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ARTICLE

Maximizing the sustainability of macroalgae biorefinery: A superstructure optimization of volatile fatty acid platform

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Macroalgae are a valuable energy source that can be transformed into numerous products most notably fuels and chemicals due to their high content of carbohydrates, proteins, and vitamins. In order to use the macroalgae on a commercial scale, it is essential to evaluate various potential pathways into value-added products as well as intermediate components and technologies. Furthermore, the prospective processes have to be economically competitive while simultaneously offer minimum environmental impact in terms of carbon and other waste emissions. This in turn presents a large decision-making problem with a significant combinatorial complexity. This study addresses this problematic by utilizing a superstructure process design approach for a seaweed biorefinery which produces mixed alcohols and mixed organic acids via anaerobic digestion/volatile fatty acid route. Seventeen design alternatives have been proposed to determine the optimal design and technical feasibility by maximizing the net present value in the most environmentally beneficial fashion. The results indicate that biofuel production from macroalgae is economically viable at a minimum ethanol selling price of \$1.17/gal. Furthermore, the optimal design enables a 90% reduction in carbon dioxide emissions. Results of the sensitivity analysis show that seaweed price is the most important parameter that can contribute in improving the economics, thereby confirming that the cost-effective and efficient large-scale seaweed cultivation is utmost important to the success of macroalgae based biofuel production.

Introduction

An impending energy crisis owing to the rapid depletion of petroleum reserves and unabated environmental damage resulting from carbon dioxide emissions (CEs) has prompted researchers to find a carbon-neutral energy infrastructure. Global oil demand has already reached to 96.6 million barrels/day last year and is anticipated to reach 105.4 million barrels/day by 2030.¹ With the current pace of oil extraction, depleting petroleum reserves could become a pressing issue 50–100 years from now.² Bhowmick et al. reported that oil production from post-peak oil fields are expected to decline from 70 million barrels/day in 2007 to 27.1 million barrels/day by 2030, considering a 6.7% decline.³ Based on the current energy consumption trends, it is expected that by 2030, CEs will increase by 25–90% from 9.7 Gt/yr in 2014.^{4,5} There is an inevitable gap between the supply and demand. It is an even challenging issue because the gap should be filled in the most economically feasible and sustainable manner. The development of biofuel production from renewable sources such as biomass is emerging as a promising alternative to meet the growing energy demand while producing less CEs.⁶

Ideally, biofuel can be produced from all biomasses such as food crops, and lignocellulosic or aquatic biomass. However, all biomasses are not well-suited for large-scale biofuel production due to limited biomass availability or ethical issues such as food competition, land and irrigation water requirements for their cultivation. Among various biomass feedstocks, aquatic biomass from the brown algae *Saccharina japonica* (SJ), which is a 3rd generation feedstock, is considered a promising candidate. This is because SJ can be cultivated sustainably, has a high carbohydrate content (32–60 wt.%) with high photosynthetic efficiency (6–8%), and has comparatively simple processing requirements owing to a lack of lignin.^{7–10} Furthermore, the advantage of brown algae for biofuel is that it does not compete directly or indirectly for land with food, and does not require irrigation water and fertilizers for cultivation.^{11,12} The primary carbohydrates of SJ are 1) laminarin (14 dry wt.%), a beta-1,3 linked glucan, 2) cellulose (6 dry wt.%), a linear chain of $\beta(1\rightarrow4)$ linked D-glucose, 3) mannitol (12 dry wt.%), a sugar alcohol, 4) fuco-dan (5 dry wt.%), a sulfonated fucan, and 5) alginate (23 dry wt.%), an anionic polysaccharide composed of mannuronic and guluronic acids.⁸ The chemical composition of carbohydrates varies depending upon the growth conditions and the time of harvest.⁸ SJ can be harvested four to six times per year owing to its rapid growth and high sequestration capability of up to ~36.7 tonnes per ha.¹³ Global production of SJ increased from 5.1 Mt in 2010 to 8.2 Mt in 2016.¹⁴ This indicates SJ harvesting infrastructure is well developed and its market is growing rapidly. From an industrial point of view, Murphy et al. calculated that through anaerobic

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digestion of SJ biomethane can be produced, up to 20,800 m³.ha⁻¹.yr⁻¹.¹⁵ Fasahati et al. determined a breakeven electricity price of 18.81 ¢/kWh by producing 35,760 kW of renewable electricity at plant scale of 400 kt/yr.¹⁶ This represents that SJ offers tremendous potential for producing biofuels and well-suited for large-scale biofuel production. Taking into consideration the benefits of brown algae, its versatile chemical composition, and growing global market, and excellent potential for producing biofuels, the present study utilizes SJ as a potential feedstock for producing biofuels and value-added chemicals.

Biofuels can be produced from SJ by two alternative biochemical pathways: the volatile fatty acid platform (VFAP) and the sugar platform (SP). In the former pathway, volatile fatty acids (VFAs) consisting of acetic acid, propionic acid, and butyric acid are produced by the partial anaerobic digestion of biomass using a mixed culture bacterial ecosystem. VFAs have numerous applications in the chemical, food and pharmaceutical industries. They are important precursors of biopolymers—e.g., polyhydroxyalkanoates (PHAs)—and other valuable products such as aldehydes and ketones.¹⁷ Therefore, VFAs can be separated and sold as the main products of a biorefinery. Alternatively, VFAs can be hydrogenated to produce mixed alcohols consisting of ethanol, propanol, and butanol, which can be sold as renewable transportation fuels. However, compared to the VFAP, the SP only utilizes hexose and pentose sugars extracted or converted from plant bodies to produce bioethanol. Several bench-scale studies are conducted to investigate the yields of biofuels and biochemicals production from seaweeds using the SP.^{18–21} Regarding industrial-scale techno-economic studies, Dickson et al. investigated the optimal design of bioethanol and dry distillery solid (DDS) production from SJ via the SP.²² They concluded that biofuel production via the SP is economically viable at a minimum ethanol selling price (MESP) of \$1.97/gal at a plant scale of 612 kt/yr. Subsequently, they performed process integration of the SP to utilize all waste streams from the manufacturing process, and achieved a MESP of \$1.31/gal for the same plant capacity.²³ Sadhukhan et al. conducted techno-economic and life cycle sustainability assessments of a macroalgal biorefinery.²⁴ However, an industrial-scale techno-economic assessment, coupled with an environmental assessment of biofuels and chemicals produced via the VFAP, remains limited and should be investigated systematically to determine which pathway is more promising.

