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# Toward Competitive Biofuel from Marine Algae Using Innovative Green Chemistry

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## Abstract

The biofuel production from marine algae is feasible but not yet economically viable compared to fossil fuel production. This work displays key reactions, processes and combination of innovative green chemistry in order to lead to a competitive biofuel production. The evaluation of chemical contents of two marine algae revealed that the major components of them are proteins, carbohydrates and lipids. To produce biofuel from marine algae with economically sustainable cost, each added value chemical content has to be valorized. This work demonstrates that each marine algae is unique and presents specific added value products specifically their secondary metabolites. Re isolation and reproducibility of specific metabolites from red alga, *Portieria hornemannii* and the cultured marine diatom, *Phaeodactylum tricornutum* were successful. Examples of formulation products from *Portieria hornemannii* and *Phaeodactylum tricornutum* are given to illustrate the feasibility of the process.

## Keywords

Biofuel, Biodiesel, Bio Ethanol, Lipids, Carbohydrates, Secondary Metabolites, Red Algae, Diatoms

## 1. Introduction

The notion of biofuel production from marine algae is very palpable and substitutable to fossil fuels because they have acquired biomass yield, oils which contain a relative amount of lipids, rapid growth rate, prospect of using uncultivable fields, ability to grow in wastewater, marine water as well as in moist soil, capability of

solar light utilization and acceptance of carbon dioxide as a source of their nutrient [1]. However, the cost of biofuel production from marine algae is still expensive compared to the present cost of fossil fuels production. The objective of this present article is to present sustainable green chemistry process in order to decrease the cost of biofuel production from marine algae by using innovative valorization of all added value products from the biomass sources. Marine environments inhabit more than 70% of the earth's surface, combining very diverse habitats with specific characteristics [2]. For simplicity of the illustration and example, we use two different marine algae sources; the Madagascar Red Marine Alga *Portieria hornemannii* and the cultured marine diatom, *Phaeodactylum tricornutum*.

## 2. Literature Review

Advancements in algal biotechnology are critical for both innovative and sustainable renewable sources, which involve the modification and targeting of bioactive components among the marine algal species in order to meet modern niche product requirements [3]. The knowledge in algae derived carbohydrates has grown significantly, with numerous research advances on their elemental composition variability as well as biological/biomedical applications documented in the published literature [3]. As cultivation and species selectivity can influence the quality and quantity of biorefinary products, low-cost microalgae biomass based biofuel manufacturing techniques must be developed. Improvements in algae biomass harvesting and extraction methods, high-quality biomass production, and greater oil-producing efficiency via genetic manipulation will be the prospects of algal biotechnology. Thus, incorporating modern algal biomass harvesting approaches, the biorefinery concept, advancements in photobioreactor design, and additional downstream processes would reduce the expenses of algal biofuel production, enabling it to become an economically viable option in the future [3].

The increase in the consumption of fossil fuels has resulted in reduction of natural resources. Thus, hunt for alternate energy sources is getting much attention nowadays [4]. Diatoms a class of photosynthetic microalgae available naturally are best suited class of microorganisms utilized for the production of biofuels. Because of their universal presence, ability to grow rapidly, diatoms can be utilized for production of biofuel [4]. One of the most useful outcomes of these is biodiesel. "Biodiesel" used as a form of sustainable diesel fuel is derived from natural sources. Conventional approach involved in lipid production from diatoms and later transforming it into bio-oil includes a list of stages such as cell harvesting and also involves applications of stressed condition so as to maximize the assembly of lipids, cell lysis to extract out the lipid content, transformation of lipid content into biodiesel by the method of transesterification [4]. The process of Extraction initiates with disruption of diatom cell wall and further the lipid extraction process can be carried out by performing several processes. Namely spontaneous oozing pulsed electric field, mechanical pressure, High-pressure homogenization, microwave oven and ball mill and so forth [4]. Out of all microwave oven and

Solvent assisted ultrasound are considered as an effective process for cell wall disruption, however, for extraction of lipids, above mentioned procedures utilize high energy input and also it is hard to scale up. Diatom-based biofuel comes under third-generation biofuel which ultimately contributes approximately 60% to 90% less greenhouse gases as compared to traditional fuel sources. Extraction steps in biofuel production need to be renewed because it sometimes causes destruction in entire diatom biomass. The extraction and purification process yields organic wastes which result in the demand of a significant amount of energy inputs. So, it is preferable to develop eco-friendly purification processes in order to keep the diatom cells alive during extraction [4].

Diatom frustules are considered as a sustainable source for several industrial applications because of their high biocompatibility and the easiness of surface fictionalization, which make frustules suitable for regenerative medicine and as drug carriers [5]. Frustules are made of hydrated silica, and can be extracted and purified both from living and fossil diatoms using acid treatments or high temperatures. Biosilica frustules have proved to be suitable for biomedical applications, but, unfortunately, they are not officially recognized as safe by governmental food and medical agencies yet [5]. Frustules can be purified from both living culture-derived algal biomass and diatomite stocks. The impurities of diatom frustules mainly consist of organic matters adhered to their surface [5].

The red seaweed is a type of marine macroalgae that can be harvested annually as a renewable living resource. In addition to being used for food, feed, and fertilizer, seaweeds are used in many other fields. There are more than sixty trace elements found in seaweeds, which are found in higher concentrations than in terrestrial plants. Aside from bromine, vitamins, protein, and iodine, seaweeds are also rich in substances of a stimulatory, antibiotic, and antimicrobial nature. Many secondary metabolites were derived from macroalgae, including fucoxanthin, terpenes, polyphenols, steroids, halogenated ketone, alkanes, and polyphloroglucinol or bromophenols [6]. The importance of seaweeds in the food and pharmaceutical industries is a result of their ecological and nutritional importance to both the food and pharmaceutical industries. According to several scientific studies, macroalgae have a wide range of bioactive compounds that exhibit numerous biological properties viz., anti-aging, antimicrobial antimalarial, dietary, anti-inflammatory, anticoagulant, antiallergic, antiproliferation, antibiotic, anticancer, antioxidant and hypolipidemia properties [7]-[9]. Phlorotannins, a class of polyphenolic compounds found in seaweeds, are polymeric forms of phloroglucinol and have been found to possess strong antioxidant properties and possess a greater ability to scavenge free radicals than monophenols and other polyphenols commonly found in terrestrial plants [10].

