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Macroalgae Biorefinery from *Kappaphycus alvarezii:* Conversion Modeling and Performance Prediction for India and Philippines as Examples

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Abstract Marine macroalgae are potential sustainable feedstock for biorefinery. However, this use of macroalgae is limited today mostly because macroalgae farming takes place in rural areas in medium- and low-income countries, where technologies to convert this biomass to chemicals and biofuels are not available. The goal of this work is to develop models to enable optimization of material and exergy flows in macroalgal biorefineries. We developed models for the currently widely cultivated red macroalgae *Kappaphycus alvarezii* being biorefined for the production of bioethanol, carrageenan, fertilizer, and biogas. Using flux balance analysis, we developed a computational model that allows the prediction of various fermentation scenarios and the identification of the most efficient conversion of *K. alvarezii* to bioethanol. Furthermore, we propose the potential implementation of these models in rural farms that currently cultivate *Kappaphycus* in Philippines and in India.

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Introduction

Our civilization today is based on fossil fuel consumption. Fossil resources and their derivatives are used in all productive sectors of the economy. In addition to being a non-renewable resource, fossil fuel extraction, processing, and end product uses are involved in numerous negative environmental impacts including climate change, water quality degradation, and pollution of air and land [1]. Moreover, the unequal distribution of fossil fuel is known to be a source of geopolitical tensions [1]. Such impacts are driving and will continue to drive changes to economies, notably by moving the global economy out of fossil-based energy, long before the full depletion of fossil resources [2–5]. Societies need to develop new sources of energy and materials, which will support long-term development of a human civilization while preserving ecosystems and their biodiversity [1, 6]. The bioeconomy provides a possible solution for the demand on the resources by substitution of the non-renewable resources with resources derived from renewable biomass [7–9].

A fundamental unit that will enable the bioeconomy implementations is the biorefinery [10]; this is a collective term for the complex system that includes biomass production, transportation, conversion into products, and distribution of the latter [11–14]. Current strategies for food production and renewable energy generation rely mostly on the classic agriculture. However, a key issue for biomass for energy production is land availability [15, 16]. At the same time, an expanding body of evidence has demonstrated that marine macroalgae (seaweeds), cultivated offshore, can provide a

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sustainable alternative source of biomass for the sustainable generation of food, fuel, and chemicals [17–24]. Macroalgal biorefineries can contribute to regeneration in a circular economy and thus play a role in environmental restoration [23] and in mitigating climate change [25].

Design of a sustainable macroalgal biorefinery process, which will generate sustainable food, fuels, and chemicals, is a complex task and is largely influenced by local raw material availability, advances in multiple technologies, and socio-economic conditions [10, 26]. The key biorefinery design questions relate to the location of the systems and to how to choose the feedstock and processing and conversion technologies [16, 27]. Economically efficient and socially and environmentally sustainable conversion of biomass into valuable products is a major contemporary challenge for science, governments, and businesses worldwide [5, 12, 28]. A key challenge is to determine the products and the process that will maximize the value of the biomass. Biorefinery models, which include materials, energy, and information fluxes, are essential for the optimization and implementation of this approach in economy [29–31]. Even though modeling for biorefineries is an active field of research [11, 23, 31–33], very few models have been applied to marine macroalgae biomass [34]. Moreover, models developed for other types of biomass are rarely applicable to marine macroalgae biomass setup due to carbohydrate differences [35], cell wall composition, and absence or low contents of lignin. These limitations emphasize the importance of the development of dedicated models for macroalgae biorefineries.

The goal of this work is to develop models to enable optimization of material and exergy flows in macroalgae biorefineries. In this study, we specifically focus on the potential of the red commercial species *Kappaphycus alvarezii*. This species is of particular interest as it is currently one of the most widely cultivated macroalgae species [36]. *K. alvarezii* shows relatively higher growth rate compared to other *Kappaphycus* macroalgae with biomass yield ranging from 12 to 45 dry tons ha^{-1} year^{-1} [37, 38]. Carrageenan derived from this macroalgae makes *K. alvarezii* highly valuable so its cultivation provides jobs and commercial opportunities to numerous poor communities in coastal areas of developing countries [39]. After carrageenan extraction, approximately 60 to 70% resultant solid fraction is considered today as waste [40]. However, this waste contains high concentrations of carbohydrates, which can be hydrolyzed to monosaccharides and then converted into biofuels [41–43]. In addition, the production of liquid biofertilizer (sap) from fresh *K. alvarezii* prior to drying and processing for carrageenan production has been reported [44]. This biofertilizer has proven to have many benefits on local crop yield and resistance and is easy to produce and use allowing the consideration of such process for rural applications.

