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Simultaneous design of macroalgae-based integrated biorefineries and their heat exchanger network



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ABSTRACT

In this work we propose a model for the optimal design of macroalgae-based integrated biorefineries for the production of chemicals and biofuels, through superstructure generation including the simultaneous heat exchanger network (HEN). We formulate MINLP problems with sustainability (RePSIM) and economic (NPV) objective functions, respectively. As novelty, simultaneous design of the process and its HEN is carried out in a large-scale problem, with more than 50,000 continuous and 10,000 binary variables. Experimental data was obtained in our laboratory for brown algae conversion into sorbitol. Heat integration provides a reduction of 70.7% in utility costs with respect to the non-integrated case in NPV maximization. When RePSIM is the objective function, heat integration provides 2.3% increase, with 79.0% utility savings. Simultaneous Process and HEN design has proven to be efficient and robust, as well as a valid approach for energy savings in the optimal design of large-scale sustainable processes.

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1. Introduction

According to the United Nations (2019) was the second warmest year ever recorded and carbon dioxide (CO_2) levels and other greenhouse gases (GHG) reached record values in the atmosphere (United Nations, 2019). Although the decrease in anthropogenic activities during the COVID-19 pandemic have dropped global carbon dioxide emissions with little positive impact on the environment, this will presumably be temporary (Fyfe et al., 2021), and climate change remains as one of the greatest challenges faced by humanity.

Carbon dioxide atmospheric sequestration through Blue Carbon programs, based on increasing the organic carbon stored, has mainly focused on the conservation and restoration of seagrass, saltmarsh and mangrove ecosystems (Wu et al., 2020). However, the discussion of the role and potential of algae as a carbon sink in the Blue Carbon context still persists (Macreadie et al., 2019). Additional studies are required to know to which extent seaweed farming and wild harvest could contribute to climate change mitigation through carbon dioxide sequestration (Krause-Jensen et al., 2018).

* Corresponding author. *E-mail address:* sdiaz@plapiqui.edu.ar (H.A. Pedrozo). Both macroalgae and microalgae can produce biofuels and a vast array of high-value compounds used in pharmaceutical, nutraceutical and cosmetical industries (Suganya et al., 2016). Macroalgae can be sustainably harvested from the natural environment, while for microalgae it is not a feasible option. On the other hand, the growth of macroalgae is not carried out in photobioreactors and their cultivation is carried out in geographical regions where the environmental conditions are adequate

Macroalgae (or seaweeds) are a promising source of biomass, as alternative to the fossil-based production of chemicals, materials and biofuels in the circular bioeconomy context. Although there has been an increasing interest in the last decade, the number of scientific publications related to macroalgal biorefineries is still far from those focused on lignocellulosic biomass, which have technologies incompatible with macroalgal biomass processing (Kostas et al., 2021). The key advantages of macroalgae for sustainable bioproduction are: high growth rates which translates into high carbon dioxide sequestration, efficiency and biomass yields (Dickson and Liu, 2021), renewable biomass resource that do not compete with human food, no requirements for arable land and industrial fertilization (Øverland et al., 2019), less energy for biomass pretreatment due to lack of a recalcitrant lignocellulosic structure in cell walls (Kostas et al., 2021), presence of unique polysaccharides such as hydrocolloids, bioactive compounds and platform molecules (Alba and Kontogiorgos, 2019; Casoni et al., 2020), among others.