## 3. Methodology

The methodological approach consists of analyzing the chemical composition of the selected marine algae. Following the determination of chemical composition,

a series of valorization of primary metabolites, lipid and carbohydrate, into biofuel and bioethanol respectively, are undertaken. The remaining major component of the marine algae is valorized according to its importance in the industrial market. The secondary metabolite and the specific composition of the given marine algae are then valorized according to their added value importance in the pharmaceutical market. The main approach is to find biomass valorization through the cascade process in order to decrease the cost of biofuel production.

## 4. Results

### 4.1. Evaluation of Chemical Contents from the Madagascar Red Marine Alga *Portieria hornemannii*

Many species of red algae synthesize primary and secondary metabolites. Among these secondary metabolite natural products are those that contain bromine, chlorine, and occasionally iodine atoms [11]. *Portieria hornemannii* was collected in the south of Madagascar. It was found growing on shallow reef rocks and was taxonomically identified by its distinctive branching pattern and pungent odor when crushed. *Portieria hornemannii* was collected by hand using scuba from southern Madagascar (Bay of Fort Dauphin). The alga was stored at −20˚C in 70% EtOH until workup.

Chemical composition of primary metabolites:

All the chemical content was determined in standard method [12]. By using the oven method at 105˚C, the moisture content was determined until a steady weight was attained. The AOAC, 1995 [13] was used to determine the crude protein concentration after converting total nitrogen into crude protein using a conversion factor of 6.25. The carbohydrate content (%) was estimated by James, (1995) [14]. The seaweeds were incinerated for 16 hours at 550˚C in a muffle furnace to estimate the amount of ash content using a gravimetric method. (Bligh and Dryer, 1959) [15], a Soxhlet extractor was used to extract the lipid from seaweed powder using methanol (2:1, v/v). After drying the extract overnight in an oven at 80˚C, the crude lipid content was determined gravimetrically. An enzymatic-gravimetric method was used to determine the amount of total, soluble, and insoluble dietary fiber in each sample [12]. The chemical content of *Portieria hornemannii* is shown in **Table 1**.

The major difficulty to explore and valorize secondary metabolites from marine algae is the re-isolation and reproducibility of the results. In order to reproduce previous results, in this work we performed re-isolation of specific metabolites from *Portieria hornemannii* [16].

The alga (100 g dry wt) was extracted four times with $CH_2Cl_2$-MeOH (2:1) to give a crude organic extract (5.93 g). This crude extract was used to assess specific secondary metabolites of the *Portieria hornemannii.* A portion of the extract was fractionated on silica gel by Normal Phase Vacuum Liquid Chromatography to give nine fractions using a stepwise gradient of hexanes-EtOAc and EtOAc-MeOH.

**Table 1.** Chemical composition of *Portieria hornemannii*.

| Chemical composition | *Portieria hornemannii* (% from 1 g) |
|---|---|
| Protein | 32.8 |
| Carbohydrate | 22.0 |
| Lipid | 3.7 |
| Total dietary fiber | 2.1 |
| Soluble fiber | 1.0 |
| Insoluble fiber | 1.1 |
| Moisture | 13.0 |
| Ash | 20.1 |

Fraction A, eluting with 100% hexanes, was further chromatographed on preparative normal-phase HPLC (Phenomenex Maxsil 10 silica 10 ím, 500 10.0 mm, 100% hexanes) and yielded three fractions, A1 to A3. Further fractionation of A3 by analytical NP-HPLC yielded the known compound halomon (**1**) and analogue **6** as the major components. Fraction A1 was also subjected to subsequent analytical normal-phase HPLC (Phenomenex Luna silica 10 µm, 250 4.60 mm, 100% hexanes) to yield successively compounds **2** and **3**. Purification of sub fractions from A1 (A1a and A1d) by HPLC led to the isolation of the compounds **4** and **5**. The identity of all known halogenated monoterpene compounds was established by direct comparison of 1H and 13C NMR, HR-MS, and specific rotation with literature values. **Figure 1** displays all known halogenated monoterpene compounds from Madagascar *Portieria hornemannii.*

Red Pigment: It is known that the Phycobiliproteins (phycoerythrin, phycocyanin, allophycocyanin) components of phycobilisomes in Rhodophyceae (Species of Porphyra or Gracilaria gracilis) play a key role in photosynthesis. These natural pigments are used in cosmetics. These pigments are stable in the solution that has a pH ranging between 5 and 9. Phycobiliproteins from Portieria species exhibited antioxidant, anti-inflammatory properties and are used as colourants in cosmetics [17] [18]. These features make the pigments an important alternative ingredient in eye shadows and lipsticks.

### 4.2. Evaluation of Chemical Contents the Cultured Marine Diatom *Phaeodactylum tricornutum*

One of the most important photosynthetic eukaryotes in marine ecosystems is the diatoms, single-celled algae surrounded by a silica-derived wall [19]. Diatoms contain a wide variety of lipids, including membrane bound polar lipids, triglycerides, and free fatty acids. Compounds such as sterols, waxes, and acyl lipids have also been identified. Increased lipid concentrations within different species of diatoms have been observed by the modification of nutrient availability and other requisite growth conditions [20].