However, to the best our knowledge, there has been no analysis on the integration of the multiple products from *K. alvarezii* so far. In this work, we developed and optimized a model of the integrated *K. alvarezii*-based biorefinery, which produces carrageenan, ethanol, fertilizer, and biogas for the local coastal communities in developing countries. To demonstrate the potential of *Kappaphycus* biomass biorefinery, we consider the production scenario in existing small farms in India and the Philippines, countries with dynamic seaweed markets that support national bioethanol production with relevant policies (Philippines' Biofuel Act in 2006 and India's National Policy on Biofuels from 2009).

Methods

Flux Balance Analysis Model of Seaweed Biomass Fermentation for Biorefinery Exergy Optimization

Optimization of energy and mass flow efficiency is essential in sustainable management of any process [45, 46]. Early works on optimizing systems for producing energy and chemicals focused on optimizing energy flows using the first law of thermodynamics. This direction led to the development of one of the more widely used methods in resources accounting—life cycle assessment (LCA). However, LCA and its variations do not take into account all the energy carriers and the inevitable irreversibility of processes [47]. These irreversibility effects are addressed in the context of the second law of thermodynamics [48]. Studies addressing the irreversibility of the process that occurs in anthropic energy conversion systems led to the concept of "energy available to do a work," [49] coined "exergy" [50]. The goal of the optimization is to maximize the exergy produced by the system per invested exergy, as was shown for energy, chemical, and metallurgical processes [51]. In the biorefinery field, the goal of a process designer is to reduce the exergy losses during biomass processing, increasing the efficiency η_{mbr} of the process (Eq. 1) [13, 52, 53].

$$\eta_{mbr} = \frac{e_f + e_e + e_c}{e_{s\_e} + e_{m\_e} + e_m + e_k + e_l + e_{eco}} \tag{1}$$

where the inputs to the process are represented by an exergy stream of solar energy supply (e_{s_e}), mechanical energy supply, (e_{m_e}), materials (e_m), capital inflow (e_k), and human labor (e_l), and ecosystem services represented by eco-exergy (e_{eco}). The outputs are the delivered exergy contained in food products such as carrageenan (e_f), useful energy such as biofuels (e_e), and chemicals, such as fertilizers (e_c). The irreversibly destroyed exergy in this process includes the streams of exergy rejection to the environment (e_{en}), material waste

(e_w), and eco-exergy information loss (or gain) ($e_{eco\text{-}c}$). This section describes a computational approach to reduce the exergy losses by optimizing the bioconversion process, in which a macroalgae biomass is converted into bioethanol in addition to the existing production of phycocolloids, extracted from macroalgae biomass.

Macroalgae-derived biomass mainly consists of high amounts of various polysaccharides, like cellulose and carrageenan in *K. alvarezii* [54]. Other prevailing molecules are carbohydrates (up to 27%), amino acids (16%), and fatty acids (1%) [55]. Indeed, such feedstock is very heterogeneous and finding an optimal setup for the biomass processing unit is not trivial. To simplify this task, it is possible to use various simulation approaches in silico prior to testing the process in situ. One of these computational approaches is a linear programming approach called flux balance analysis (FBA).

FBA analyzes internal reaction fluxes based solely on simple physical-chemical constraints without requiring exact enzyme kinetic data. Specifically, this methodology enables the prediction of biomass production rates based only on reaction stoichiometry and directionality. FBA-based approaches have a broad range of applications including phenotype analysis, bioengineering, and metabolic model reconstruction [56–58].

There are two constraint types typically used in various FBA-based methods: (i) mass-balance constraints imposed by network stoichiometry (Eq. 2) and (ii) maximal/minimal feasible reaction flux constraints (Eq. 3). They describe the FBA basic setup, where *S* is a stoichiometric matrix, in which $S_{m,r}$ corresponds to the stoichiometric coefficient of metabolite *m* in the reaction *r*, and $\overrightarrow{v}$ is a vector of reaction fluxes.

$$S \cdot \overrightarrow{v} = 0 \tag{2}$$

$$v_r^{LB} \leq v_r \leq v_r^{UB}, \forall r \in reactions \tag{3}$$

Although the bounds v^{LB} and v^{UB} are usually unknown and therefore set to [−*Inf*; *Inf*] for most of bidirectional and to [0; *Inf*] for unidirectional reactions, we can still reduce the solution space to physically possible values by limiting the growth media uptake rate [62]. In our specific case, the knowledge of actual media uptake rate is not critical, because we are not interested in reaction rates, but rather in total conversion yield (in %) of dry algal biomass into ethanol. Therefore, we assumed the uptake rate of 1 g DW h^{-1} of *K. alvarezii* and calculated the *Kappaphycus*-to-*ethanol* conversion yield accordingly.