Nomenclature	Continuous
Acronyms	
AD anaerobic digester	C _{equip} St
CHP combined heat and power unit	C 12
DF dark fermentation	C _{land} in
DW dried weight	Criming Di
HENS heat exchanger network synthesis	Cworking W
HEN heat exchanger network	E CO
HPS high pressure steam	EC _u el
MINLP mixed-integer nonlinear programming model	Ec ec
NVS non-volatile solids	En ei
RePSIM renewable process synthesis index metric	F&F _A lo
SDG sustainable development goals	po
VS volatile solids	F&F _B ef
Indices	F CO
c index of cold streams	Fcp he
<i>h</i> index of hot streams	$HX_{h,c,k}$ he
j index of components	
k index of stages	
r index of reactants	HX ^{HU} by
u, u1, u2 index of units	W W
Sets	I to
<i>C</i> set of cold streams and cooling utilities	IT to
CU coldest cooling utility	JS jo
<i>H</i> set of hot streams and heating utilities	M CO
HU hottest heating utility	NPV ne
J components	P pi
ST set of stages	RM CO
U CONDITIONAL UNITS	So so
U_u, U_u subsets of units that define the connection between units	
UNR pop-reactive units	
U^R reactive units	IIT ne
Daugua ataun	V _{rec} re
Purumeters RM big M parameter	W CO
$C_{\rm ext}$ carbon tax	dt _{h,c,k} te
Comment annualized coefficient	h
ECR_{ii} energy consumption ratio per unit of mass flowrate	dt_h^{CU} te
relative to unit <i>u</i>	tr
$U_{h,c}$ heat transfer coefficient for the match of hot stream	at _c te
h and cold stream c	f m
U_h^{CU} heat transfer coefficient for the hot stream h with	$J_{u1,u,j}$ III
the extreme utility	St
$U_c^{(10)}$ heat transfer coefficient for the cold stream c with	q_{h}^{CU} co
the extreme utility	a_c^{HU} he
Greek letters	$t_{h,k}$ te
α_0 fixed cost associated with heat exchanger units	t _{c,k} te
α_1 and α_2 parameters of the capital cost correlation	Binary varie
β_h cost of the heating utility h	v _u bi
p_{CU} cost of the bottest beating	le
β_{HU} cost of the cooling utility c	z _{h c k} bi
β_c cost of the cooling utility c	st
θ interest rate	th th
$\xi_{u,r,i}$ mass coefficient for component <i>j</i> from the main	z_h^{CU} bi
reactant <i>r</i> in reactive unit <i>u</i>	st
au project life	WHU
φ_1 tax contingency factor	
φ_2 grass-root factor	SL
Dig-M parameter	vv
52 Dig-IVI parameter	

Continuo	us variables
В	CO ₂ mitigation due to by-products
C_{equip}	sum of the equipment cost
Cgeneral	general cost
Cland	land cost
C _{manu}	manufacturing cost
C _{piping}	piping and instrumentation cost
C _{working}	working capital
E	CO_2 emissions due to the energy consumption
EC_u	electrical energy consumption
EC En	economic pillar
EN F&F	loss of food production for using land for other pur-
IGIA	noses
F&F₽	effect of fuel vs food competence
F	CO_2 emissions related to the fertilizers,
Fcp	heat capacity flow rate of streams
$HX_{h,c,k}$	heat exchanger cost corresponding to the match of
	hot stream h and cold stream c at stage k
HX_h^{CU}	heat exchanger costs of the match of hot stream h
	with utilities
HX_c^{HU}	heat exchanger costs of the match of cold stream <i>c</i>
	with utilities
l IT	total investment
	total income from sales
JS М	JODS generation for the main product
NPV	net present value
P	production cost
RM	CO_2 emissions associated with raw materials
So	social pillar
T ⁱⁿ	input temperature of stream
T ^{out}	output temperature of stream
T _{income}	income taxes
UT	net annual profit or losses
V _{rec}	recovery value at the end of the project
W	CO ₂ emissions derived from water consumption
$dt_{h,c,k}$	temperature approach of the match between the
ьсц	hot stream h with the cold stream c at the stage k
at_h^{co}	temperature approach of the not stream <i>n</i> with ex-
d+HU	temperature approach of the cold stream c with ex
ul _c	treme utilities
f.	molar flowrate from unit $u1$ to u of component i
Ju1, u, j	heat exchanged between the hot stream <i>h</i> and cold
чп,с,к	stream <i>c</i> in the stage <i>k</i>
q_{h}^{CU}	cooling utilities for hot stream <i>h</i>
q_c^{HU}	heating utilities for cold stream c
t_{hk}	temperature of hot stream at hot end of stage k
$t_{c,k}$	temperature of cold stream at hot end of stage k
Rinary va	riables
V.	binary variable which is equal to one if unit u is se-
yu	lected and zero otherwise
Zh a h	binary variable which is equal to one when the hot
- <i>n</i> ,c, <i>k</i>	stream h exchanges heat with the cold stream c at
	the stage k and zero otherwise
Z_{h}^{CU}	binary variable which is equal to one when the hot
п	stream <i>h</i> requires extreme utilities, and zero other-
	wise
z_c^{HU}	binary variable which is equal to one when the cold
	stream <i>c</i> requires extreme utilities, and zero other-
	wise

The brown algae Macrocystis (Giant kelp) is a member from the Order Laminariales (Class Phaeophyceae) widely distributed throughout the cold temperate water of the Southern and Northern hemispheres (Macaya and Zuccarello, 2010). Alginate is the main commercial product from brown algae and constitutes the most abundant carbohydrate (about 30 %) of Macrocystis biomass in dry weight. Together with Laminaria hyperborea and Ascophyllum nodosum, Macrocystis pyrifera is used for alginate commercial production in USA, Japan, China, France, and Norway (Gomez et al., 2009). Driven by the search for sustainable biotechnologies and biomass valorization, research has been carried out on the use of *M. pyrifera* biomass for the production of bioactive compounds (Leyton et al., 2020), functional food (Díaz et al., 2017), biogas (Fan et al., 2015; Vergara-Fernandez et al., 2008), bioethanol (Camus et al., 2016), hydrogen and volatile fatty acids (Zhao et al., 2017), among other products.