In the literature, numerous studies have demonstrated that the VFAP has a higher product yield than the SP.²⁵ This is primarily owing to the ability of anaerobes to digest all the non-lignin components of the biomass, including carbohydrates, proteins, and lipids, whereas in the case of the SP, only the carbohydrate content of the biomass is converted to bioethanol.²⁶ Furthermore, unlike the SP, the VFAP does not require aseptic conditions, and does not utilize expensive enzymes and capital-intensive fermenters.²⁷ Despite the promising yields and simple digestion process, the design of effective and economically viable separation technologies for the dehydration of aqueous VFAs is a major obstacle to the industrial-scale application of the

VFAP. This is mainly because water and acetic acid have similar boiling points, which makes their separation by distillation difficult and energy-intensive. Another challenge associated with the VFAP is the significant production of carbon dioxide during the fermentation of biomass. Bonfim-Rocha et al. demonstrated that the CEs produced by the fermentation-based biorefinery processing of 2–3.5 Mt/yr amount to approximately 110–193 kt/yr.²⁸ A potential method of mitigating direct CEs from the VFAP is microalgae (MA) based biological utilization. Davis et al. reported that 100 t of algal biomass fixes approximately 193 t of carbon dioxide, which make it a suitable candidate for reducing the CEs produced by the VFAP.²⁹ There is also an indication that the water footprint of a biorefinery is quite high. Approximately 13 gals of wastewater are produced when one gal of corn ethanol is refined.³ This level of water consumption is alarming and must be reduced by reusing the wastewater from processing.

Based on the presented arguments, the goals of the present study are to determine the optimal topology for the VFAP as well as to utilize all waste streams including CEs, wastewater, and undigested biomass from the manufacturing process to value-added chemicals. The novelty of the present work is the utilization of a self-sustaining SJ feedstock and a comprehensive network of process alternatives to identify the optimal VFAP and waste streams design. To utilize all waste components of the manufacturing process, microalgae and a wastewater treatment network are embedded in the superstructure. The mathematical model of the superstructure is formulated as a mixed integer non-linear programming (MINLP) problem, which determines the optimal design of a biorefinery using a rigorous objective function called net present value (NPV). Once the solution is computed, the resulting optimal topology provides: (1) the operating conditions and flow rates in each stream; (2) the process economic indicators including total capital investment (TCI), total cost of manufacturing (TCOM), MESP, maximum seaweed price (MSP), and NPV; (3) environmental performance indicators including the net CEs from the process and the water footprint; and (4) a sensitivity analysis of the key model parameters.

Methodology

Problem statement

The main objective of the optimization problem is to determine the optimal design of the biorefinery from the given superstructure by maximizing the NPV as well as minimizing the environmental impact of the biorefinery by integrating waste streams utilization technologies. The major decision variables include: technology selection for the VFAP and carbon dioxide utilization; the mass flow rate of each species in every stream; the heat and power consumption of each piece of equipment; the capital cost and the operating cost required for economic evaluation; and all emissions required for environmental evaluation.

Superstructure development

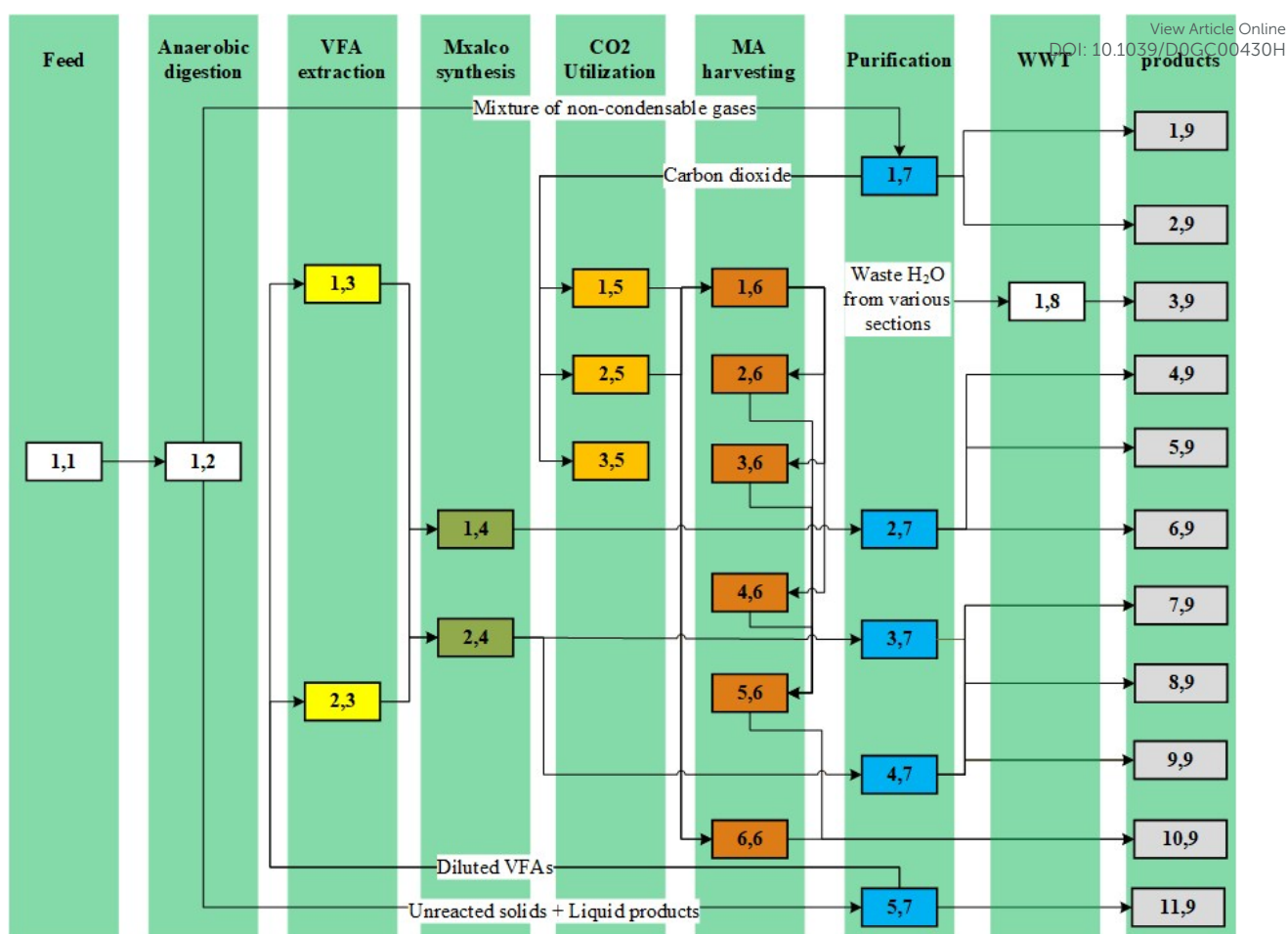


Fig. 1. Superstructure of biorefinery for producing biofuel and chemicals from *Saccharina japonica*.

A superstructure containing the entire potential design alternatives at the various processing stage of biorefinery is illustrated in Fig. 1.³⁰ Seven major sections are included in the superstructure: anaerobic digestion, VFA extraction, mixed alcohol synthesis, carbon dioxide utilization, harvesting, purification, and wastewater treatment (WWT).

Seventeen alternative processing technologies are embedded in the previously mentioned sections. Each alternative is represented in the superstructure by two indices. The first index refers to the alternative, whereas the second index refers to the processing stage. For example, "1, 1" refers to alternative 1 in processing stage 1. White blocks are used in the superstructure to represent certain processing stages where no topology (structural) decisions are involved. Simplified depiction of the superstructure is given in the graphical abstract. Based on the given alternatives, biorefinery can produce eleven products. The nomenclature of the superstructure including references is listed in Table S.1. Each processing stage and their alternatives are briefly explained in the following subsections.