The FBA framework assumes that the modeled organism metabolic network is regulated to maximize some cellular function under the predefined set of constrains (Eqs. 2 and 3). The most common cellular target for unicellular organisms is maximization of organism growth rate, which leads to the framework presented by Eq. 4, in which v_{biomass} is an artificial growth reaction converting all the organism biomass constituents into units of biomass and Eqs. 2 and 3 are the constrains. A metabolite flux $\overrightarrow{v}$ that attains a max as below is one that is a feasible one for the organism modeled.

$$\max_{\overrightarrow{v}} v_{biomass}\ s.t.: \begin{bmatrix} S \cdot \overrightarrow{v} = 0 \\ v_r^{LB} \leq v_r \leq v_r^{UB} \end{bmatrix} \tag{4}$$

Indeed, there may be multiple such solutions, namely, vectors of reaction fluxes both satisfying all the predefined constrains as well as maximizing organism growth rate. This means that each non-biomass reaction, and particularly the ethanol-producing one, may have a range of possible values. This range is estimated using flux variability analysis (FVA) formulation [59], as presented in Eq. 5, where v_{ethanol} is the flux in the ethanol-producing reaction.

$$\max/\min_{\overrightarrow{v}} v_{ethanol}\ s.t.: \begin{bmatrix} v_{biomass}\ is\ a\ solution\ to\ Eq.4 \\ S \cdot \overrightarrow{v} = 0 \\ v_r^{LB} \leq v_r \leq v_r^{UB} \end{bmatrix} \tag{5}$$

To summarize, Eq. 5 estimates maximal and minimal possible metabolic fluxes passing through the ethanol-producing reaction under the assumption that the organism maximizes its growth rate and under a given organism reaction stoichiometry model and lower/upper limits on fluxes in each reaction. The feed medium composition is considered by appropriately setting the upper limits of the input flux variables.

In all simulations, we were interested in two main output numbers of the FVA process: ethanol production yield and carbon utilization yield. The simulations were performed under anaerobic conditions assuming 1 g of seaweed uptake for 1 g dry weight of organism in 1 h. Carbon utilization yield was calculated as the ratio of carbons in the ethanol output to carbons in the media input.

Two-Step Fermentation of Complex *K. alvarezii* Biomass

The natural first candidate for production of bioethanol is a standard fermentation yeast *Saccharomyces cerevisiae* [42]. However, this strain of yeast poorly utilizes a significant part of the seaweed carbohydrates such as xylose, rhamnose, and galactose, leading to low carbon utilization yield. One approach to this issue and to improving bioethanol yields is to genetically modify *S. cerevisiae* to improve sugar uptake mechanisms. Although studies in this direction were conducted over the past years, it remains an open challenge [60]. Here we describe an alternative, namely, a two-step fermentation approach [13, 52], to address this same issue (Fig. 1). In the first step, decomposed seaweed biomass is fed to *S. cerevisiae* for conversion into ethanol. In the second step, fermentation leftovers and the *S. cerevisiae* biomass resulting from the first step are fermented by *Escherichia coli* to produce additional ethanol.

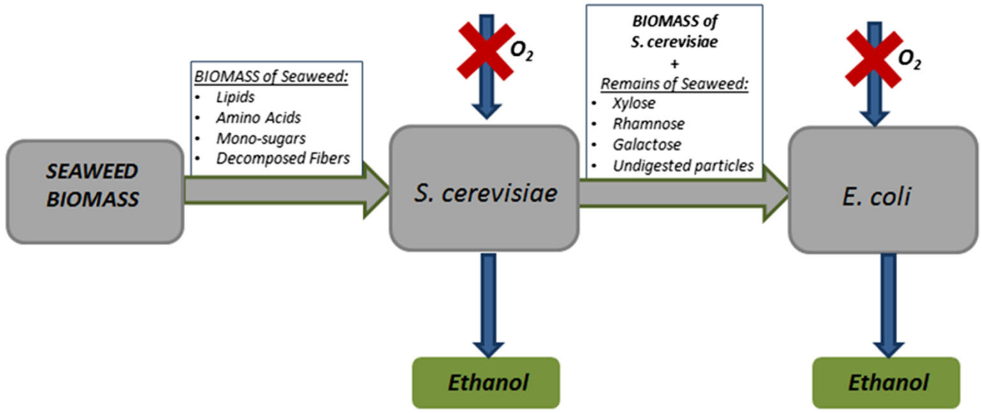

Fig. 1 Schematic representation of the two-step bioconversion of seaweed feedstock into bioethanol

To simulate the two-step process, we performed FVA analysis twice. First, we take seaweed biomass as media and inspect the upper and lower fluxes for ethanol-producing reaction in the metabolic model of the first organism. Second, the undigested remains of the original media and the biomass of the first organism were taken as growth media for the second organism. We then investigate the total flux in ethanol-producing reactions in the system (Fig. 1).

All the simulations were performed using the BioLEGO web service [52]. We used the Yeast5 model [61] for *S. cerevisiae* simulations and the iJO1366 model [62] for *E. coli* simulations.

