbohydrates, 8.0–47.0% protein, and 7.0–37.0% ash; and green seaweed contains 29.8–58.1% carbohydrates, 8.7–32.7% protein, and 11.0–73.0% ash. The lipid content in seaweed is generally low—0.1–4.5% of dry weight [20], but even so, seaweed is still a very attractive substrate for bioenergy production thanks to its high carbohydrate content. For this reason, several researchers have investigated the potential of seaweed for biofuel production [21–24].

It has been estimated that 48 million km² of the of the oceans are suitable for the sustainable production of seaweed [25]. The success of marine biorefinery systems proposed in this article relies mainly on seaweed cultivation at a very large scale. For this, it would be valuable to establish pilot seaweed demonstration farms of at least 10 km² each. The location of the seaweed farm could be in shallow water near the coastline or integrated with the wind farms (for example, wind farms in the North Sea).

This farm can be used to carry out economic, farming, and environmental studies on seaweed production. The main points of these studies should include the following:

1. Optimisation of seaweed production (types, quantity, and quality) using different farming methods and tools.
2. Optimisation of harvesting and dewatering of seaweed.
3. Estimating the cost of seaweed production over the world's economical seaweed farming area (48 million km²) using different tools and techniques.
4. Estimating the seaweed biomass production from the world's economical seaweed farming area (48 million km²) and the potential for the production of biofuels, HVC, salts, and freshwater.
5. Estimating the CCS capacity of different types of seaweed over the world's economical seaweed farming area (48 million km²) and their ability to reduce the atmospheric CO₂ level and the surrounding temperature.
6. Estimating the effect of intensive large-scale seaweed farming on the atmospheric humidity and the probability of rain.
7. Predicting the effect of large-scale seaweed production on sea level.
8. Estimating the effect of large-scale seaweed farming on the marine environment including the seawater pH, seawater pollutants, and seawater dissolved oxygen.
9. Estimating the effect of seaweed production on the variety and density of marine microorganisms, fishes, and mammals.
10. Estimating the economic cut-off supply distance between the seaweed farms and the locations of the biorefinery.

4.1.4. Marine Yeast

Marine yeasts are those yeast strains that have been isolated from marine environments and usually are able to grow better on a seawater-based medium. They can be isolated from fish, marine animals, sea sand, seaweeds, and many other marine substances, but the main source of marine yeast is seawater. The number of yeasts decreases in the seawater as the distance increases from the coast; however, yeast density is higher in deep-sea sediments [8,26].

Marine yeasts can be divided into two main groups: facultative and indigenous or obligate. The facultative marine yeasts are species that are originally derived from the terrestrial environment. They may have reached the marine environment through rivers, wind, birds, or human activities and are usually found near the coast. They have adapted to the marine environment over time and may have developed a higher tolerance to osmotic pressure, salts, and other inhibitors compared with their terrestrial counterparts. Indigenous or obligate marine yeasts are the yeast species that are native inhabitants of marine environments. They may be able to grow in freshwater-based media, but they grow better in marine-based media (made with seawater) [8,26]. Recent research has indicated that marine yeasts show high tolerance to salts and many inhibitors usually present in fermentation media. They also demonstrated higher fermentation ability and tolerance to sugar and ethanol concentrations compared with current industrial yeast strains [9,12,27]. Therefore, marine yeasts are suitable candidates for a marine biorefinery where seawater and seaweed are used for the production of biofuels.

4.1.5. Marine Microalgae

Microalgae are a broad range of microorganisms that include cyanobacteria, unicellular green and red algae, and diatoms [28]. They are unicellular, primarily photoautotrophic organisms, existing either in isolation or in colonies. They are ubiquitous in aquatic environments from cold glacier ice to hot springs and in freshwater, seawater, and brackish water, and feature low down on the food chain as food for higher organisms such as plankton [29,30]. So far, about 30,000 species of microalgae have been identified and analysed [31].