Anaerobic digestion

The proposed biorefinery process starts with the anaerobic digestion of SJ. Anaerobic digestion consists of four stages: hydrolysis, acidogenesis, acetogenesis, and

methanogenesis.^{31,32} In the first stage, the complex structure of brown algae including carbohydrates, proteins, and lipids are broken down by bacteria into simple sugars, amino acids, and fatty acids, respectively. Acidogenic bacteria then convert the simple sugars into volatile fatty acids, ammonia, carbon dioxide, and hydrogen sulfide. These resulting volatile fatty acids are then digested by acetogens to produce acetic acids along with additional ammonia, hydrogen, carbon dioxide, and other acids including propionic acid and butyric acid. Finally, methanogens convert products from the preceding stages into methane, carbon dioxide, and water. Methanogenesis must be prevented to produce VFAs as the final product of fermentation. This is accomplished using inhibitor such as iodoform.²⁷ The operating conditions for anaerobic digestion are: 13 wt.% solid loading; a retention time of 120 h; an inhibitor loading of 30 ppm; a digestion temperature of 35 °C, and a yield of 0.35 g VFA/g of dry feed.²⁵ The stoichiometric reactions of anaerobic digestion are given in Table S.2. The outlet stream from the digester consists of solid (unreacted biomass), liquid, and gaseous products. These fermentation products are sent to the purification section for further processing. The liquid products recovered from the solid purification are sent to the VFA extraction section.

VFA extraction

The main goal of this section is to dehydrate and recover VFAs. Owing to the energy-intensive dehydration process, two alternative technologies are embedded in the superstructure: classical dehydration and hybrid dehydration. The main separation equipment of the classical dehydration comprises an extraction column, a rectification column, a stripping column, and a decanter. Dilute VFAs at 5 wt.% concentration enter the extraction tower where 95 wt.% of the VFAs are separated in the extract phase. Methyl tert-butyl ether (MTBE) is used as an extraction agent because it has a lower enthalpy of vaporization (322 kJ/kg), and a lower boiling point (55 °C) compared to other reported extraction agents such as ethyl acetate, isopropyl acetate, and methyl propyl ketone.³³ The extract stream is sent to a rectification column to separate the VFAs from the MTBE. The extraction agent and water are recovered in the distillate and the VFAs are recovered at the bottom of rectification column, resulting in a VFA concentration of ~99.99 wt.%. The raffinate in the extraction tower is saturated with MTBE which is recovered in a downstream stripping tower. A low-pressure steam is used to strip 99 wt.% of the MTBE. The extraction agent recovered from the top of the stripping and rectification column is condensed and sent to a decanter to separate the organic phase from the aqueous phase. The organic phase is recycled to the extraction column and the aqueous phase is sent to the stripping column. The hybrid process involves the combination of membranes and the classical dehydration process described previously. In this alternative, a mordenite membrane (pervaporator) is integrated prior to the classical process. This increases the concentration of VFAs from 5 wt.% to 10 wt.% by removing ~50 wt.% of the total water flow. Retentate in which the VFA concentration has reached 10 wt.% is sent to the extraction/distillation section for further dehydration to ~100%.

Mixed alcohols synthesis

Once the VFAs have been recovered, there are two alternatives for further processing. The first alternative is to bypass hydrogenation and send the concentrated VFAs to the purification section where the acids are separated into pure compounds. This alternative produces mixed acids consisting of acetic acid, propionic acid, and butanoic acid. Alternatively, the VFAs can be hydrogenated to produce mixed alcohols consisting of ethanol, propanol, and butanol. Hydrogenation process is a gas phase process that takes place at 290 °C and 60 bars in the presence of a cobalt catalyst, and produces a high alcohol yield of 97 wt.%.³⁴ The catalyst consumption is 0.46 mg catalyst/kg mixed alcohols, and the hydrogen requirement is a molar ratio of 2.1:1 (H₂/VFA).³⁵

The alternatives of this processing stage are modeled in such a way that either a standalone facility producing only mixed alcohols or an integrated facility producing both mixed acids and alcohols can be selected as the optimal process design. If the latter is selected as an optimal decision, an upper limit is set on mixed acid production, because the main objective of the proposed biorefinery is to produce biofuels. Hence, 30 wt.% of the VFAs from the VFA extraction section can be used to produce mixed acids. The split ratio of VFAs between mixed acid synthesis and mixed alcohol synthesis is an important decision

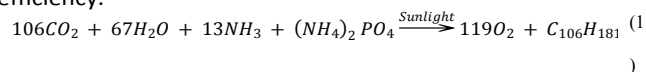
variable and should be occurred to ensure improved process economics.

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Carbon dioxide utilization

Non-condensable gases produced from the partial anaerobic digestion of biomass consist of carbon dioxide, hydrogen, and hydrogen sulfide. These gases are first sent to the purification section where pressure swing adsorption (PSA) technology separates hydrogen from carbon dioxide (greater than 99 wt.% purity each). The highly pure carbon dioxide gas can be readily utilized to produce value-added chemicals. The microalgae production process is embedded in the superstructure because it uses carbon dioxide as a primary feedstock, and therefore contributes to managing carbon dioxide in a sustainable manner. Two alternative processes are considered in the superstructure: microalgae production and venting carbon dioxide to the environment.

It is assumed that *Scenedesmus acutus*, a freshwater algae strain, is produced. The microalgae grow throughout the year, although its productivity varies with the seasons. An average microalgal annual productivity of 25 g/m²/day is assumed.^{36,37} The cultivation of microalgae requires carbon dioxide, nutrients such as nitrogen and phosphorus, sunlight, and water. Two alternative processes for the cultivation of microalgae—open ponds and photobioreactors (PBRs)—were included in the superstructure. In each alternative, carbon dioxide and nutrient are delivered in stoichiometric amounts based on Eq. (1), assuming an algal composition of [C₁₀₆H₁₈₁O₄₅N₁₅P] based on the Redfield ratio.^{29,38} In addition to the stoichiometric requirement for raw materials, 10 wt.% excess raw materials were delivered to accommodate for possible variations in efficiency.



The design parameters of microalgae cultivation in the open ponds and PBRs are given in Table S.3.

Microalgae harvesting

The harvesting and dewatering of microalgae biomass are energy-intensive processes owing to the dilute concentration, water-like density, and small sizes of the algal cells. Hence, six design alternatives for harvesting and dewatering were included in the superstructure to select optimal technology. The potential combinations of harvesting and dewatering technology include: (1) a gravity settler (GS) followed by hollow filter membranes (HFMs) and a centrifuge; (2) a GS followed by diffused air flotation (DAF) employing chitosan flocculants and a centrifuge; (3) a GS followed by electrocoagulation (ECA) and a centrifuge; and (4) a GS followed by a belt filter press. The design parameters of these dewatering technologies are provided in Table S.3.