Estimation of Annual Bioethanol Production Potential of *K. alvarezii* Biorefineries

To estimate the potential annual bioethanol production from *K. alvarezii* in a two-step process, we used Eq. 6:

$$\mathrm{BPP} = yield \cdot production \tag{6}$$

where BPP ($L\ ha^{-1} year^{-1}$) is the bioethanol production potential, yield (kg DW $ha^{-1} year^{-1}$) is an average seaweed biomass yield, and production (L ethanol kg DW^{-1}) is the conversion efficiency of dry seaweed into bioethanol through fermentation predicted by BioLEGO.

Results and Discussion

Computational Analysis of *K. alvarezii* Fermentation to Reduce Wasted Exergy

We evaluated ethanol production by simulating the following four configurations: two possible orderings of *S. cerevisiae* and *E. coli* and two single organism fermentations. To simplify the computational simulations, we assumed that all macromolecules have been completely depolymerized before the bioconversion process. The summary of chemical composition of *K. alvarezii* used in our modeling is shown in Table S1. The composition of the decomposed biomass used as fermentation media is detailed in Table S2.

As demonstrated in Table 1, we predict maximal bioethanol production rate in a two-step fermentation setup with *S. cerevisiae* as first organism in the process. In this configuration, we expect, based on simulation, a ~ 70% product increase (decrease in the wasted exergy content $e_{en} + e_w$ led to η_{mbr} increase by 4–4.5%) compared to *S. cerevisiae* alone. Notice that switching the order of organisms is not beneficial, since *E. coli* consumes all available *K. alvarezii* components leading to predicted zero-growth rate of the *S. cerevisiae.* The predicted results for *K. alvarezii* fermentation using two-step fermentation (94.1–97.6 g ethanol/kg biomass) correspond well to the experimentally observed results (81.9 g of ethanol/kg dry biomass in a study using a special *S. cerevisiae* strain which ferments galactose [43]). In Table 2, we show the potential production of ethanol from the residual biomass after 12% DW was extracted as carrageenan. We show that in this case of co-production, up to 81.7 g of ethanol/kg biomass can be produced in addition to 120 g/kg of carrageenan.

In addition, we performed sensitivity analysis of the ethanol production as a function of biomass chemical composition. Biochemical analysis of biomass shows that total fiber and protein contents vary as a function of season and nutrient availability [63–68]. The increase in the fiber content is compensated by the decrease of the protein content [63–68]. Therefore, for sensitivity analysis we simulated variation of the fiber/protein ratio, keeping their total content constant (45%). This sensitivity analysis could provide some insights into the expected changes in bioethanol yield from *K. alvarezii* biomass according to season. Simulation results are shown in Table S3 and Fig. 2. Increasing the fiber content from 9 to 36% (fiber/protein ratio from 0.25 to 4) increased the predicted growth rate of *S. cerevisiae* from 0.0098 to 0.0168 h^{-1}, *E. coli* from 0.001 to 0.0017 h^{-1} (Fig. 2a, Table S3), ethanol yield from 44.2–74.9 to 103.1–105.1 g kg^{-1} (Fig. 2b, Table S3), and carbon utilization yield from 8.8–14.9 to

Table 1 Simulation results of fermentation of whole *K. alvarezii* biomass

Configuration	*E. coli* growth (h^{-1})	*S. cerevisiae* growth (h^{-1})	Min ethanol		Max ethanol	
			Production (g/kg)	Carbon utilization (%)	Production (g/kg)	Carbon utilization (%)
S. cerevisiae	–	0.02	49.4	9.9	57.2	11.4
E. coli	0.05	–	69.9	14.0	72.2	14.4
S. cerevisiae ⇒ *E. coli*	0.04	0.02	94.1	18.8	97.6	19.5
E. coli ⇒ *S. cerevisiae*	0.05	0.0001	69.9	14.0	74.5	14.9

21.1–23.5% (Fig. 2c, Table S3). The increase, however, reaches saturation, indicating the limitation other metabolites impose on growth and ethanol production at higher fiber content (Fig. 2).

Kappaphycus-Based Biorefinery Design for Rural Farms in the Philippines

In the previous section, we introduced a method for optimizing the bioconversion of seaweeds into bioethanol using modeling by FBA. Here, we show the potential of the seaweed biorefinery to generate additional value from *Kappaphycus* biomass and other coastal communities in the Philippines, a rapidly developing country and one of the world's largest producers of *Kappaphycus* [36].