Marine microalgae are cultivated in photobioreactors. These can be open, usually large open ponds or raceways, or closed—consisting of usually glass or Perspex tubing or flat plate vessels [32,33]. Their main cultivation requirements are seawater; light; a carbon

source (organic or inorganic); and inorganic nitrogen, phosphorous, and trace elements. Temperature, salinity, and pH must also be adjusted to maintain a high growth rate [34]. The current annual global microalgae production is estimated at 20,000 tonnes [35]. They are mainly cultivated to produce food supplements for humans, animals, and aquaculture [36]. However, recently, microalgae are increasingly cultivated for the production of biofuels and high value products [37,38].

Several marine microalgae species such as *Nannochloropsis oceanica*, *N. gaditana*, *Dunaliella salina*, *Tetraselmis suecica*, and *N. salina* have been proposed for the production of biodiesel [39–42]. They have a higher lipid content compared with terrestrial biodiesel feedstocks and are not used as a primary food source [43]. Furthermore, they have a lower land requirement per kilogram of biodiesel produced, which minimises the land needing to be dedicated to their cultivation, freeing up land for agriculture and ensuring food security. This can be improved further by cultivating marine microalgae on coastal sites that are usually not suitable for agriculture [44].

4.2. Assessment of the Coastal Marine Biorefinery (CMB) System for the Production of Bioethanol (Route 1)

In this system, seaweed is used instead of terrestrial biomass as a carbon and nutrient substrate, and seawater is used instead of freshwater for preparing the fermentation medium. Marine yeast is used instead of the conventional industrial strains in the fermentation process (Figure 3).

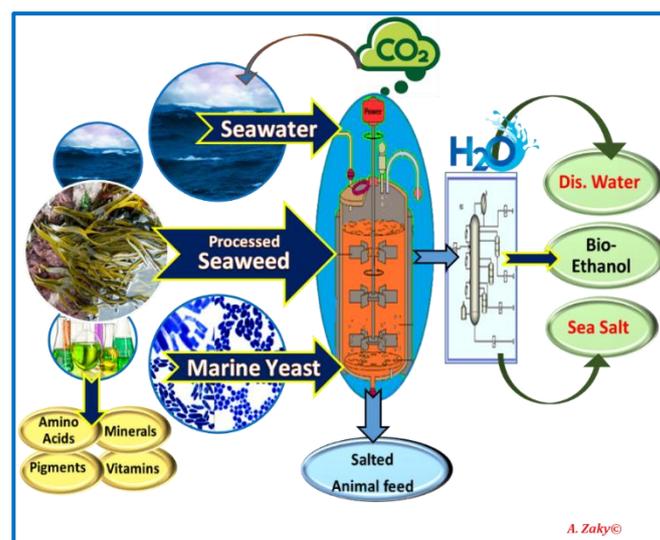


Figure 3. CMB system for the production of bioethanol (Route 1).

1. Optimisation of seaweed hydrolysis using new methods based on seawater for the maximum production of fermentable sugars and HVC. The seaweed can be cultivated, collected from the sea, or obtained from retailers such as provided by GreenSeas, <http://www.greenseas.co.uk/>, 16 October 2021.
2. Development and optimisation of extraction methods for the HVC from seaweed hydrolysates.
3. Optimising bioethanol production from seawater-seaweed hydrolysates using marine yeast strains, such as *S. cerevisiae* AZ65.
4. Assessment of the water footprint (WF) and carbon footprint (CF) of bioethanol and HVC of the CMB system and comparison of the results with the conventional system.
5. Conducting an LCA of the bioethanol and HVC obtained from the CMB system and comparison of the results with those obtained from the CSB system and the conventional system.

- Conducting a TEA of the products obtained from the CMB system and comparing with the results obtained from the CSB system and the conventional system. Sensitivity analysis should be performed to identify the impact of several process variables on the financial and environmental viability. This should detect trade-offs for optimisation of the production pathways.