Purification

Hydrogen and carbon dioxide purification

Non-condensable gases consisting of hydrogen, carbon dioxide, and traces of hydrogen sulfide are purified by PSA. The purity of the recovered hydrogen is 99 wt.%, and it can be sold or utilized during the hydrogenation of VFAs. Likewise, carbon dioxide

recovered by PSA has purity of 99 wt.% and is sent to a carbon utilization section for further processing into value-added chemicals.

Mixed acid purification

Mixed acid purification aims to achieve 99.5 wt.% purity for each acid by distillation. Concentrated mixed acids are fed to the first distillation column, which separates butyric acid in the bottom stream from a mixture of acetic acid and propionic acid in the top stream of the column. This mixture is then fed to the second distillation column where acetic acid is recovered in the distillate and propionic acid is recovered in the bottom.^{39,40}

Mixed alcohols purification

The separation of mixed alcohols is challenging owing to the formation of azeotropes between water and the mixed alcohols, which make a simple distillation process inefficient and highly energy-intensive. Therefore, water is first removed from the mixed alcohols using molecular sieves or a pervaporator. Subsequently, the dried mixed alcohols are sent to the distillation column to separate ethanol from propanol and butanol. Ethanol is recovered in the distillate, and the mixture of propanol and butanol recovered in the bottom of the distillation column is fed to the second column to separate propanol in the distillate from butanol in the bottom. This method can achieve 99.5 wt.% purity.^{26,41}

Unreacted biomass purification

A report by Pacific Northwest National Laboratory indicated that the protein content of residual solids obtained from the anaerobic digestion of brown algae (kelp *Macrocystis*) could be similar to that of distillers' dried grain with soluble, the protein-rich byproduct of corn fermentation.⁹ Hou et al. have reported that the protein concentration in the solid residues collected after brown algae fermentation is 2-3 times greater than that present in raw brown algae.⁴² They further have shown that the amino acid distribution in these residues is unchanged.

Therefore, the unreacted solid from the anaerobic digestion is a valuable byproduct. However, it contains a large quantity of moisture that must be removed before it can be stored the byproduct for a long period. The unreacted wet solids are processed into a centrifuge, where moisture is partially removed. It is assumed that 60 wt.% of the liquid will be removed by this operation.⁴³ The desired level of moisture in the final byproduct is below 10 wt.%. Therefore, the wet solids are dried using a steam bundle dryer and can be sold as cattle feed.

Wastewater treatment

A complete wastewater treatment network is embedded in the superstructure that will purify the wastewater from various process units, and the blowdown from the cooling towers and boilers. The WWT design consists of screens, anaerobic digestion, aerobic digestion, and reverse osmosis system. The treated water from the WWT network is assumed to be clean and is recycled to the process. It is assumed that 2 wt.% of the wastewater entering the anaerobic digester will be discharged in the blowdown to mitigate the buildup of salts and other inorganics.

Mathematical model

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The mathematical model of the superstructure is formulated as an MINLP problem which can simultaneously determine the optimal design, operating conditions, and waste reduction network for the biorefinery. The MINLP model involves four major types of constraints, which are mass balance, energy balance, capital and operating costs constraints. The complete mathematical model of the superstructure is provided in the Supplementary Material.

Objective function

The objective function for the model is the NPV that should be maximized and is defined as

$$NPV = \sum_{n=0}^{20} \frac{NCF_n}{(1+r)^n}, \quad (2)$$

where NCF_n is the non-discounted cash flow for the year n and is defined as

$$NCF_n = -r_n T_{CI} + a_n W_C + (Rev - T_{COM})(1 - tax) + D \times tax, \quad (3)$$

where r_n is the ratio of TCI consumed during year n , D is depreciation, and W_C is working capital. a_n is a parameter equal to -1 during year 3, 1 during the last year of the project, and zero for all other years.

Optimization scenarios

Three optimization scenarios are investigated to design a sustainable biorefinery. This approach will enable to quickly compare strength and weakness of different processing configuration obtained in each scenario.

Scenario 1

The base case is an unrestricted scenario where no limit on TCI is set. In addition, carbon dioxide utilization alternatives are deactivated in this scenario. Therefore, according to this scenario, the result with a focus on the process economics and CEs of the biorefinery process by maximizing the NPV is obtained. The solution obtained from this scenario will act as a reference point for evaluating other scenarios in terms of economics and the environment issue.

Scenario 2

All binary variables denoting carbon utilization in the initial model and the scenario 1 are relaxed. Regarding carbon emission, it is important to mention that two sources of CEs from the biorefinery should be considered: direct and indirect emissions. The former originate explicitly from various process stages such as anaerobic digestion and degassing from open ponds. Indirect emissions, however, originate from the heat and power required to power-up the processing facilities. The objective here is to focus on direct emissions only. The goal of this scenario is to find optimal flowsheet that has better process economics and environmental performance than that achieved in the base case by maximizing the NPV.

Scenario 3

Owing to the integration of the carbon utilization processes, the TCI of the biorefinery may increase significantly. Therefore, in this scenario, further optimization based on limited funds is performed. Specifically, optimization is conducted for three scenarios: Cases A, B, and C, where the fund allocated to each scenario are 20%, 30%, and 40% of the base case TCI, respectively.

Results and discussion

The proposed process synthesis MINLP model was implemented in GAMS (25.0.2) and its solution was computed using DICOPT solver. The model contained 7,476 continuous variables, in which 1,680 variables are nonlinear, 22 variables are binary, and the remaining variables are linear, and 6,517 equality and inequality constraints. The chemical composition (wt.%) of the SJ species reported by Roesijadi et al.⁸ was used in the present study. An upper limit of 400 kt/yr (dry basis) is set on the SJ supply. Three different optimization scenarios were investigated to gain greater insight into a macroalgae-based biorefinery.

Scenario 1 results

The optimal flowsheet of the base case is an integrated biorefinery producing both mixed acid and mixed alcohols. The optimal pathway is given in Fig. 2. It consists of anaerobic digestion, extraction followed by distillation, partial bypass and hydrogenation, venting carbon dioxide to the atmosphere, hydrogen purification via PSA, the distillation of mixed acid, the dehydration of mixed alcohols using molecular sieves followed by distillation, DDS purification, and WWT. In the integrated design, 30 wt.% of the concentrated VFAs are utilized to produce mixed acids, whereas the remaining VFAs are utilized to produce mixed alcohols. The NPV, TCI, and cost of manufacturing (COM) are \$27.65 MM, \$147.74 MM, and \$89.86 MM/yr, respectively.

The products obtained in this scenario are mixed alcohols, mixed acids, and DDS. Their production rates are given in Table

1. The biorefinery utilizes 400 kt/yr biomass. It produces 24 Mgal/yr mixed alcohols and 11 Mgal/yr mixed acids as main products and 111.8 kt/yr DDS as a byproduct. The CEs of the base case are 64 kt/yr.