In Argentina, *M. pyrifera* is the major component of the kelp forests (Boraso et al., 2006), and it is distributed along more than 4800 km of the Patagonian coast (including provinces of Río Negro, Chubut, Santa Cruz and Tierra del Fuego). Nevertheless, due to the agricultural livestock tradition, these resources are not currently exploited. There are local experimental studies for sustainable *M. pyrifera* extraction (Boraso de Zaixso et al., 1982) and regulatory legislation for seaweed exploitation (Law 3273, Santa Cruz; Law 939, Chubut).

Advanced biorefineries such as the ones that produce third generation biofuels, aim to explore the use of algal biomass as feedstock in order to produce biofuels, biomaterials and biochemicals. Bathia et al. (2020), states that even though third generation biorefineries have many advantages than other biorefineries, more investment needs to be focused on research to reduce production costs. In this sense, we decided to further study a macroalgae biorefinery based on the current status of macroalgal biomass for third generation biorefineries (Gonzalez-Gloria et al., 2021).

In this work, we address the optimal design of an integrated biorefinery, potentially based on macroalgae, and its heat exchanger network (HEN) through a superstructure optimization approach. To the best of our knowledge, simultaneous optimal design of a macroalgae biorefinery and HEN of a large-scale problem, with more than 50,000 continuous and 10,000 binary variables including more than 500 potential stream matches, has not been addressed in the literature. The objective is to sustainably produce a platform molecule (isosorbide) and derived chemicals, biogas and fertilizers (Casoni et al., 2020; Ramos et al., 2021), as well as biohydrogen through dark fermentation. Different processes are included downstream isosorbide for high value-added chemicals. In this integrated biorefinery, M. pyrifera and Lessonia vadosa are used as potential renewable feedstock, together with corn starch. L. vadosa is a species belonging to the order Laminariales that is part of the assemblage of the kelp forests of the Argentinean Patagonia. The model includes experimental data obtained in our laboratory from the acid hydrolysis of algae biomass samples collected in Ushuaia (Tierra del Fuego, Argentina). The resulting model is a mixed-integer nonlinear programming (MINLP) problem and we consider two alternatively objective functions: the Renewable Process Synthesis Index Metric (RePSIM), developed by Martín (2016) to address sustainability assessment, and Net Present Value (NPV). The superstructure embeds four major sections: (1) Sorbitol Production, (2) Isosorbide Production, (3) Isosorbide Conversion, and (4) Biofuels and Fertilizers Production. As energy consumption is one of the highest operating costs (Kong et al., 2017; Pedrozo et al., 2021), the superstructure also includes a Heat Exchanger Network Synthesis (HENS) model, based on Yee and Grossmann (1990). Algal-based integrated biorefineries are one of the most promising options to achieve some of the United Nations Sustainable Development Goals (SDG) and to move forward to circular bioeconomy (Espinosa et al., 2008; García Prieto et al., 2017). Numerical results show that the proposed MINLP models constitute useful tools to evaluate the sustainable production based on unexploited renewable coastal resources in the context of holistic zero waste biorefinery approach (Rajak et al., 2020).

2. Materials and methods

2.1. Algae hydrolysis and sorbitol quantification

In order to hydrolyze the algal carbohydrates, we have modified the experimental procedure presented by Ravanal et al. (2017) as follows: dried biomass samples were mixed with sulfuric acid (2 % m/m) in a 0.05 biomass-to-acid rate. The reactions were performed at 121°C for 15 min under a nitrogen atmosphere (90 psi) in a 50 mL stainless steel reactor (Parr 4848).

Sorbitol and other saccharides quantification was carried out through gas chromatography coupled with mass spectrometry (GC-MS Perkin Elmer, CLARUS 500). Peak identification was carried out using NIST MS library with global matches higher than 800. Peaks with lower signal than 1% were not considered. Chromatographic conditions were: injector 260°C, Split 1:15 and column: Elite-5MS (60 m, 0.25 mm ID and 0.25 lm df). The samples were derivatized before the analysis, applying the silylation procedure proposed by Ravanal et al. (2016). For this, after the reaction completion, the supernatant was neutralized with CaCO₃. Then, an aliquot of 1 mL was mixed with 1 mL of acetone and evaporated at 60°C under a nitrogen atmosphere. Next, 1 mL of pyridine was added to redissolve the hydrolyzed carbohydrates. Finally, the solution was mixed with 0.5 mL of BSTF (N,O-Bis(trimethylsilyl)trifluoroacetamide) and 0.1 mL of TMCS (Trimethylchlorosilane) and the mixture was incubated at 60°C during 20 min.