In 2006, Philippines passed the Biofuel Act, making it mandatory to use bioethanol in fuel blends. Initially, four potential crops were identified as feedstock for the local bioethanol industry: sugarcane, corn, cassava, and sweet sorghum. However, almost 10 years after the Biofuel Act was passed, Philippines still produced less than 50% (85 million liters as for 2012) of their local demand, importing the rest of the required bioethanol [69]. Moreover, as mentioned above, terrestrial biomass production is limited due to limited land and freshwater availability, due to the use of fertilizers, and due to potential competition with food production.

In previous works, using life cycle analysis, we have shown the advantage of macroalgae feedstock for biofuel production potential in comparison with corn and cassava fresh roots in terms of land, potable water, fertilizer, and herbicide usage [13]. The Philippines have a history of almost 50 years of commercial seaweed farming, with *K. alvarezii* as a major cultivated crop [36]. The industry, which mostly targets seaweeds for carrageenan processing, has already generated thousands of jobs and improved the quality life to multiple families in the rural coastal areas. In the Philippines, the current area for seaweed farming in the major producing regions of ARMM (Autonomous Region in Muslim Mindanao) is about 24,000 ha with the potential expansion to 103,000 ha [36]. The average productivity using current cultivation methods in the Philippines is 31 t DW ha^{-1} $year^{-1}$ [36]. Several previous studies have investigated the conversion of *K. alvarezii* into ethanol by a single-step process [42, 43].

Table 2 Simulation results of fermentation of residues of *K. alvarezii* biomass after carrageenan extraction (120 g/kg) (calculation per total *K. alvarezii* biomass)

Configuration	*E. coli* growth (h^{-1})	*S. cerevisiae* growth (h^{-1})	Min ethanol		Max ethanol	
			Production (g/kg)	Carbon utilization (%)	Production (g/kg)	Carbon utilization (%)
S. cerevisiae	–	0.02	49.4	12.5	57.2	14.5
E. coli	0.04	–	52.9	13.4	56.4	14.3
S. cerevisiae ⇒ *E. coli*	0.03	0.02	77.6	19.6	81.7	20.7
E. coli ⇒ *S. cerevisiae*	0.04	0.0001	52.9	13.4	58.1	14.7

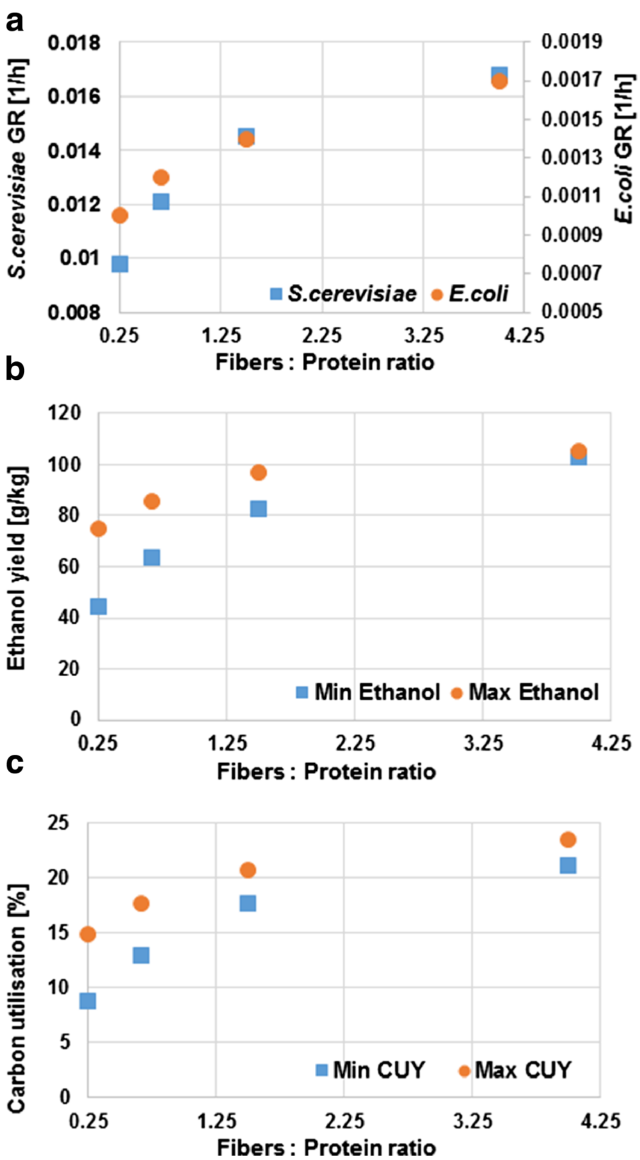

Fig. 2 Sensitivity analysis of fibers and protein content variation, expected with nutrient availability and seasonal changes, impact on **a** *S. cerevisiae* and *E.coli* growth rates, **b** ethanol yield from the two-step fermentation, and **c** carbon utilization yield in the two-step fermentation. For this analysis, the sum of protein and fibers content was kept constant on 45%

The predicted output of an *S. cerevisiae*-based biorefinery is in the range of experimentally obtained data (1963–2273 L ha^{-1} year^{-1} predicted versus 710–4000 L ha^{-1} year^{-1} reported in [42, 43]) (Table 3).