Scenario 2 results

The optimal flowsheet obtained for this scenario is different from that for Scenario 1, as illustrated in Fig. 2. The optimal pathway obtained for mixed acids and mixed alcohols production is similar to that of the base case. Microalgae production was selected as the optimal pathway for carbon dioxide utilization. The optimal pathway of microalgae production includes cultivation in open ponds, harvesting by GS, and dewatering by HFMs followed by centrifuge were selected as optimal technologies. The products obtained in this scenario are mixed acids, mixed alcohols, DDS, and microalgae. Their production rates are reported in Table 1. In this scenario, a 90% reduction in net CEs was achieved relative to the base case. Only 6 kt/yr of carbon dioxide is released to the environment. This surplus can accommodate the possible variation in efficiency; otherwise, the carbon dioxide utilization will be too optimistic. In terms of process economics, the NPV of this scenario is 1.60 times higher than in the base case. The TCI and COM are \$215.34 MM and \$101.57 MM/yr, respectively.

Scenario 3 results

As indicated in Scenario 2, the NPV and CEs are improved by 160% and 90%, respectively, compared to the base case. However, these improvements are achieved by investing 1.46 times more than the capital investment in the base case.

Table 1. Mass balance summary of various scenarios for 400 kt/yr plant capacity.

Scenarios	Mixed acids (Mgal/yr)			Mixed alcohols (Mgal/yr)			Byproducts due to utilizing waste streams of biorefinery (kt/yr)	
	Ethanol	Propanol	Butanol	Acetic acid	Propanoic acid	Butyric acid	MA	DDS
1	14.00	6.00	4.00	6.00	3.00	2.00	0.00	111.8
2	14.00	6.00	4.00	6.00	3.00	2.00	28.17	111.8

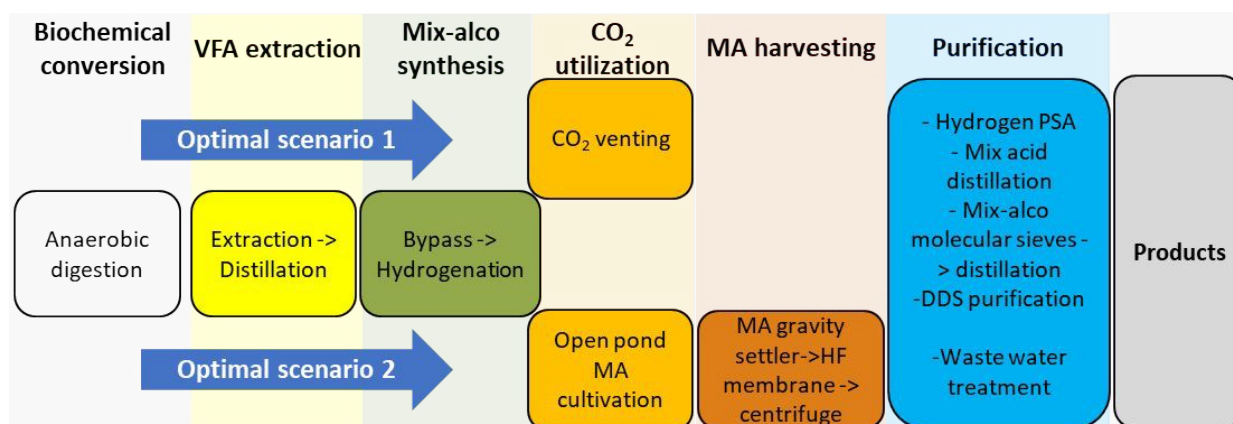


Fig. 2. Optimal pathway for various scenarios.

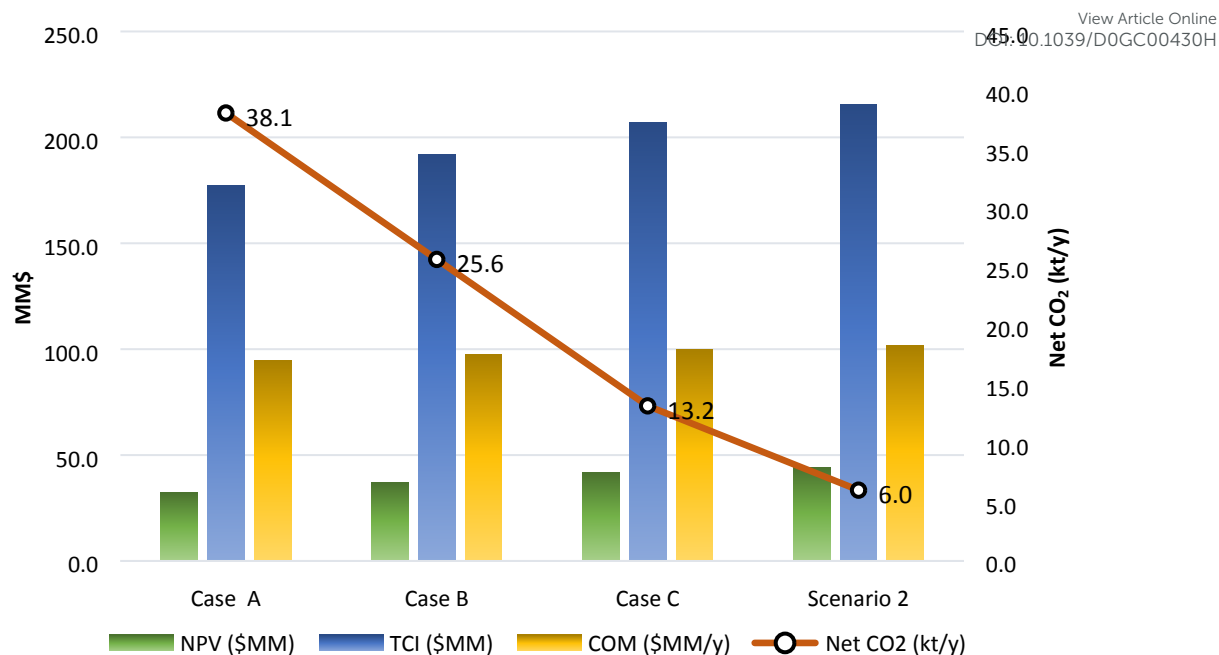


Fig. 3. Effect of investment on process economics (bars) and environmental performance (line with markers).

Therefore, it was of interest to investigate the effect of investment on the process economic and environmental performance of a sustainable biorefinery. As illustrated in Fig. 3, reducing the TCI budget by 17.6% (Case A) of the TCI in Scenario 2 increases the CEs by 6.32 times, and reduces the NPV by 37%. As investment increases in the remaining cases, the process economics and environmental performance start improving.

Optimal design

When all previous scenarios are compared, it can be seen that Scenario 2 is the most expensive process design: 46% more expensive than the base case and 4% more expensive than Case C. Despite a capital-intensive process design, Scenario 2 offers a 1.60-times higher NPV than the base case and a 1.06-times higher NPV than Case C. Moreover, Scenario 2 utilizes 12% more CEs than Case C. Based on the improved performance, Scenario 2 was selected as the optimal design. The topology of the optimal design is shown in Fig. 4. The overall product yield of anaerobic digestion was calculated to be 29%, which is 7% higher than the yield calculated by Dickson et al.²³ via an SP.

The total capital cost was calculated to be \$215 MM. The VFA section consumes 69% of the TCI owing to the large volume of mixed alcohols and mixed acids produced, whereas the MA section consumes 31% of the TCI, and its cost depends on the carbon dioxide evolved from anaerobic digestion. The total installed cost breakdown of the integrated biorefinery is shown in Fig. 5. Wastewater treatment, cultivation of microalgae, and anaerobic digestion and DDS production are the most dominant areas in terms of investment, with a 73% cumulative contribution.