2.2. Thermo-gravimetric analysis

Raw and hydrolyzed algae were characterized through Thermo Gravimetric Analysis (TGA) to determine volatile solids and nonvolatile solids content. The analyses were carried out using TA Instrument Discovery- TGA 5500 equipment. Before each analysis, the scale was purged for 20 min with nitrogen. Next, approximately 10 mg of biomass were heated at 10°C.min⁻¹ from room temperature to 900°C under an inert atmosphere. It is worth noting that final solid residue in TGA varies with heating rate, which could affect volatile and non-volatile fractions since these parameters depend on operating conditions. In this case, the variation in the final solid yield among heating rates is most slight. Hereby, it was considered that the values obtained at 10°C/min are representative.

3. Process description

The integrated biorefinery includes four main sections: sorbitol production, isosorbide production, isosorbide conversion, and biofuels and fertilizers production. We consider the possibility of including a two-stage process for hydrogen (H_2) and methane (CH₄) sequential production. Hydrogen is produced by dark fermentation (DF) in the first-stage, while methane is produced by anaerobic digestion (AD) in the second-stage. In this approach, the hydrolysis and acidogenesis in the first stage are separated from acetogenesis and methanogenesis, carried out in the second stage (Kumar et al., 2021). A detailed description of biohydrogen, methane, and fertilizers production processes is provided in Section 3.4. This section presents a brief description of process alternatives embedded within the superstructure (Fig. 1). For a detailed description



Fig. 1. Simplified superstructure of process alternatives showing the four considered sections: Sorbitol Production, Isosorbide Production, Isosorbide Conversion, and Biofuels and Fertilizers Production Potential products of the integrated biorefinery are shown in bold. Chloride acid and methanol are byproduct.

of the production technologies see Casoni et al. (2020). The potential processing routes are: macroalgae for chemicals production with biofuels and fertilizer production considering potential sorbitol sale (40 routes), macroalgae for chemicals production without biofuels and fertilizer production considering potential sorbitol sale (10 routes), corn starch for chemicals production considering potential sorbitol sale (5 routes), chemicals production from commercial sorbitol (4 routes). The superstructure for integrated biorefinery systems includes 59 alternative possible process designs.

3.1. Sorbitol production

In the first step, two brown macroalgae species biomass are considered as raw material for sorbitol (sugar) production, *M. pyrifera* and *L. vadosa*, as well as corn starch. An additional embedded alternative is directly purchasing sorbitol from market suppliers.

Two different streams are obtained after the acid hydrolysis of macroalgae biomass. The aqueous one is initially treated to neutralize the remaining acid and sent to an exchange column to isolate sorbitol, which is then processed in the isosorbide production section. The hydrolyzed solid, mainly composed of proteins, lipids and ashes, is fed to the biofuels and fertilizers production section (Fig. 3).

In the case of corn starch as raw material, it is hydrolyzed and saccharified into glucose to be finally hydrogenated to obtain sorbitol. Directly purchasing sorbitol from market suppliers does not involve any pretreatment process step.

3.2. Isosorbide production

The sorbitol stream is transformed into a platform molecule, isosorbide. The process stream is purified by distillation, and then liquid-phase dehydration of sorbitol to isosorbide is carried out in the presence of a sulfated zirconia catalyst. Next, xylene is used to promote impurities precipitation and, therefore, purified isosorbide is obtained and fed to the isosorbide conversion section (Fig. 3).

3.3. Isosorbide conversion

This process step involves isosorbide transformation into four potential products:

- (1) Vasodilator drug (isosorbide dinitrate, ISDN) used in the treatment of coronary artery diseases (Khazanie et al., 2016). The isosorbide stream reacts with nitric and a sulfuric acid mixture and it is then washed with water to precipitate the ISDN. After a filtration step for recovering the desired product, the drug is mixed with ethanol for dissolution and crystallization and it is finally filtered to obtain the final product.
- (2) Flame-retardant precursor for safety materials manufacture (Sheth et al., 2020). This precursor can be obtained by a polycondensation reaction between isosorbide and a phosphorus-containing monomer such as phenyl phosphonic dichloride. It is worth mentioning that this reaction also generates chloride acid as a byproduct. In this process, methanol is required to remove impurities generated when the polycondensation reaction occurs.
- (3) Isosorbide-based precursor for polyester polymers (Lomelí-Rodríguez et al., 2018). It is produced by mixing and heating isosorbide with succinic acid using titanium (IV) n-butoxide as a catalyst. Here, methanol purification is also required before a centrifugation step to obtain the final product.
- (4) Biosolvent applied in pharmaceutical additives and in personal care products (dimethyl isosorbide, DMI) (Aricò et al., 2017). The dimethyl isosorbide production process involves mixing isosorbide with dimethyl carbonate and a catalyst based on a Mg and Al mixed oxide that can be synthesized calcinating hydrotalcite. After a distillation operation process, the biosolvent is obtained as the main product, while methanol is a byproduct.