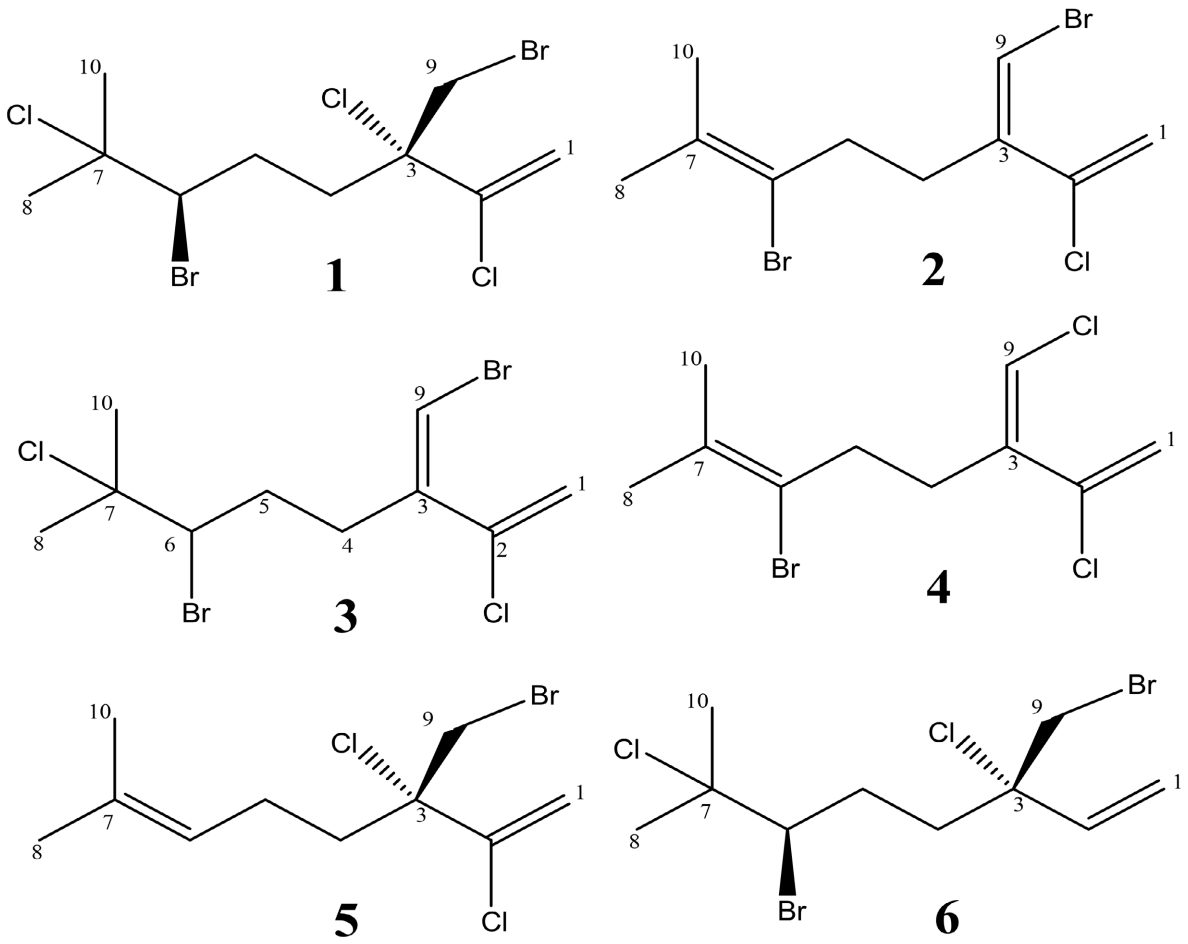


**Figure 1.** Halogenated monoterpenes re isolated from the Madagascar red marine alga *Portieria hornemannii*.

The marine diatom, *Phaeodactylum tricornutum*, was cultured in an F/2 medium at 18˚C under constant light (100 μmol·m$^{-2}$·s$^{-1}$). Cultures were grown in medium made from 0.2 μm filtered, autoclaved seawater supplemented with filter-sterilized vitamins and inorganic nutrients. Sterility was monitored by occasional inoculation into peptone-enriched media to check for bacterial growth. Diatom cells were harvested by centrifugation for 15 min at 4000g, and pellets were frozen instantly in liquid $N_2$ and stored at −80˚C before further workup [21].

Chemical composition of primary metabolites:

The same protocols as previously described were performed and the result is in Table 2.

For the assessment and reproducibility of specific secondary metabolite of the cultured marine diatom, *Phaeodactylum tricornutum*, the material (80 g) was extracted three times with MeOH to give a polar crude organic extract (840 mg). A portion of this extract (30 mg) was tested for apoptosis induction. The crude organic extract was found active and subjected to fractionation using a solid-phase extraction cartridge (normal-phase silica) to give four fractions, F1 to F4, using hexane, $CH_2Cl_2$, EtOAc, and MeOH as an increasingly hydrophilic solvent system series. The fraction eluting with EtOAc (F3) had apoptosis induction activity. This

fraction was further chromatographed on analytical RP HPLC (Phenomenex luna C18, 250 × 4.60 mm) using isocratic elution with 100% MeOH (flow rate 1 mL/min) to yield successively 10 mg of **2** (tR) 5.65 mn) and 20 mg of **1** (tR) 6.45 min). Chemical structures shown in Figure 2 of these two compounds (1 and 2) were ascertained by direct comparison of their 1 D and 2 D NMR as well as HR MS data to the published record data [21]. It is demonstrated that reproducibility is again verified from this species.

Table 2. Chemical composition of cultured marine diatom *Phaeodactylum tricornutum.*

| Chemical composition | *Phaeodactylum tricornutum* (% from 1 g) |
|---|---|
| Protein | 36.4 |
| Carbohydrate | 26.1 |
| Lipid | 18.0 |
| Total dietary fiber | 2.4 |
| Soluble fiber | 1.1 |
| Insoluble fiber | 1.3 |
| Moisture | 3.0 |
| Ash | 15.9 |