If total transportation bioethanol demand in the Philippines is 283 million liters per year [70], ~ 73,000 ha will be required on the national level to cultivate *K. alvarezii* using current methods for the reported two-step fermentation process, using the high-end prediction at up to ~ 3879 L of ethanol production ha^{-1} year^{-1}. These yields are close to the maximum yields of ethanol predicted in previous studies that used only the sugar to ethanol ratio calculation [42].

Table 3 Bioethanol production potential (BPP) of whole *K. Alvarezii* biomass per hectare per year, given the current biomass productivity of 31 t DW ha^{-1} year^{-1}

Fermentation configuration	Min ethanol (L ha^{-1} year^{-1})	Max ethanol (L ha^{-1} year^{-1})
S. cerevisiae	1963	2273
E. coli	2778	2869
S. cerevisiae ⇒ *E. coli*	3740	3879
E. coli ⇒ *S. cerevisiae*	2778	2961

Results are based on FBA simulations

Considering a local processing facility for carrageenan extraction, which can be the potential local fuel producers, bioethanol production from currently wasted seaweed biomass material could generate additional profit streams. For example, two representative farms in Zamboanga, Philippines, reported on 2.85 t DW year^{-1} (cultivation area of 0.05 ha, farm A) and 8.5 t DW year^{-1} (cultivation area of 0.27 ha, farm B) [36]. If 70–92% of the residual produced biomass from carrageenan extraction, which is lost today, is converted into bioethanol, this can generate additional 162–214 kg of ethanol from the seaweed production of farm A and 486–638 kg of ethanol from the production of farm B (results are based on simulations in Table 3, where waste after carrageenan extraction was fermented).

Importantly, until now, seaweed farming has contributed to improving the socio-economic status of coastal communities in the Philippines. The farms generate employment for tens of thousands of coastal families, providing diversified livelihoods to meet basic family needs such as food, shelter, education of children, and health care, among others, and enhance community cohesion through cooperation among farmers. In addition, seaweed farming was shown to strengthen stewardship of marine environment and resources, promoting development of and enhancing viability of small and medium enterprises [36]. We believe that the development of low-cost processing systems to convert seaweeds and the waste of their current processing into platform chemicals and biofuels will further contribute to the sustainable development in the poor rural areas assuming that the algae are processed in their native regions, which is currently not always the case [71]. Moreover, the development of additional products from macroalgae, such as bioethanol, through fermentation, could address the current challenges of the industry such as low income of farmers, which is mostly due to seasonal and unstable production, and poor market linkages that deprive seaweed farmers of benefits of the seaweed value chain.

Kappaphycus-Based Biorefinery Design for Rural Farms in India

According to India's National Policy on Biofuels (2009), renewable fuels are encouraged for motor vehicles, targeting a 5% blending rate for ethanol [69]. However, this target has not been yet achieved because of the unavailability of local ethanol and barriers for ethanol import (although 155 million liters have been imported from the USA alone, in 2014). Marine biorefineries provide an opportunity for local biofuels and chemical production in India [13].

The main part of seaweed industry in India is at Tamil Nadu and Gujarat state coasts mainly based only on the natural stock of agar and alginate-producing seaweeds. Previous work demonstrated the production of bioethanol from red algae *Gracilaria verrucosa* residual biomass after extraction of agar [72]. An integrated biorefinery approach was demonstrated for local to India *Ulva fasciata* [73], *Gelidiella acerosa*, and *Gracilaria dura* [74].

K. alvarezii was cultivated in India at the coast of Tamil Nadu state, during 1995 to 1997, by obtaining few vegetative fragments from the Philippines. PepsiCo invested in seaweed cultivation project as corporate social responsibility (CSR) and started contract farming successfully from March 2003 for commercial cultivation of *K. alvarezii* by fishing communities in coastal districts of Tamil Nadu state with the technology supported by Gujarat state-based Central Salt and Marine Chemicals Research Institute (CSMCRI). At 2008, AquAgri overtook this project [75] and started cultivation commercially for various purposes. The cultivation of *K. alvarezii* on a large scale has given a yield of 25 t DW ha^{-1} $year^{-1}$ by net bag method, 40 t DW ha^{-1} $year^{-1}$ by raft method, and 45 t DW ha^{-1} $year^{-1}$ by open culture method in eight harvests [38].