4.3. Assessment of the Coastal Marine Biorefinery (CMB) System for the Production of Biogas (Route 2)

Many researchers reported that methanogens isolated from marine sediments are able to digest biological materials and produce methane [45–48]. Therefore, marine sediments are a potential source for microbial consortia to be used in a marine-based biogas system. In this system, seaweed is used instead of terrestrial biomass as a substrate for biogas production in the anaerobic digestion (AD) plant. Seawater is used instead of freshwater if needed. Halotolerant or marine methanogenic consortia are used instead of the conventional consortia for the AD process and the production of biogas (Figure 4).

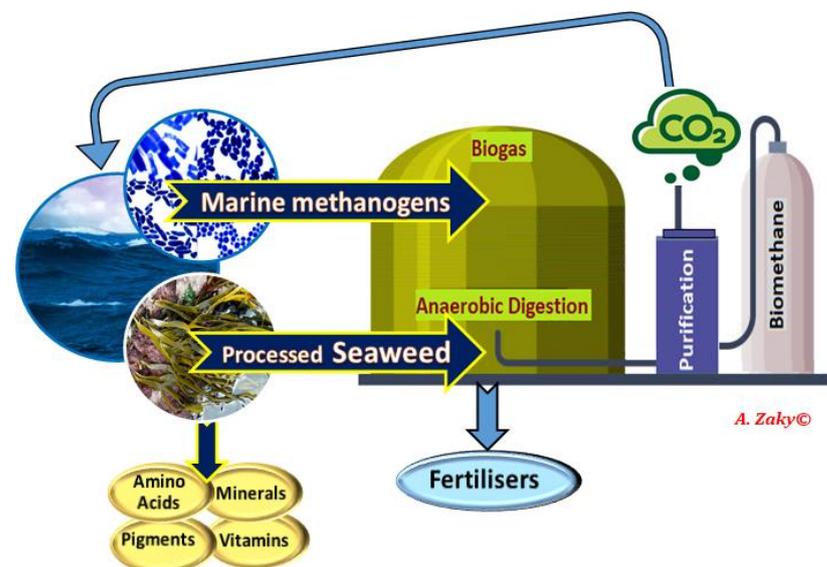


Figure 4. CMB system for the production of biogas (Route 2).

The research study should address the following questions:

- Optimisation of seaweed hydrolysis using new methods based on seawater to facilitate the extraction of the HVC and prepare the seaweed for efficient biogas production through AD.
- Isolation of marine methanogens or screening for halotolerant methanogens for biogas production from seaweed hydrolysates.
- Optimisation of biogas production using seaweed hydrolysates and a mix of seaweed and other biological residues available in the coastal locations.
- Assessment of the water footprint (WF) and carbon footprint (CF) of biogas and HVC of the CMB system and comparison of the results with the conventional system.
- Conducting an LCA of the biogas and HVC obtained from the CMB system and comparison of the results with those obtained from the conventional system.
- Conducting a TEA of the products obtained from the CMB system and comparison with the results obtained from the conventional system.

4.4. Assessment of the Coastal Marine Biorefinery (CMB) System for the Production of Biodiesel and HVC (Route 3)

In this system, marine microalgae strains only and seawater are used for cultivation and biomass production. Inorganic carbon and sunlight or organic carbon derived from

marine substrates are used as a carbon source, and seawater is used instead of freshwater for preparing the fermentation substrate and media (Figure 5).

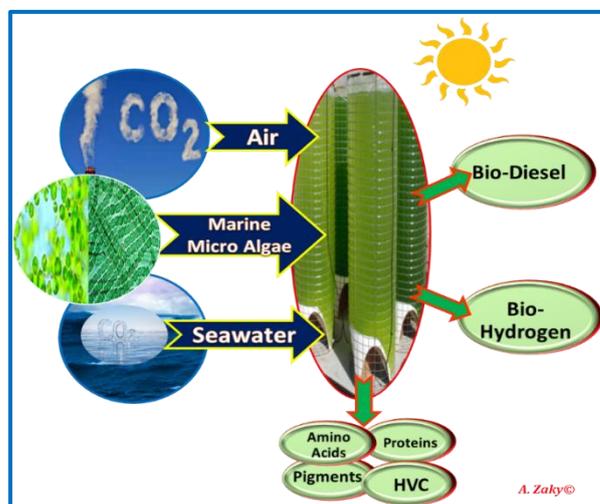


Figure 5. CMB system for the production of biodiesel and/or biohydrogen (Route 3).