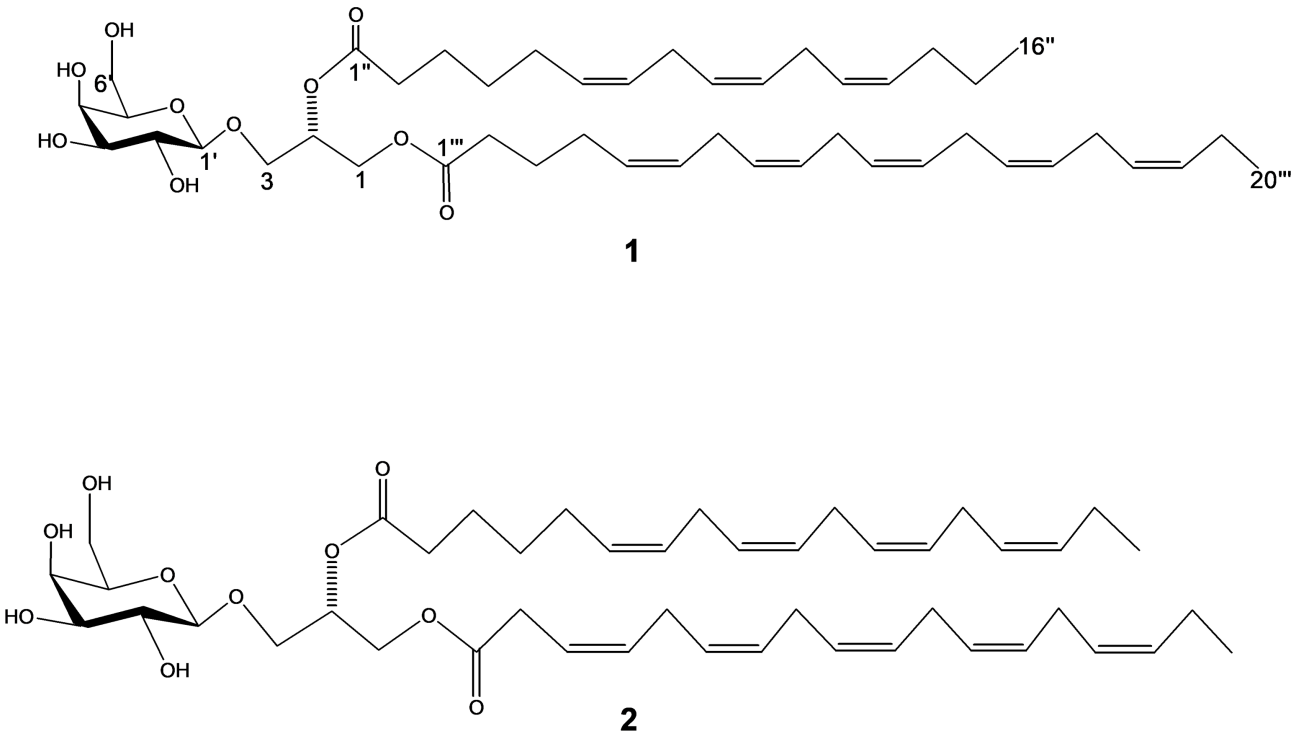


Figure 2. Galactolipids re isolated from a cultured marine diatom, *Phaeodactylum tricornutum.*

## 5. Valorization of Primary Metabolites

Marine macro algal stores carbon mainly in the form of sugars rather than

lignocelluloses, like terrestrial biomass, which is suitable as input raw material for biorefineries. Seaweed biomass has high growth rates, does not require fresh water or arable land, and therefore does not compete with conventional food production [22]. In order to make seaweed based biorefineries economically viable the valorization of biomass has to be maximized through cascade processes with the production of several high-value products such as pharmaceuticals/chemicals, nutraceuticals, cosmetics, food, fertilizers/biostimulants and low-carbon fuels [23]. The composition of macro algae, which varies depending on the species (green, red, or brown), the region in which it is grown, and the time of year, determines the variety of goods that can be made from it. Fuels must be made from seaweed leftovers since the market value of pharmaceuticals and chemicals is substantially larger than that of fuels [24].

## 5.1. Lipid into Biofuel

Diatoms are one major group of algae in oceans that account almost half of marine primary food production and have also been identified as a promising candidate for biofuel production for their high level accumulation of lipids [25]. They have gained increasing attention for their potential applications in pharmaceuticals, cosmetics, nutrient supplements, and biofuels [26]. Cultured marine diatom, *Phaeodactylum tricornutum*, is a promising oil feedstock and energy source as it accumulates a large amount of lipids consisting of Triacylglycerols about 34% of total lipids and diverse fatty acids mainly hexadecanoic acid (C16:0), palmitoleic acid (C16:1), and eicosapentaenoic [25]. Transesterification; this step is involved in the triglyceride conversion into long chain fatty acid alkyl esters (FAAEs) also known as biodiesel under the combined activity of catalyst and alcohol as shown in **Figure 3** [27].

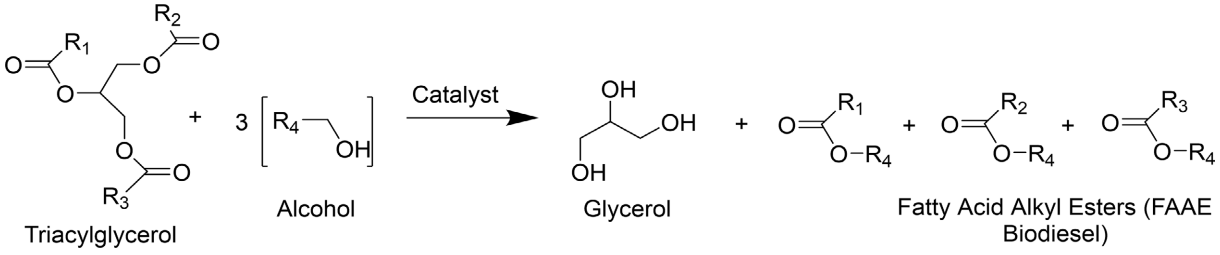


**Figure 3.** Transesterification of Triacylglycerol (TAG).

## 5.2. Carbohydrate into Bio Ethanol

Red algae contain carbohydrates that can be converted into fermentable sugars and at the end into ethanol. *Portieria hornemannii* is one of the red algae that has a high ratio of carrageenan which is estimated at 24.2% of all carbohydrate content [28]. The major driver of the carrageenan market is the rising demand for processed foods. Carrageenan is an essential ingredient in many foods and beverages consumed every day, including nut and soy milk, deli meats, protein shakes and powders, chocolate milk, yogurt, popsicles, prepared meals such as frozen burritos

and pizza, ice cream, and infant formula [29]. On the other hand, carrageenan is a well-known additive in the pharmaceutical, cosmetic, and home care industries, where it can be used as a thickener or film-forming agent [29]. The focus of this present work is to valorize carrageenan by converting it into bio ethanol. Carrageenan undergoes hydrolysis acid to cleave the sugar polymer. The products of the hydrolyses acid are 3,6-Anhydro-D-galactose and D-galactose. These sugars will be converted to ethanol through enzymatic fermentation. The production of D-AnG from κ-carrageenan by acid hydrolysis is optimal at temperature of 80˚C with reaction time of 120 min by using nitric acid ($HNO_3$) as shown in **Figure 4**. The reaction is selective and no 5-hydroxymethylfurfural (HMF) is formed. $HNO_3$ can easily be recycled using known processes [30] [31].

Wild-type *Saccharomyces cerevisiae* has been reported with good performance of galactose fermentation. A wild-type *S. cerevisiae* strain with the ability to ferment galactose to ethanol was isolated from grape with ethanol tolerance of 15%. Immobilization of yeast cells has been performed to increase the ethanol production. The immobilization of the isolated wild-type *S. cerevisiae* is performed in PVA-alginate beads. Batch fermentation of galactose by immobilized wild-type *S. cerevisiae* obtained ethanol concentration of 9.4 g/L and a yield efficiency of 92% [32].