The TCOM of the optimal design is \$101.57 MM/yr. The VFA section accounts for 89% of the TCOM, whereas the MA section accounts for only 11%. The TCOM breakdown is given in the

Supplementary Material. Variable costs are one of the main contributors to the total manufacturing cost and are dominated by raw material costs. The raw material costs of the VFA and MA sections account for 53% and 22% of the TCOM, respectively. The seaweed purchasing cost alone accounts for 35% of the TCOM. Utility costs are the second dominant factor in the TCOM. The total utility cost of the biorefinery is \$24.8 MM/yr. As already pointed out, the cost of seaweed is one of the biggest expenses, and accounts for up to 35% to the TCOM. Therefore, the MSP at which the NPV becomes zero was also calculated. The results in Table 2 indicate that the base case is more sensitive to changes in the price of seaweed. For example, if the seaweed price increases from \$90/t to \$104/t, the NPV of the base case decreases to zero. In contrast, the MSP for the optimal design is \$112/t for achieving zero NPV, which is 8% higher than that of the base case.

Table 2 shows that the MESP of the optimal design is \$1.17 /gal, which is 18% lower than the base case and 36% lower than the current wholesale price (\$1.82/gal) of ethanol. Moreover, the MESP obtained from the VFAP is 10.7% lower than the MESP reported by Dickson et al.²³ via SP. This demonstrates that the VFAP is superior to the SP. The calculated MESP of the optimal design is comparable with those reported in the other studies.^{26,44,45}

Table 2 Minimum selling and maximum purchasing price of ethanol and seaweed.

	MESP (\$/gal)	MSP (\$/ton)
Scenario 1	1.42	104
Scenario 2 (Optimal design)	1.17	112
Scenario 3 (Case A)	1.35	106
Scenario 3 (Case B)	1.27	110
Scenario 3 (Case C)	1.21	111

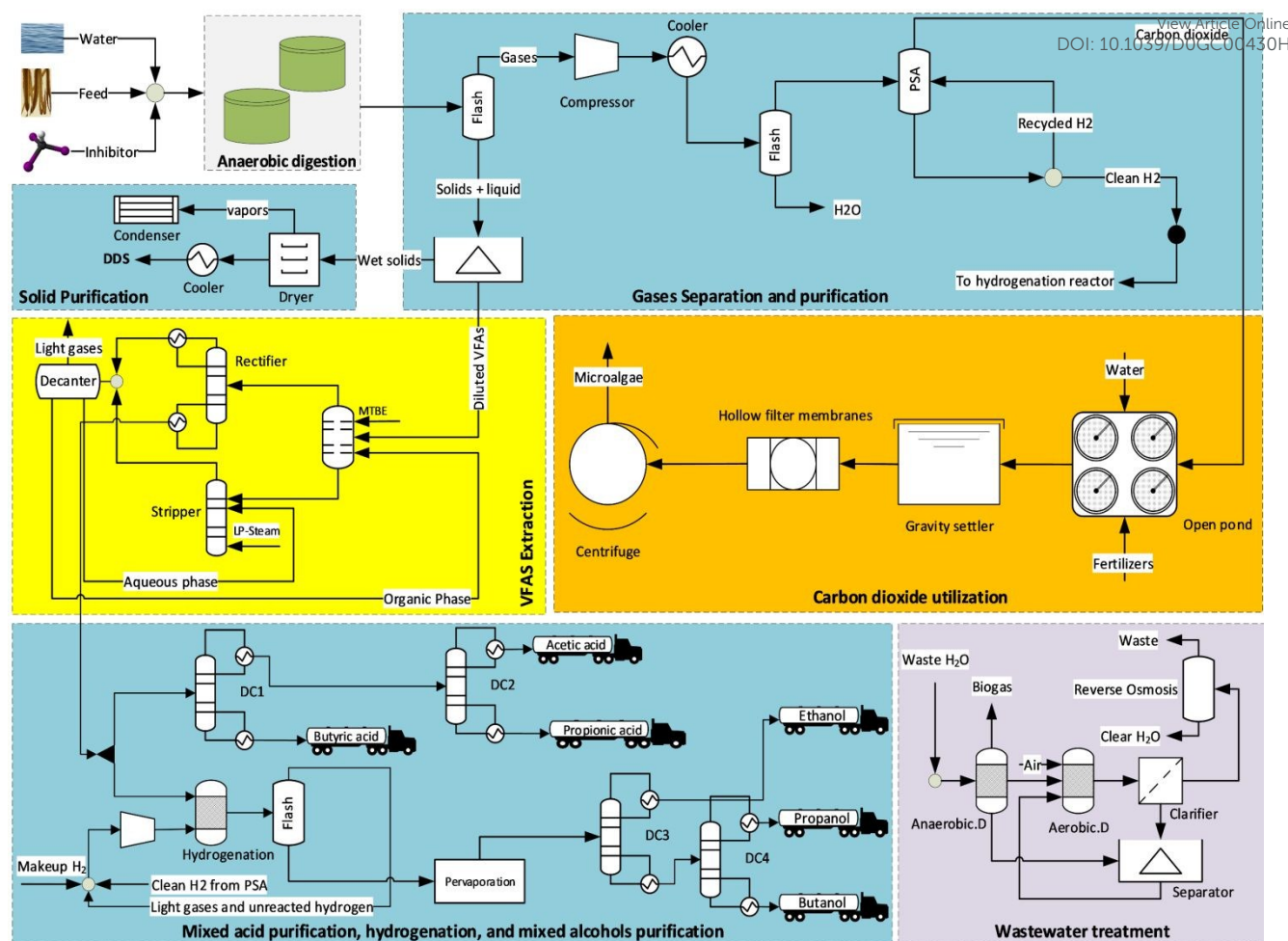


Fig. 4. Optimal biorefinery structure.

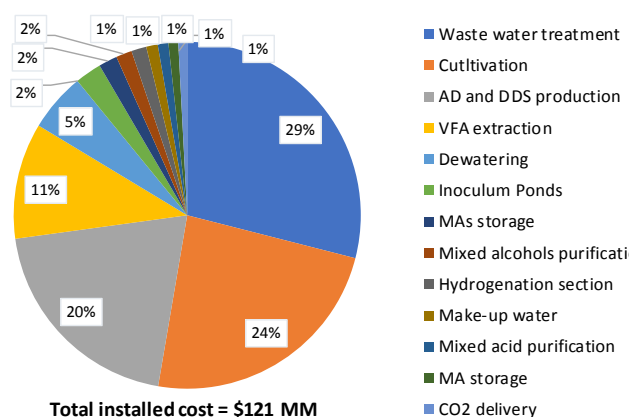


Fig. 5. Total installed cost breakdown of optimal design.