Fig. 2. Biofuels and fertilizers section simplified superstructure.

3.4. Biofuels and fertilizers production

Fig. 2 shows a simplified superstructure for the biofuels and fertilizers section. The hydrolyzed biomass for both *M. pyrifera* and *L. vadosa* contains volatile (VS) and non-volatile (NVS) solids, which can be harnessed to directly produce methane and fertilizers in an anaerobic digestor (AD). In this case, methane and carbon dioxide are produced, based on the amount of VS entering the AD (0.3222 g CH₄ /g VS; 0.2148 g CO₂ /g VS) (Casoni et al., 2020; Ramos et al., 2021). Methane is sent to a combined heat and power unit (CHP) to generate electricity and heat power. Furthermore, the AD unit produces fertilizers as a byproduct in a 0.95:1 fertilizer-to-NVS ratio

We have also embedded the possibility to include a dark fermentation (DF) step prior to the AD. In this unit, 0.004 g H_2/g VS (Ding et al., 2020) can be generated and sold at 1.76 \$/kg (He and You, 2015). This process produces 0.164 g CO₂ /g VS (Cooney et al., 2007), considering a VS conversion of 21.31 % (Zhang et al., 2017). The non-converted VS along with the NVS are sent to the AD unit for further transformation. It is worth mentioning that the fertilizer-to-NVS ratio, which is 0.95:1 respectively, remains constant even if a DF step exists upstream the AD. Conversely, methane and carbon dioxide generation parameters differ according to the selected scheme. In this sense, when the process stream goes through a DF step, Ding et al. (2020) reported 0.202 g CH₄ /g VS and Cooney et al. (2007) suggested a conversion of 0.164 g CO₂ /g VS in the AD. As the previous alternative (hydrolyzed solid fed to AD), methane is intended for the production of heat and electric power in the CHP unit.

An additional feed stream of raw *M. pyrifera* to this section has also been included, in the case that energy production turns out to be less than 20 % of the total consumed energy in the entire process. This value is incorporated as a model constraint to meet the Argentinean Law 27191, which sets that at least 20 % of the total consumed electrical energy must be renewable. The raw macroalgae biomass can follow the two different paths described hereinabove concerning methane generation and the potential hydrogen production. If this alternative is selected, a thermal pretreatment at 121°C is required prior to the AD process, rendering biomass compositions of 0.799 g VS/g DW (Ding et al., 2020) and 0.201 g NVS/g DW (Ohlsson et al., 2020).

4. Mathematical model

We formulate a mixed-integer nonlinear programming (MINLP) problem, implemented in GAMS 35.2.0 (McCarl et al., 2016), to determine the optimal design of an integrated macroalgal based biorefinery. The model superstructure includes the integrated process and its heat exchanger network design.

Equations for the integrated biorefinery model include: mass and energy balances, equipment design calculations, capital cost correlations, mixed-integer constraints, and objective function definition. Mass balances for nonreactive units are formulated as shown in Eq. (1)

$$\sum_{u1\in UI_u} f_{u1,u,j} = \sum_{u2\in UO_u} f_{u,u2,j} \ j \in J, \ u \in U^{NR}$$
(1)

where $f_{u1,u,j}$ is the flowrate from unit u1 to u of component j; Ul_u and UO_u are unit subsets that define the connection between units.

 $UI_u = \{u1 : u \text{ has input flowrate from } u1\}$

 $UO_u = \{u2 : u \text{ has out put flowrate to } u2\}$

In case of reactive units, mass balances are as follows,

$$\sum_{u2 \in UO_u} f_{u,u2,j} = \sum_{u1 \in UI_u} f_{u1,u,j} + \sum_{r \in R_u} \left(\xi_{u,r,j} \sum_{u1 \in UI_u} f_{u1,u,r} \right) j \in J, \ u \in U^R$$
(2)

where $\xi_{u,r,j}$ corresponds to the mass coefficient for component *j* from the main reactant *r* in reactive unit *u*. This coefficient is positive for products and negative for reactants. It should be noted that main reactor models are formulated as yield-based models based on experimental data, where process operating temperature is fixed, therefore they are considered as parameters in the model.