Chrysolaminarin is a linear polymer of glucose monomers linked through $\beta$(1,3) glycosidic bonds with some $\beta$(1,6) linkages. It is the major component of carbohydrate found in diatoms *Phaeodactylum tricornutum*. Hydrolysis acid of the glucose polymer will give glucose monomer which in turn fermented by enzyme into bio ethanol [33].

A large quantity of glycerol is produced through the conversion of triglyceride into long chain fatty acid alkyl esters (FAAEs biodiesel). It is known that the conversion of glycerol into ethanol by enzymatic fermentation with relatively high yield (less than 60%) [34]. A new route using synergistic catalysis by Pd/CoOx and Cu/SBA-15 (Santa Barbara Amorphous-15 (SBA-15)) was recently established as shown in **Figure 5** [35].

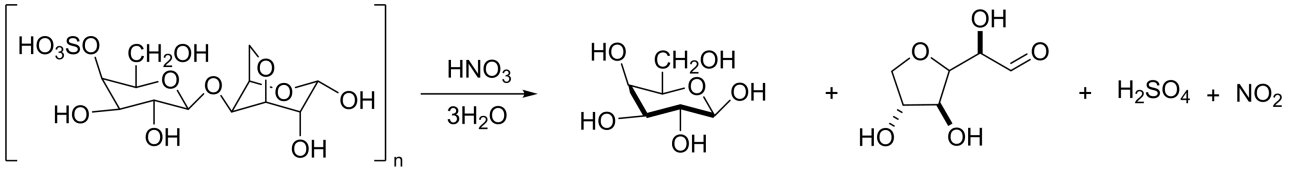


**Figure 4.** Formation of D-galactose and 3,6-Anhydro-D-galactose by acid-catalyzed hydrolysis of Kappa carrageenan.

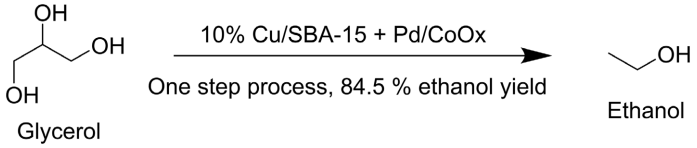


**Figure 5.** From glycerol to ethanol using mixed catalysts 10% Cu/SBA-15 and Pd/CoOx.

The direct hydrogenolysis of glycerol to ethanol in liquid phase was feasible and the use of Pd/CoOx gave high ethanol selectivity and good reusability. The yield of ethanol reaches 84.5%, which is the highest value ever reported in glycerol conversion into ethanol [27].

### 5.3. Proteins and Pigments

Proteins are the most abundant biological macromolecules found in macro and microalgae, existing either in single (amino acid) or complex (heteroproteins like glycoproteins, and phycobiliproteins) forms, accounting for 20% and 67% respectively [36]. The seaweed/macroalgal proteins have all of the essential amino acids that are comparable to those recommended by the FAO/WHO. These proteins have antiaging, anti-inflammatory, antitumor, and antioxidant activities, which makes them useful in the diagnosis as well as the treatment of neurodegenerative disorders, malignancies, chronic gastritis, DNA replication, biochemical reactions, molecule transfer, and other conditions [37].

Phycobiliproteins, another important class of water soluble fluorescent proteins, are of three types: 1) Blue pigment, 2) Red pigment, and 3) Light blue pigment, and the most abundant pigment in several red macroalgal species is red pigment [38].

Phycobiliproteins have antiangiogenic, antioxidant, anti-inflammatory, anticarcinogenic, neuroprotective, and antiobesity properties, according to recent reports [39] [40].

Due to the absorbance, the phycobiliproteins are classified into four categories depending on their light absorption capabilities and bilin type. Allophycocyanin (APCs) ($\lambda_{max}$ = 650 - 655 nm), Phycoerythrin (PEs) ($\lambda_{max}$ = 540 - 570 nm), Phycocyanin (PCs) ($\lambda_{max}$ = 610 - 620 nm), Phycoerythrocyanin (PECs) ($\lambda_{max}$ = 560 - 600 nm) [38].

The market of phycobiliproteins was 69.19 M USD in 2022 and its anticipated to reach 129.64 M USD in 2031 with the constant annual growth rate (CAGR) of 23.28%. The red algae *Portieria hornemannii* is one of the rich source of phycobiliproteins with a concentration of 12.87 mg/g of fresh weight of the algae [41]. The structures of Phycoerythrin, Phycocyanin and Allophycocyanin monomer are shown in **Figure 6**.

## 6. Valorization of High Added Value Secondary Metabolites

The global market for Marine Biotechnology was US$6.7 Billion in the year 2022, and is projected to reach US$13.1 Billion by 2030 with a constant annual growth rate (CAGR) of 8.7% [42]. The growth in the Bioactive Substances segment is estimated at 8.5% CAGR for the next 8-year. Marine drugs, extracted from a variety of marine organisms such as bacteria, viruses, algae, fungi, and sponges, exhibit significant potential as therapeutic agents for addressing conditions like cancer, drug-resistant bacteria, viral diseases, and immune suppressive disorders [36]. **Figure 7** and **Figure 8** display all possible added values from red algae, *Portieria hornemannii* and diatoms, *Phaeodactylum tricornutum*, respectively.