According to the India National policy on biofuels, the governmental goal is to produce 5% of the ~ 156 million tons from local biomass [69]. This is equal to ~ 11.7 million tons of bioethanol (given 1.5:1 ratio of ethanol to gasoline energy density). Given 97.6 g of bioethanol kg^{-1} of DW *K. alvarezii* biomass (or 81.7 g of bioethanol kg^{-1} of DW residual *K. alvarezii* biomass after carrageenan extraction) (Tables 1& 2) and *K. alvarezii* biomass production rates of 40 t DW ha^{-1} $year^{-1}$, this will require ~ 30,000 km^2 of offshore cultivation facilities (~ 36,000 km^2 for the residual biomass if carrageenan is extracted in the first step). While the total exclusive economic zone of India is 2,305,143 km^2, the estimated coastline area suitable for macroalgae cultivation of India is 451,000 km^2 [76]. These results suggest that macroalgae have a potential to provide for a significant part of India's transportation biofuels in the future.

In addition, an important positive social impact of the development of marine biorefinery industry will be jobs in rural areas. More than 250 million people from rural areas in India are living in coastal areas. Many rural and coastal populations in India are mainly dependent on agriculture, and with the globalization of economy, the agricultural sector of India is facing poor infrastructures and inefficient bureaucratic procedures, small landholdings of farmers, and weather-dependent farming systems, which all make farmers and rural people more economically sensitive. The development of seaweed cultivation will play a key role in economically supporting such population. The cultivation does not require skilled and well-educated people; the rural people who face various challenges such as illiteracy, weak socio-economic conditions, and lack of technical knowledge would benefit from additional job opportunities as well as local economic development.

Indian economic growth depends on the fuel sources, which make India dependent on oil-producing countries [77]. The Middle East covers more than 60% of total oil import. Such dependency on fossil fuel with unstable supply, because of the current geopolitical situation and frequent wars, and fluctuant price is a hurdle and a hazard for India's economy. However, locally cultivated macroalgae biofuel has potential to reduce this dependency at least for a few percentages and will be beneficial for rural and coastal India in terms of other economic benefits. For the local population, prices of biofuel may be similar to those of petrol-based fuel, but we expect better supply and less price volatility than for imported fossil fuel. Moreover, the overall cost-benefit of using them is much higher as it is a locally produced renewable fuel. The economic stability will be achievable with large production of biofuel from macroalgae, which will definitely play an important role in Indian energy security.

Integrated Biorefinery for Carrageenan, Ethanol, Biofertilizer, and Energy Production

In this paragraph, a selection of two additional products that could contribute to the sustainability of macroalgae biorefineries in a developing country is presented. Parameters for such selection include the low-capital requirement, direct benefit for local population, and attenuation of exergy losses. Local production of additional products would benefit not only the stakeholders of the seaweed industry in the Philippines or India but also the local community including the local agriculture sector. For example, a process allowing for the production of a liquid biofertilizer named "sap" from fresh *K. alvarezii* prior to drying and processing for carrageenan production has been reported [44]. The biofertilizer has proven to have many benefits on local crop yield and resistance and is easy to produce and use allowing the consideration of such process for rural applications. From 20 kg of fresh algal biomass, production of 13 kg of sap (67% yield) along with 1.62 kg of dry residue was reported; the latter can be subsequently used for carrageenan extraction and ethanol production with similar yield than for non-extracted algae. Moreover, while the sap is usually used locally