The electrical energy consumption (EC_u) in process units is determined through linear functions, as shown in Eq. (3).

$$EC_u = ECR_u \cdot \left(\sum_{u1 \in UI_u} \sum_{j \in J} f_{u1,u,j} \right) u \in \left\{ U^{NR} \cup U^R \right\}$$
(3)

where ECR_u is the energy consumption ratio per unit of mass flowrate relative to unit *u*. Mass and energy coefficients are taken from Casoni et al. (2020) and are provided in the Supplementary Material.

Conditional units are associated with binary variables in the superstructure through Big-M formulations. The corresponding mixed integer constraints are formulated as follows

$$\sum_{u2\in UO_u}\sum_{j\in J} f_{u,u2,j} - BM.y_u \le 0 \ u \in U^C$$

$$\tag{4}$$

where y_u is the binary variable associated with the selection of conditional unit u; and BM is a big M parameter. It should be noted that output flowrates of conditional units u are forced to be zero when the binary variable y_u is equal to zero.

Regarding equipment design equations and capital cost correlations, we include standard capital cost models from the literature (Casoni et al., 2020; Ramos et al., 2019; Ulrich and Vasudevan, 2004) and are provided in the Supplementary Material.

4.1. Objective function

We formulated two MINLP problems with different objective functions. In the first design problem, Net Present Value (NPV) is maximized to focus the analysis on a detailed economic evaluation of the integrated biorefinery and its heat exchanger network. NPV is calculated as shown in Eq. (5.1), where I denotes the total investment; UT is the net annual profit or losses; V_{rec} is the recovery value at the end of the project. We consider an interest rate (θ) of 15 % and a project lifespan (τ) of 20 years. As shown in Eq. (5.2), total investment (I) includes the sum of equipment cost (C_{equip}) , considering tax contingency factor ($\varphi_1 = 1.18$) and a grassroot factor (φ_2 = 1.3), land cost (C_{land}), piping and instrumentation cost (C_{piping}), and the working capital ($C_{working}$). Regarding Eq. (5.3), the net annual profit (UT) takes into account revenues from products and by-products sales (IT), manufacturing cost (Cmanu), general cost ($C_{general}$), and income taxes (T_{income}). The recovery value is calculated based on selling the equipment units, and the working capital, as shown in Eq. (5.4).

$$NPV = -I + UT \frac{(1+\theta)^{\tau} - 1}{\theta(1+\theta)^{\tau}} + \frac{V_{rec}}{(1+\theta)^{n}}$$
(5.1)

$$I = C_{equip}(\varphi_1 + \varphi_2) + C_{land} + C_{piping} + C_{working}$$
(5.2)

$$UT = IT - \left(C_{manu} + C_{general} + T_{income}\right)$$
(5.3)

$$V_{rec} = C_{working} + 0.2I \tag{5.4}$$

In the second MINLP, the Renewable Process Synthesis Index Metric (RePSIM) (Martín, 2016) is maximized to evaluate the sustainability of the integrated biorefinery. This objective function includes economic (Ec), environmental (En), and social pillars (So), as shown in Eq. (6.1). The economic pillar is shown in Eq. (6.2) and considers the production cost (P) and the annualized investment $(I \cdot C_{annual})$. As shown in Eq. (6.3), the environmental pillar is weighted with the carbon tax (C_{CT}) and takes into account CO_2 mitigation of the main product (M), CO_2 mitigation due to byproducts (B), CO_2 emissions related to the fertilizers (F), CO_2 emissions associated with raw materials (RM), CO₂ emissions due to energy consumption (E), and CO_2 emissions derived from water consumption (W). Finally, the social pillar has three terms: jobs generation (JS), the loss of food production for using land for other purposes ($F \& F_A$) and the effect of fuel vs food competence ($F \& F_B$) (see Eq. (6.4)).

$$RePSIM = Ec + En + So \tag{6.1}$$

$$Ec = -P - I(C_{annual}) \tag{6.2}$$

$$En = (M + B - F - RM - E - W)C_{CT}$$
(6.3)

$$So = JS + (F\&F_A + F\&F_B) \tag{6.4}$$

 CO_2 mitigation due to the main product is considered in the term *M*, which accounts for the mitigation effect of replacing current fossil-based fuels, power and chemicals by renewable based ones on carbon dioxide emissions.

$$M = Prod.Capacity . C_F . C_M$$
(6.5)

where C_M is a factor related to carbon dioxide mitigation, C_F is the correction factor when a fossil based chemical is substituted by a renewable one. C_F is 1 when the chemical is produced from renewable resources. *Prod.Capacity* is the amount of chemical produced in the process in kg/y.