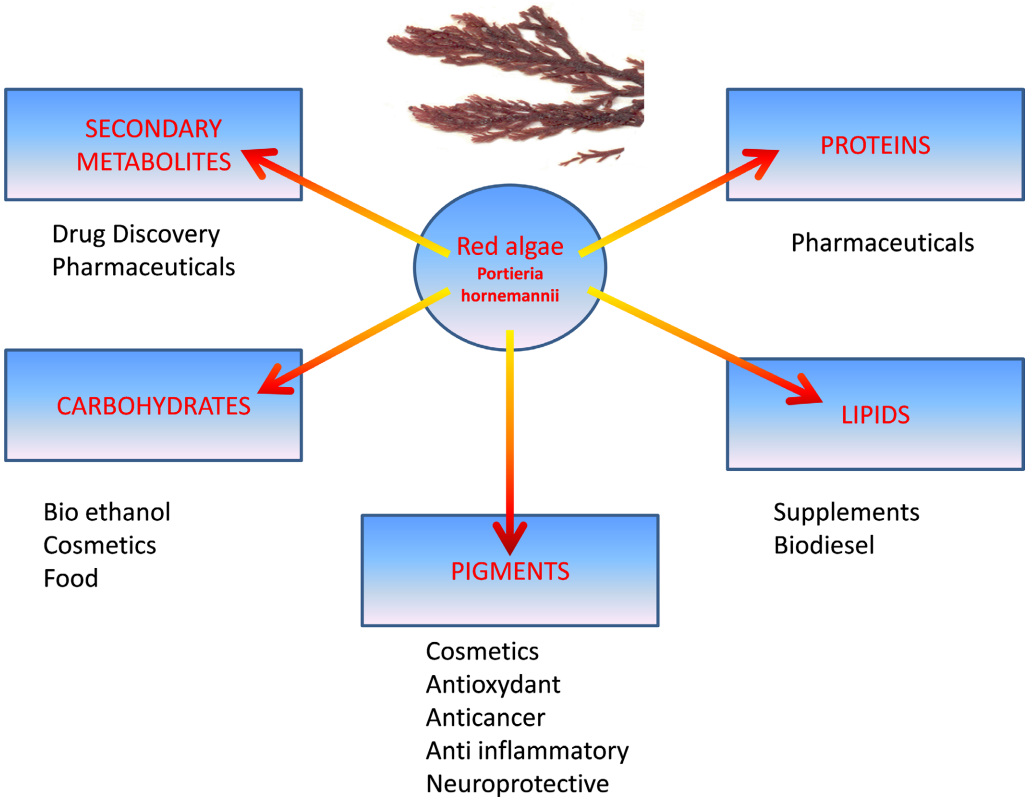


**Figure 6.** Structures of Phycoerythrin, Phycocyanin and Allophycocyanin monomer.

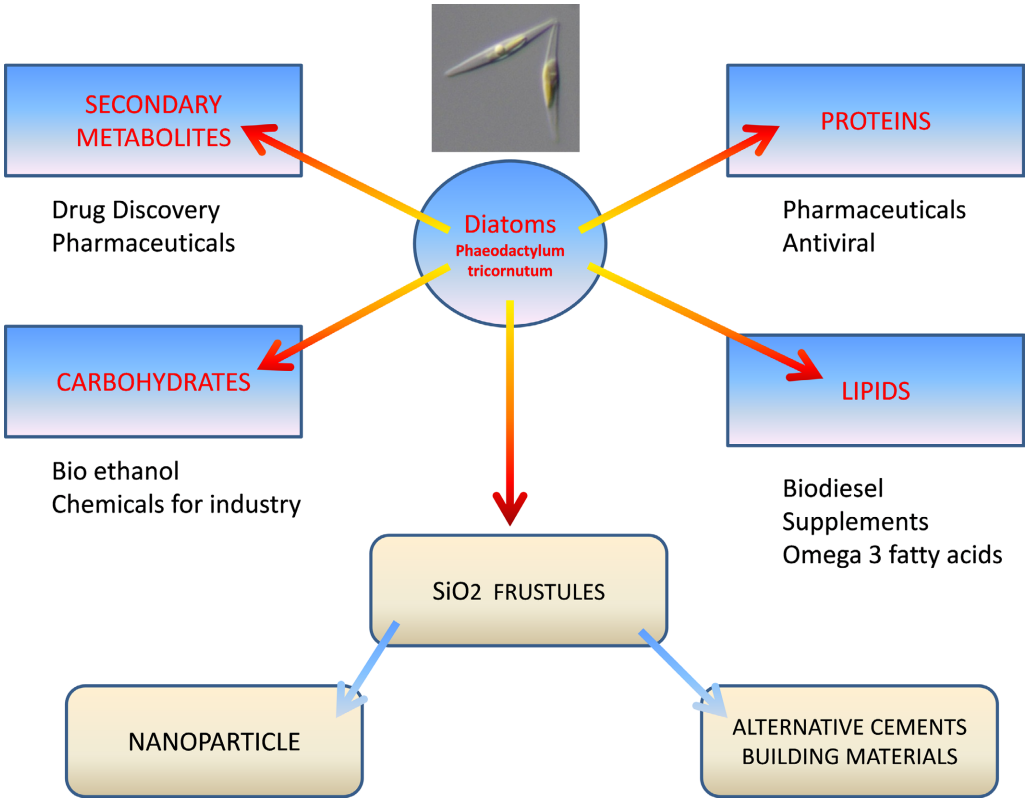


**Figure 7.** Natural products with high added value from red algae, *Portieria hornemannii.*

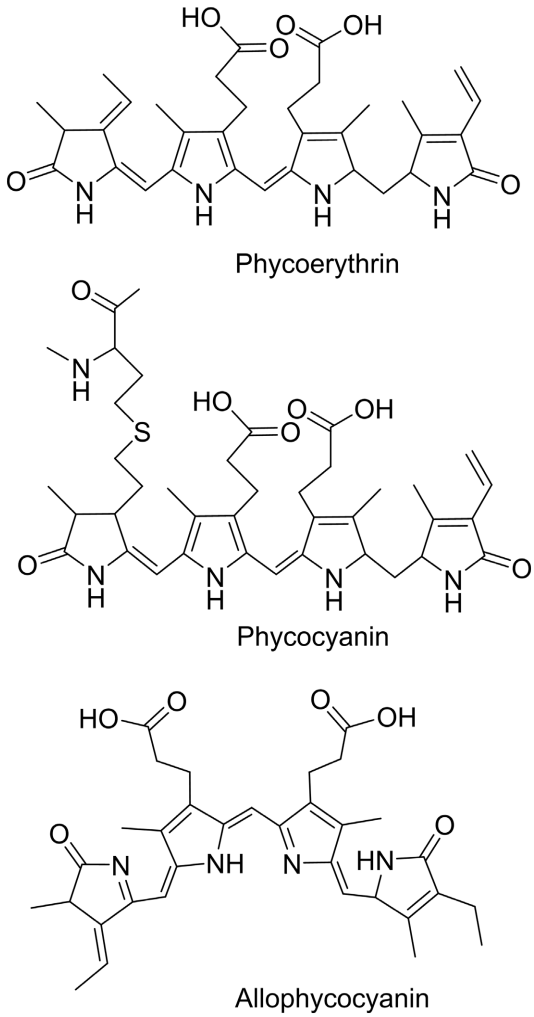


**Figure 8.** Natural products and high added value products from diatoms, *Phaeodactylum tricornutum.*

The pharmaceutical industry will have a promising future in the development of new drugs by exploring chemical structures derived from marine sources [43]. The vast majority of the world's biodiversity is in the ocean, which provides untapped reservoir of potential pharmaceutical resources [44].