The main research areas for this system should include the following:

1. Selection of a suitable marine microalgae strain from a culture collection or by isolating a new strain from the marine environment. For example, *N. oceanica* CCAP 849/10 is a potential strain for this system as it has a high content of lipids and HVC, as well as high cell and lipid productivity.
2. Optimising the microalgae cell production as well as lipid and HVC production using seawater and different carbon sources including air, CO₂, CH₄, solid inorganic carbon, and organic carbon.
3. Optimising microalgae biomass recovery and dewatering using low energy methods and using renewable energy sources such as solar energy.
4. Development and optimisation of lipid and HVC extraction methods.
5. Optimisation of biohydrogen production.
6. Assessment of the water footprint (WF) and carbon footprint (CF) of biodiesel, biohydrogen, and HVC of the CMB system and comparison of the results with the conventional system.
7. Conducting an LCA of the biodiesel, biohydrogen, and HVC obtained from the CMB system and comparison of the results with the conventional system using freshwater.
8. Conducting a TEA of the products obtained from the CMB system and comparison with the results obtained from the conventional system.

5. Coastal Integrated Marine Biorefinery (CIMB) System for the Production of Biofuels, HVC, and Co-Products

Seaweed and microalgae have been studied separately for the potential of biofuel and/or HVC production. The studies have been mainly based on inland sites and focused on the utilisation of the freshwater for the process. Despite the proven positive environmental impact, they were usually found to be economically unviable. Therefore, this article, for the first time, proposes the investigation of the synergy impact of utilising both types of biomass in a single production system for the complementary production of biofuels, high value chemicals (HVC), and co-products, in a complete marine-based system based on coastal sites. The system can be a vehicle for CCS on a large scale with the potential to play a key role in the global effort to tackle the climate emergency, reaching the net-zero carbon emissions target and beyond.

The core of this system is the cultivation of seaweed in huge marine farms covering millions of square kilometres of oceans and seas for several years. The biomass, in the

3. Investigating the possibility and impact of upgrading the biofuels obtained from the biological routes into higher value biofuels (such as jet fuels) and chemicals.
4. Investigating the production of hydrogen fuel based on seawater and comparison with conventional methods that use freshwater.

7. Additional Studies Related to the CIMB System

1. Assessment of the hydrothermal liquefaction (HTL) of marine biomass for biofuels and co-products production. HTL is a promising method for the production of bio-crude oils that can be upgraded into fuels and HVC from marine biomass, as this method is ideally suited to wet biomass, significantly lowering the prohibitive energy required for biomass drying.
2. Investigation of the potential corrosion issues in bioreactors because of the use of seawater. Furthermore, investigating ways to overcome this issue, for example, using coating materials or using corrosion-resistant materials in new bioreactors.
3. Investigating the effect of the produced marine-based animal feed on meat and the production other animal products and the effect on methane reduction (experimental, LCA, and TEA).

8. Conclusions

The marine environment is a massive source of water, minerals, valuable materials, and biological substances, yet it is still underutilised. However, the high salt content of seawater has been seen as a disadvantageous characteristic that limits the exploitation of such a large resource in industries, agriculture, and other human activities. This should not be the case and the salt content in seawater should be considered as a valuable source of minerals. The intensive use of seawater, seaweed, marine microalgae, and marine microorganisms in biomass bioenergy and biochemical production though the proposed CIMB system could play a key role in global warming mitigation, and thus controlling of the rise in sea level in coastal areas protecting islands and coastal cities around the world from inundation. The flexibility and system integration described in the CIMB system is a significant driver for the biofuel system to be integrated into future energy systems as a means to facilitate intermittent renewable hydrogen and electricity systems. The exploitation of the marine environment in this way will multiply the food and energy productive area on the planet for the benefit of humankind and create numerous jobs and wealth. Hence, an intensive investment in research and industrial projects in this arena is urgently required.

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