It should be noted that the conventional fossil-based production routes were not considered within this model since the traditional route involves corn-starch as raw material and the consecutive production of sorbitol. The traditional route for sorbitol production is bio-based, and the base case is to use sorbitol as raw material to produce high-value products. Therefore, we considered the production of the chemicals from sorbitol ($C_{M0} = 0$). In this sense, the other C_M values are obtained by calculating the difference between the net CO₂ emissions of the base case and the corresponding one. In particular, we consider that the macroalgae can be harvested in ten days through boats. In this sense, we calculate the amount of CO_2 emitted due to the engine combustion. The starch and sorbitol CO₂ emissions data were obtained from the Ecoinvent database (Wernet et al., 2016). Then, the C_M values were calculated by differences considering the sorbitol-based production emissions as the base case. It should be noted that final products yield factors (kg prod/kg macroalgae) were taken into account in this C_M calculation.

Byproduct mitigation is considered in the term B for producing others chemicals or fuels as byproducts within the process, as shown in Eq. (6.6). Similar to M, the factors C_B computes the kg of CO₂ mitigated per kg of byproduct. A detailed explanation of the RePSIM environmental pillar can be found in the Supplementary material.

$$B = ByProduct \ . \ C_B \tag{6.6}$$

4.2. Heat exchanger network

This work addresses simultaneous biorefinery and heat exchanger network design, as proposed in Yee et al. (1990) and Yee and Grossmann (1990). According to the consulted literature, simultaneous optimal design of a macroalgae biorefinery and HEN has not been applied to a large-scale problem like the one addressed in this work (50482 constraints, 49530 continuous variables and 10640 binary variables), with variable stream flowrates, which constitutes a novelty in this work. Kong and Maravelias (2018) provide the first approach addressing simultaneously the design of a chemical process and the complete HEN problem, where the most complex case study includes 1660 constraints, 1035 variables, and 256 binary variables. We include multiple utilities for both, heating and cooling. So, the coldest cooling utility and the hottest heating utility are referred to by using the superscript CU and HU, respectively; while the other utilities are included as hot or cold streams. In this way, the set H includes both hot streams and heating utilities, while the set C comprises cold streams as well as cooling utilities.

Furthermore, we formulate the design problem considering fixed stream temperatures based on the available data of process operating conditions (Casoni et al., 2020). This simplification reduces the number of model variables. However, process streams are variables in the optimization process, and this fact significantly increases the number of continuous variables and nonlinear matrix entries in the model. Thus, there is an increase in the complexity of the problem, as compared to the case of the sequential heat exchanger network design (Yee and Grossmann, 1990).

Eqs. (7.1) and (7.2) are overall heat balances for hot and cold streams, respectively.

$$Fcp_h(T_h^{in} - T_h^{out}) = \sum_{k \in ST} \sum_{c \in C} q_{h,c,k} + q_h^{CU} h \in H$$

$$(7.1)$$

$$Fcp_c(T_c^{in} - T_c^{out}) = \sum_{k \in ST} \sum_{h \in H} q_{h,c,k} + q_c^{HU} \ c \in C$$

$$(7.2)$$

where Fcp is the heat capacity flow rate of streams; T^{in} and T^{out} are the input and output temperatures of streams, respectively; $q_{h,c,k}$ is the heat exchanged between the hot stream h and cold stream c at stage k; q_h^{CU} and q_c^{HU} are cooling and heating utilities for hot and cold streams, respectively.

Eqs. (8.1) and (8.2) are heat balances at stage k. For hot streams, the coldest cooling utility can be used after the last stage (Eq. (8.3)), while the hottest hot utility for cold streams can be submitted before the first stage (Eq. (8.4)).

$$Fcp_h(t_{h,k} - t_{h,k+1}) = \sum_{c \in C} q_{h,c,k} \ k \in ST, \ h \in H$$

$$(8.1)$$

$$Fcp_{c}(t_{c,k}-t_{c,k+1}) = \sum_{h \in H} q_{h,c,k} \ k \in ST, \ c \in C$$
 (8.2)

$$Fcp_h(t_{h,NOK+1} - T_h^{out}) = q_h^{CU} \ h \in H$$
(8.3)

$$Fcp_c(T_c^{out} - t_{c,1}) = q_c^{HU} \ c \in C$$

$$(8.4)$$

where $t_{h,k}$ and $t_{c,k}$ are the temperature of hot and cold streams at hot end of stage k. It should be noted that the left-hand side of Eqs. (8.1) and (8.2) are nonlinear since in the process synthesis problem, process stream flowrates are variables, as well as stage temperatures. This is an important difference from the case presented in the literature (Yee and Grossmann, 1990), where the synthesis of heat exchanger network is carried out sequentially for a fixed process flowsheet.