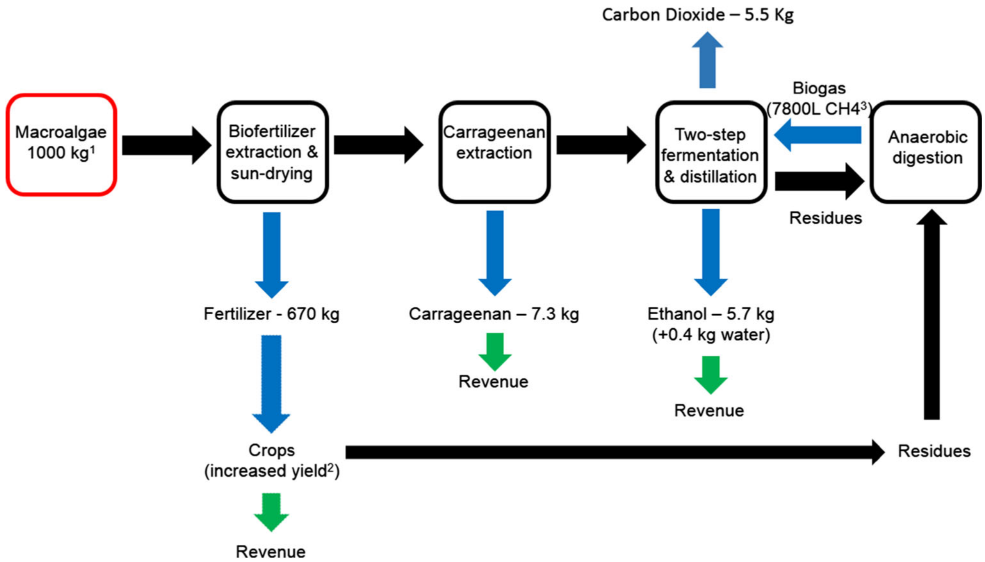

Fig. 3 *Kappaphycus*-based biorefinery for the co-production of fertilizers, carrageenan, ethanol, and biogas. kilogram of freshly harvested algae (fresh weight) (1), [44] (2), and yield from digestion of algal biomass only (3) Park et al. (2012). Calculations were done using the following yield and assumption: fertilizer yield (67%), residue moisture content (25%), carrageenan yield (12% g/kg dry algae), ethanol yield (minimum scenario of 77.6 g/kg dry algae from Table 2), ethanol purity after distillation (95:5 *v*/*v* ethanol water mixture), 1 mol of produced ethanol = 1 mol of produced CO_2, and 141 L CH_4 kg^{-1} of algal dry matter before ethanol production

on agricultural land, the transportation cost of the residue to the processing plant is lowered due to the decrease of weight from the extraction; the residue is also richer in carrageenan leading to higher yield per mass of processed biomass [44].

Finally, in order to reduce the amount of waste produced, we considered the use of the waste stream from ethanol production (after carrageenan extraction) as a feedstock for bioenergy production by anaerobic digestion (AD) followed by the conversion of the biogas to energy for the process using a combined heat and power system. AD has proven to be a robust method for bioenergy production from agricultural waste, and therefore, such facility could be installed near algae-processing plants for bioenergy production and waste management [78]. Moreover, various feedstock can be used for AD without significantly impacting the yield (and in some cases, improving it, as different feedstock can have synergic ratio of nutrients [78]). In the case of macroalgae, Park et al. (2012) reported an energy production of 141.1 L CH_4/kg dry algae from the anaerobic digestion of the residues of red algae *Gelidium amansii* after ethanol production [79]. This energy potential of 1086 kcal/kg dry algae is enough energy to entirely replace the need of fossil energy for the ethanol production [79].

Therefore, such biorefinery (Fig. 3) could provide cheap biofertilizers for local farmers, an opportunity to sell their waste for bioenergy production by AD (biogas can be used for combined heat and electricity production) that could meet local demand in energy while giving local communities an access to an additional fuel source. The mass balance of products that can be obtained from the processing of 1 t of freshly harvested *K. alvarezii* was calculated and is shown in Fig. 3. The mass balance reported is based on the following assumptions: (1) 67% fertilizer extraction yield [44], (2) 12% carrageenan extraction yield [36], (3) minimum scenario of 77.6 g of ethanol/kg of dry residue (Table 2), and (4) 141 L CH_4/kg dry algae from residuals after ethanol fermentation [79].

In addition to the obvious positive impact of the implementation of such biorefinery on the development of rural and coastal areas, the quantity and quality of the carrageenan produced remain unchanged. However, the implementation of such integrated process will require governmental support. Although biofertilizer production is performed directly after harvesting in the farm, carrageenan extraction and the proposed additional steps require specific facilities that could be used to process algal biomass supplied by local farms. Moreover, benefits for family-size farms may be limited by the current system of multiple small farms, reducing their bargaining power on algal biomass price. Such drawback could be efficiently overcome by the creation of cooperatives [80].

Moreover, since the early 1990s, concerns over the effects of economic globalization have haunted economic and environmental thought in developing countries. Critics argued that globalization and foreign investments often distort local economies, especially when they are biased for large-scale projects, and that wealth for investors (especially in agriculture) creates poverty for local farmers and communities. "Localization" [81] was promoted as the counterpart (and antidote) to globalization, along human rights, equity, and ecological sustainability. Localization is supposed to be based on decentralized local infrastructure, knowledge, and resources, and by recreating social and environmental "commons" [82]. Macroalgal biorefineries, especially in small- and medium-size scales, could empower bioregional communities and enable them to supply their own energy requirement, based on available local resources, and thus to promote greater self-reliance and equality in distribution of economic power through decentralized market of fuel and energy. Therefore, marine macroalgae biorefineries will provide essential tools for transition to the bioeconomy in the most rapidly developing economic areas of the world.

Conclusions

Macroalgae biorefineries could provide a sustainable alternative to the fossil fuels and terrestrial biomass feedstock in multiple coastal areas. Development of seaweed-based biorefineries could preserve the arable land and drinking water by moving the biomass production offshore. Such sustainable technology has the potential of empowering communities and households through localization, and thus of promoting social and global justice. We have shown that using currently available computational methods, it is possible to predict the potential of additional revenue stream generation to the seaweed farmers in the Philippines and India by the production of bioethanol and fertilizer. This potential additional revenue stream could significantly reduce the current industry waste and open new opportunities for the further sustainable industry growth.

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