*Phaeodactylum tricornutum* microalgae is a rich source of omega-3fatty acid oil and has strong potential for value generation from human health products [45]. The estimated cost from *Phaeodactylum tricornutum* of omega-3-rich oil is 13.71 USD and 4.11 USD for high-value protein. Providing omega-3 supplements of algal origin is believed to be an eco-friendly way to get a daily dose of these supplements. An innovative process that is in line with consumer values. Algal oils are thought to be the future of the omega-3 market. The process will protect the oceans' precious marine ecosystems and specifically endangered fishes. Omega-3 fatty acids from algae are generally produced through controlled indoor aquaculture industrial systems. Therefore, if wild fish reserves are limited, micro algae like diatoms offer a consistent, plausible and sustainable source of omega-3

free fatty acids that don't rely on diminishing marine resources [46].

## 7. Valorization of Frustules from Diatoms

Unicellular diatoms are found to live in freshwater, saline water or seawater as well as in wet soils [47]. Besides their biochemical composition such as carbohydrates, lipids, proteins and vitamins, they also biosynthesize secondary metabolites which have been used for biotechnological purposes with a wide variety of applications such as pharmaceutical, nutraceutical, chemical and drug discovery industries. Additionally, diatoms possess a highly silicified cell wall, called frustules, composed by a siliceous skeleton $SiO_2$ that comprises a couple of valves connected by silica girdles along the borders [48]. Frustules of diatoms are different morphologically from species to species. The shape, size, and silica content are also different therefore these characteristics are used for the identification and classification of these organisms. When diatom cells decay, their silicified carapace forms sediments on the sea floor of the so-called diatomaceous earth or diatomite [49]. Diatomite has important applications in the industries such as sorbent, anti-caking agent, insulation material, filter material and abrasive [49]. Recently, diatom-based biosilica has been used in nanotechnology industries and considered for a wide range of utilization, such as nanoparticles [49], electronic devices, drug delivery systems, biomolecule diagnostic devices, chemical sensors and energy applications [50].

In this present work, the valorization of the silica frustules into sodium silicate and $SiO_2$ for building material was proposed. After obtaining diatom cells of *Phaeodactylum tricornutum* from culture, an extraction of organic material was performed using organic solvent MeOH like previously described. The cells were washed with deionized water and cleaned with diluted $HNO_3$ for complete removal of organic materials. Cleaned cells were baked at 600 C˚ to give an excellent purity of >90% of $SiO_2$. Almost 50% of the dry weight of the original diatom cells is in the form of $SiO_2$ meaning that a large amount of these materials needs to be valorized after extraction of organic materials (proteins, carbohydrates, lipids and secondary metabolites...). The purified $SiO_2$ is used as a starting material for sodium silicate and an important component for the stabilization of lateritic soil and brick. $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$ reaction of formation of sodium silicate with purified $SiO_2$ Frustules.

## 8. Proposed Formulation

### 8.1. Brick Stabilized with Sodium Silicate and $SiO_2$ Frustules

A binder composition for building material comprising: lateritic soil, sand, lime, $SiO_2$ Frustules, sodium silicate from purified Frustules and water. The lateritic soil used in this formulation is prepared by extraction of laterite present in the soil, drying at ambient temperature for example 21 degrees C, sifting advantageously with a sieve with an opening of 1 mm, and storage for example in a propylene bag. The $SiO_2$ Frustules are prepared as previously described to obtain > 90% $SiO_2$. The binder composition for construction material can be prepared by first dry mixing

the laterite, sand, lime, $SiO_2$ Frustules. Then water is added to the mixture thus obtained, then the alkaline silicate solution with a $SiO_2/Na_2O$ molar ratio of equal to 2, and the whole is kneaded until a homogeneous mixture is obtained. The mass of added water, also called mixing water, is between approximately 5% and approximately 15% relative to the total dry mass. The binder composition can be used to prepare construction materials, for example, bricks. The binder composition is molded or compacted depending on the plasticity index (PI) of the mixture. The plasticity index depends on the quantity of clay present in the laterite, and is determined by calculating the difference between the liquid limit and the plasticity limit of the sample studied. Once the binder composition has been molded, for example in the form of bricks, it is allowed to be set by drying in ambient air, for example for approximately 24 hours. We unmold the bricks and leave them in the open air for 14 days as shown in **Figure 9**.

A binder composition for construction material comprising:

- approximately 30% to 85% of laterite;
- approximately 8% to 15% sand;
- approximately 0% to 8% lime;
- approximately 0% to 12% $SiO_2$ Frustules;
- approximately 3% to 35% of an alkaline silicate solution with a $SiO_2/Na_2O$ molar ratio in the range from approximately 1 to 3.

And water with solubility product quotient 100%.

**Figure 9.** Compaction test and maturation in ambient air.

## 8.2. Cosmetic Formulation

1) Choice of galenic form

Emulsions are the most used in cosmetics, so we have chosen galenic for emulsion dosage form. In an emulsion, various constituents are added to the three basic elements (oil, water and emulsifier): active ingredients, thickener, flavorings, colorings, preservatives, etc. in each case, the three basic constituents must be chosen carefully in order to have an emulsion with well-defined characteristics. Aqueous creams tend to be preferred by patients because they are easily applied, refresh and penetrate the skin which is characterized by excessive production of sebum.

2) Choice of concentration of active ingredients

Ascorbic acid; Vitamin C is used as an antioxidant or anti-free radical in cosmetic formulations and we have retained the concentration of 1% (w/w).

The moisturizer; moisturizers are almost all part of preparations for topical application, on the one hand to prevent the evaporation of water from the aqueous medium, on the other hand to slow down the evaporation of water from the skin. Glycerol is the most common moisturizer. It is a hygroscopic substance capable of fixing approximately 10% water. It prevents the skin from drying out. It is used in our case at a concentration of 3%.