A better insight of promising economics can be obtained from the breakdown of MESP (Fig. 6), where a negative value indicates earnings from product sales while a positive value indicates expenses including capital and manufacturing costs. The sum of all values from each biorefinery area corresponds to MESP (\$1.17/gal). Results indicate that revenues from the sales

of mixed acids and mixed alcohols are the primary reason for the promising and cost-competitive price of fuel ethanol. This indicates that future biorefineries should produce high market value byproducts to maximize profit and economic viability. On the contrary, the capital recovery charge and raw material costs are found to be the main contributors to MESP.

Comparison of volatile fatty acid platform with sugar platform and methane platform (MP)

To compare the economic viability of the VFAP with the SP and the MP, a techno-economic assessment was performed for the SP and the MP at the plant scale of 400 kt/y. The detailed process description for the SP^{22,23} and the MP¹⁶ can be found in our previous publications, where the SP produces bioethanol and the MP produces renewable electricity. The direct comparison of the SP, VFAP, and MP, based on minimum product selling price is challenging because the nature of products (alcohols vs electricity) produced from the platforms is different. To present a fair comparison of the platforms, minimum product selling price per gasoline-equivalent was used as a key economic indicator. Calculated values of minimum product selling price for the SP, VFAP, and MP are \$2.00, \$1.79, and \$5.6/gal gasoline-equivalent, respectively. Results indicate

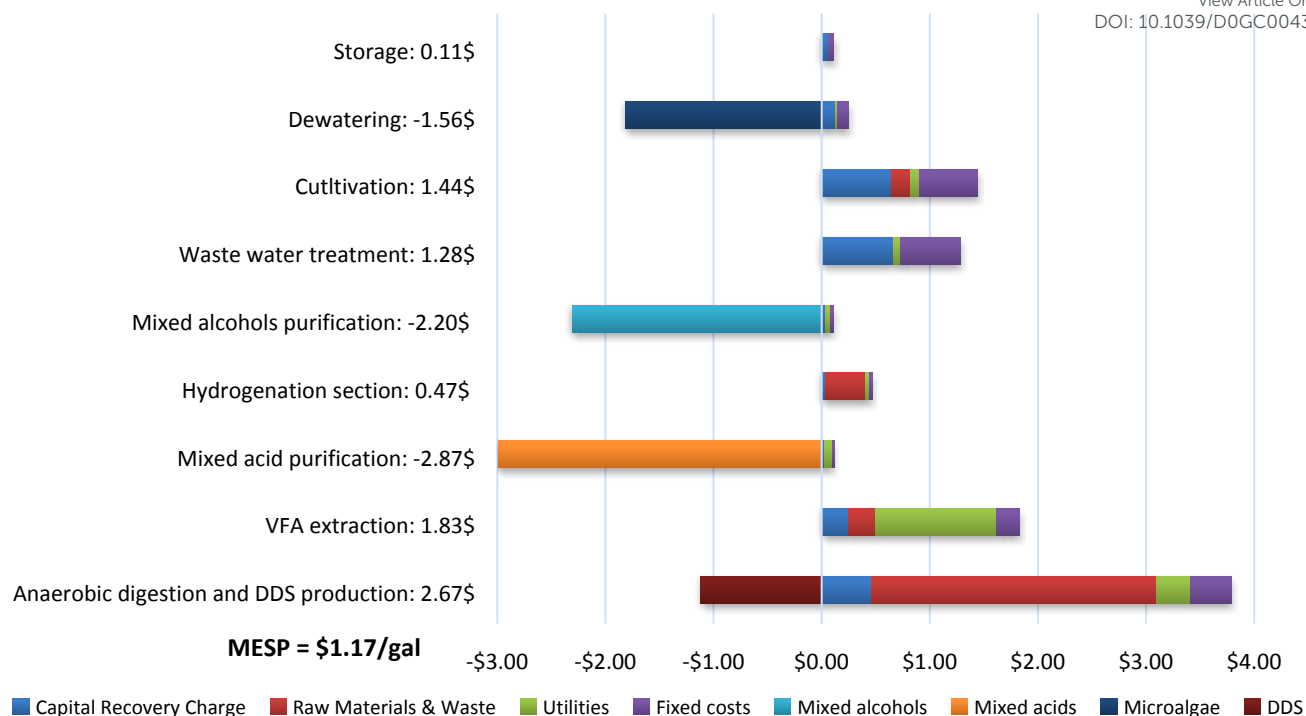


Fig. 6. Cost contribution details from each process area to MESP.

that the VFAP is economically more favourable because of high revenues from mixed acids and mixed alcohols.

Water consumption

The freshwater requirement is an important environmental factor in process sustainability. The results presented in Table 3 highlight that the overall freshwater consumption of the VFA section is 6.26 gal of water/gal of alcohols and acids. Approximately 73% of the overall water makeup is due to water evaporation in the cooling tower.

The water loss during microalgae production is higher than that from the VFA section owing to the evaporation of water from the pond surfaces. The water evaporation alone accounts for 90 wt.% of the total water loss. The total water requirement for the microalgae section is 157.7 t/h.

Table 3 Makeup water requirement of biorefinery.

Sections	Makeup water (t/h)	Freshwater consumption (gal of A ^a /B ^b)
VFA	103.7	6.26
Microalgae	157.7	9.52

a. A: water

b. B: mixed alcohols and acids

Sensitivity analysis

The optimization model also performs sensitivity analysis on 16 parameters of the biorefinery to evaluate the impact of key model parameters on the NPV. The investigated parameters are given in the tornado chart (Fig. 7) along with their limits and percentage variations.

The results indicate that fixed capital investment, the seaweed price, and the internal rate of return (IRR) are the most

important parameters for determining the economic viability of a biorefinery. As it is already indicated, 35% of the TCOM is due to the seaweed purchasing cost. When the seaweed purchasing price increases by 20%, the NPV decreases from \$44 MM to \$9 MM. Therefore, to ensure the economic viability of a seaweed-based biorefinery, efficient sea farming is necessary to increase the seaweed productivity. Indeed, several research projects including MARINER⁴⁶ and MAB4⁴⁷ are conducting research and development regarding advanced seaweeds cultivation and harvesting systems. The selling prices of ethanol and microalgae are critical parameters (as suggested by sensitivity analysis) for viable biofuel production.

Potential improvements to plant economics

The results of the sensitivity analysis suggest several potential improvements to plant economics. It is important to note that some of the biorefinery parameters—such as the market prices of the products—are based on the geographical and political situation, and therefore cannot be controlled. However, parameters related to biorefinery processing can be tuned, thereby providing room for further improvements.