3) Choice of emulsion type:

Our choice is oriented toward an aqueous emulsion of the W/O type for the following reasons:

- they have good tolerance;

- they have a strong penetrating power (unlike O/W emulsions which are weak), thanks to auxiliary substances (wetting surface agents and emulsifiers);

- they are washable with water which is not the case for O/W emulsions.

4) Choice of excipients

a) Choice of aqueous phase

We chose distilled water as the dispersion liquid.

b) Choice of oil phase

We used wax as the oil phase.

Bees wax, lanolin and its derivatives are esters of natural fatty acids, sterols or triterpene alcohols, with a relatively high content of alcohols and free fatty acids. They are more hydrophilic and have good skin penetration power, probably due to the high number of free hydroxyl groups in their constituents.

c) Choice of surfactants

We used in our formulation the Tween® surfactant which are esters of ethoxylated fatty acids and anhydrosorbitol (X = OH or O-($CH_2CH_2$)n-H or $RCO_2$). These are nonionic surfactants derived from polyoxyethylene Span® surfactants. Tween® surfactants are hydrophilic, generally soluble or dispersible in water, and soluble to varying degrees in body fluids. They are used for O/W emulsifications, dispersions or solubilizations of oils, and wetting.

Oleic acid is also used as a surfactant, it is an anionic and oil-soluble surfactant. Its crude chemical formula is $C_{18}H_{34}O_2$ and expanded $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, with a double bond of cis configuration. Its IUPAC name is cis-9-octadecenoic acid. The -COOH carboxylic acid function has an acidic hydrogen which can react with a base such as sodium hydroxide. A carboxylate ion -COO- is then formed, the presence of this group increases the solubility in water which leads sodium oleate to be a surfactant.

The surfactants used at 5% are:

- Tween®80: sorbitan monooleate, liquid and soluble in water, hydrophilic-lipophilic balance (HLB) = 14.9.

- Oleic acid: oil-soluble liquid, HLB = 1.

d) Choice of curator

Benzoic acid at a usual concentration of 0.1% was chosen as a preservative for the following reasons:

- Widely used and most available;
- Water-soluble to protect the aqueous phase;
- It is an acid preservative, so it is active at a pH below 5;
- Presents skin tolerance.

e) Choice of thickener and gelling agent

We chose carrageenan, which is extracted from red algae, as a thickener.

Depending on the desired effect, it can be used in doses ranging from 0.1% to 3%, it is soluble in water and aqueous solutions, insoluble in oil.

5) Conditioning; Since ascorbic acid is sensitive to light, an opaque bottle was chosen as primary packaging as shown in Figure 10.

The general formula is as follows:

Ascorbic acid 1 g

Wax 20 g

Tween 80 Oleic acid 5 g

Benzoic acid 0.1 g

Glycerol 98% 3 g

Carrageenan 1 g

Distilled water 75 g

Fragrance base 1 drop

Figure 10. Hot mixing and final products.

## 9. Conclusion

Two different marine algae chemical contents were analyzed and revealed that the major constituents of them are similar with different proportions; proteins, carbohydrates and lipids. The re-isolation of interesting secondary metabolites from these marine algae was successful, for example, the re isolation of Halomon from the red algae *Portieria hornemannii* and galactolipids from marine diatoms *Phaeodactylum tricornutum.* In order to valorize all high added value products in these marine algae, combination of reactions and processes are displayed. For example, the lipid content from *Phaeodactylum tricornutum* is relatively high which requires transesterification of TAG to give biodiesel and glycerol. A large quantity of glycerol has to be converted into bio ethanol with a known one-step catalytic reaction. Another example is the valorization of carbohydrates. Carrageenan is the major carbohydrate content of the red algae *Portieria hornemannii*, whereas Chrysolaminarin for *Phaeodactylum tricornutum.* Hydrolyses of Carrageenan

releases galactose but glucose for Chrysolaminarin. Two different fermentation processes are mentioned for the conversion of galactose and glucose into bio ethanol. Each marine alga has unique high-added value products. $SiO_2$ Frustules are the unique component of diatoms. This natural nanoparticle from *Phaeodactylum tricornutum* can be used as a binder composition for building material or directly as brick for building construction after proper purification. The best way to valorize all added value products from marine algae is the process known as cascade. The valorization has also to take into account the market size of each added value product, in that case, biofuel will probably be a byproduct and its production cost will be decreased dramatically. The feasibility of the process was illustrated in this work by providing formulation of products, for example, the use of carrageenan in cosmetic skin care or a binder composition using $SiO_2$ Frustules. The global biofuels world market size was valued at USD 123.97 billion in 2023 and is projected to soar around USD 257.61 billion by 2034. It is growing at a constant annual growth rate (CAGR) of 6.9% from 2024 to 2034, Figure 11 displays the projected world market size of biofuel by 2034. The North American biofuels market is growing at a CAGR of 7.10% during the forecast year.

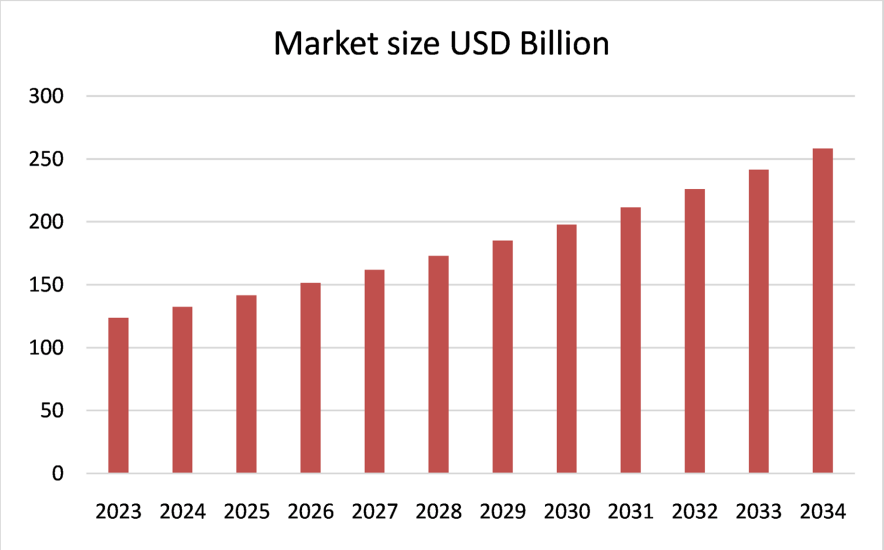


Figure 11. Projected world market size of biofuel by 2034.

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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