Seaweed price (Goal 1)

The sensitivity analysis demonstrated that the biomass purchasing price is a key factor for determining the economic feasibility of a biorefinery. The base case price of dry biomass (\$90/t) includes the cost of macroalgae cultivation (80%) and transportation (20%).⁴⁸ The latter accounts for \$18/t of the total biomass cost. In other words, the cost of transporting biomass from the seaweed farm to the biorefinery is equal to \$7.2 MM/yr. If the location of the biorefinery is properly optimized

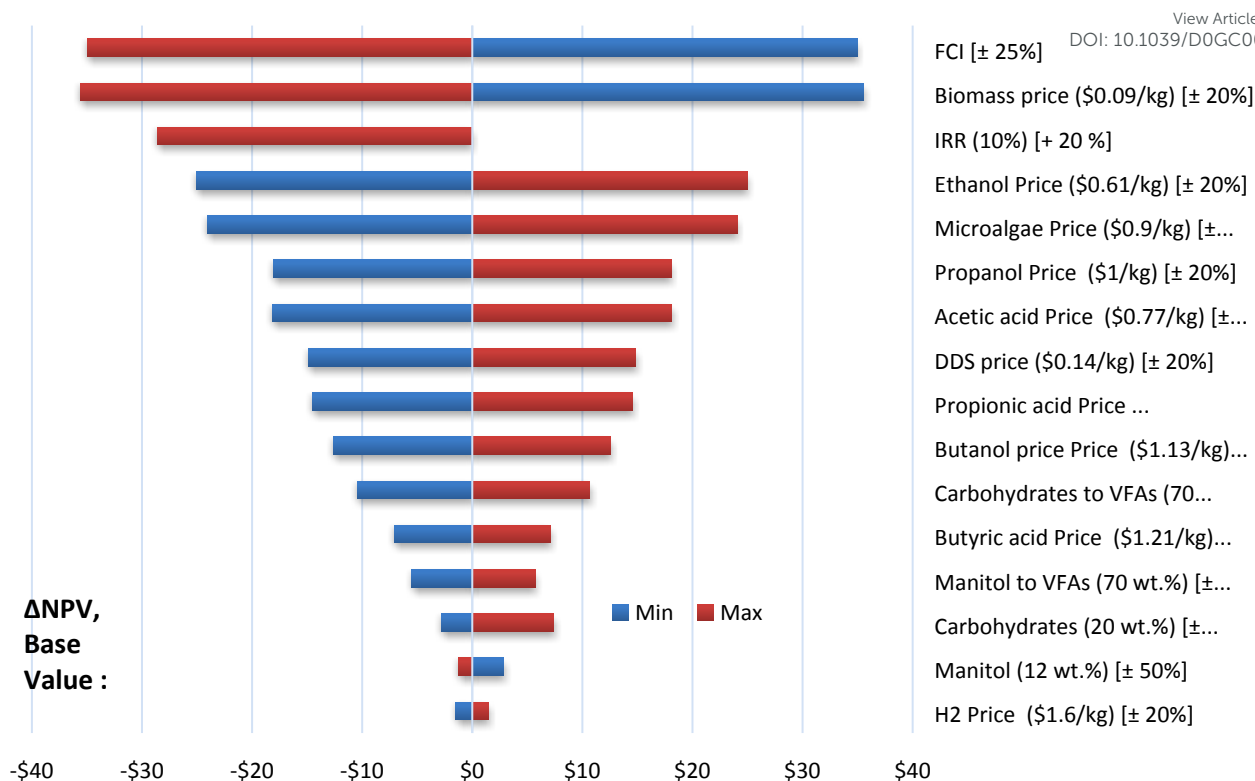


Fig. 7. Sensitivity analysis of biorefinery parameters.

the transportation cost can be reduced significantly. A 25% reduction in the transportation cost of biomass owing to optimized biorefinery location corresponds to \$84.5/t of dry feed. The results presented in Table 4 demonstrate that a 24.5% improvement in NPV can be achieved relative to the NPV of the optimal design.

Table 4 Effect of different goals on NPV.

	Base case	Goal 1	Goal 2
NPV	44.25	55.11	65.80
% improvement in NPV	0	24.5	48.7

Carbohydrates conversion (Goal 2)

Another important parameter of biorefinery processing is the conversion of carbohydrates to VFAs. In the present study, carbohydrates to VFAs conversion rate of 70 wt.% was assumed. Higher rates of carbohydrate conversion require the use of novel bioreactors such as multistage continuous high cell density reactors, in which the VFAs are extracted continuously with a solvent mixture. Once these targets are met and properly tuned, a marked improvement in performance of up to 0.5 g VFA/g of seaweed can be expected, as reported by Chang et al.³¹ By assuming a 10% increase in carbohydrate conversion to VFA, and combining this with goal 1, a 48.7% improvement in the NPV can be achieved.

Conclusions

The optimal design for the *Saccharina japonica* based biorefinery using the volatile fatty acid platform was

determined using a superstructure-based approach. To determine the optimal design, a rigorous process synthesis mixed integer non-linear model was developed that takes into accounts both process economics and the environmental impact. A techno-economic assessment indicated that the production of biofuels and value-added chemicals results in a minimum ethanol selling price of \$1.17/gal, which is 10.7% lower than the minimum ethanol selling price achieved through the sugar platform. When compared based on the minimum product selling price per gasoline equivalent, the VFAP allowed selling biofuel at price lower than that from the SP and the MP, at \$1.79/gal gasoline-equivalent compared to \$2.00 and \$5.6/gal gasoline-equivalent, respectively. The NPV of the optimal design is \$44 MM for a 20-year project life. An environmental assessment indicated that the optimal design achieves considerable emission reductions as it utilizes 90% of CEs produced by the biorefinery processing. The VFA section consumes approximately 6 gallons of water per gallon of mixed acids and mixed alcohols. A sensitivity analysis suggested a few goals that could improve the process economics of optimal design by up to 49%. Therefore, R&D on artificial seaweed cultivation is vital to increase the yield and lower the cultivation costs to make brown algae an economical and sustainable biomass resource for biofuels production. Furthermore, optimization of biorefinery location is crucial to decrease biomass transportation cost, and development of low energy and capital cost processes coupled with novel digester design are important targets for the improvement of the process economics.

Considering the general trend of increasing energy demand, the effort of diversifying energy supplying sources cannot be underestimated: more environment friendly energy sources should replace the existing climate change causing ones. At the same time the corresponding energy generation processes should be improved in terms of reducing the carbon emission. In order to transform the efforts into reality, the new energy sources and the associated energy generation processes should be economically competitive. There are much to be done in the evaluating their economic feasibility due to the existence of a large number of intermediate processing routes. The presented superstructure-based framework played an important role in the evaluation in the case of macroalgae based biorefinery. It can be further utilized in the decision-making framework of new energy systems.

Conflicts of interest

"There are no conflicts to declare".

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Notes and references

‡ Units

\$ = US dollar; ¢ = US cent; gal = US gallon; and t = metric tonne.

‡ ‡ List of acronyms

Carbon dioxide emissions (CEs)
Saccharina japonica (SJ)
 Volatile fatty acid platform (VFAP)
 Sugar platform (SP)
 Volatile fatty acids (VFAs)
 Dry distillery solid (DDS)
 Minimum ethanol selling price (MESP)
 Microalgae (MA)
 Mixed integer non-linear programming (MINLP)
 Net present value (NPV)
 Total capital investment (TCI)
 Total cost of manufacturing (TCOM)
 Maximum seaweed price (MSP)
 Wastewater treatment (WWT)
 Methyl tert-butyl ether (MTBE)
 Pressure swing adsorption (PSA)
 Gravity settler (GS)
 Hollow filter membranes (HFMs)
 Diffused air flotation (DAF)
 Electrocoagulation (ECA)
 Cost of manufacturing (COM)
 Methane platform (MP)

Internal rate of return (IRR)

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