Eqs. (9.1) and (9.2) are input temperature assignments for hot and cold processes, respectively; while Eqs. (9.3)–(9.6) impose monotonic decrease in temperature throughout each stage.

$$T_h^{in} = t_{h,1} \ h \in H \tag{9.1}$$

$$T_c^{in} = t_{c,NOK+1} \ c \in C \tag{9.2}$$

$$t_{h,k} \ge t_{h,k+1} \ k \in ST, h \in H \tag{9.3}$$

$$t_{c,k} \ge t_{c,k+1} \ k \in ST, \ c \in C \tag{9.4}$$

$$T_h^{out} \le t_{h,NOK+1} \ h \in H \tag{9.5}$$

$$T_c^{out} \ge t_{c,1} \ c \in C \tag{9.6}$$

Logical constraints (10.1)–(10.3) are included using binary variables *z* to force heat loads to be zero when the corresponding match is not selected.

$$q_{h,c,k} - \Omega \, z_{h,c,k} \le 0 \, k \in ST, c \in C, h \in H \tag{10.1}$$

$$q_h^{CU} - \Omega \, z_h^{CU} \le 0 \ h \in H \tag{10.2}$$

$$q_c^{HU} - \Omega \ z_c^{HU} \le 0 \ c \in C \tag{10.3}$$

where $z_{h,c,k}$ is the binary variable that is equal to one when the hot stream h matches the cold stream c at stage k and equal to zero otherwise; z_h^{CU} and z_c^{HU} are binary variables that are equal to one when the hot stream h and the cold stream c require extreme external utilities, respectively, and equal to zero otherwise.

Binary variables are also included to activate constraints (11.1)–(11.4) related to the calculation of temperature differences.

$$dt_{h,c,k} \le t_{h,k} - t_{c,k} + \Gamma(1 - z_{h,c,k}) \ k \in ST, \ c \in C, \ h \in H$$
(11.1)

$$dt_{h,c,k+1} \le t_{h,k+1} - t_{c,k+1} + \Gamma(1 - z_{h,c,k}) \ k \in ST, \ c \in C, \ h \in H \quad (11.2)$$

$$dt_h^{CU} \le t_{h,NOK+1} - T^{CU,out} + \Gamma\left(1 - z_h^{CU}\right) h \in H$$
(11.3)

$$dt_c^{HU} \le T^{HU,out} - t_{c,1} + \Gamma\left(1 - z_c^{HU}\right) c \in C$$
(11.4)

where $dt_{h,c,k}$ is the temperature difference corresponding to the hot stream *h* and the cold stream *c* match at the stage *k*; dt_h^{CU} and dt_c^{HU} are the temperature differences between hot stream *h* and cold stream *c* with extreme external utilities, respectively.

In this work, we address the estimation of global heat transfer coefficients based on process stream compositions, which constitutes a novelty, especially considering that there are more than 500 potential matches in the HEN. It should be noted that heat transfer coefficients accurate calculation based on flow and fluid properties is not addressed, as this approach is usually avoided in predesign evaluations (Ulrich and Vasudevan, 2004). Therefore, heat transfer coefficients approximate values are considered suitable for the model formulation, and these values obtained from industrial experience are generally appropriate for final process designs due to fouling phenomena (Perry and Chilton, 1973). Heat exchanger capital costs are evaluated using capital cost correlations (Ulrich and Vasudevan, 2004) as shown by Eqs. (12.1)–(12.3).

$$HX_{h,c,k} = \alpha_1 \left(\frac{q_{h,c,k}}{U_{h,c} (dt_{h,c,k} dt_{h,c,k+1} 0.5 (dt_{h,c,k} + dt_{h,c,k+1}))^{\frac{1}{3}}} \right)^{\alpha_2} \\ k \in ST, c \in C, h \in H$$
(12.1)

$$HX_{h}^{CU} = \alpha_{1} \left(\frac{q_{h}^{CU}}{U_{h}^{CU} \left(\left(T_{h}^{out} - T^{CU,in} \right) dt_{h}^{CU} 0.5 \left(\left(T_{h}^{out} - T^{CU,in} \right) + dt_{h}^{CU} \right) \right)^{\frac{1}{3}} \right)^{\alpha_{2}} h \in H$$
(12.2)

$$HX_{c}^{HU} = \alpha_{1} \left(\frac{q_{c}^{HU}}{U_{c}^{HU} \left(\left(T^{HU,in} - T_{c}^{out} \right) dt_{c}^{HU} 0.5 \left(\left(T^{HU,in} - T_{c}^{out} \right) + dt_{c}^{HU} \right) \right)^{\frac{1}{3}} \right)^{\alpha_{2}} c \in C$$
(12.3)

where $HX_{h,c,k}$ is the heat exchanger cost corresponding to the hot stream h and cold stream c match at stage k; HX_h^{CU} and HX_c^{HU} are the heat exchanger cost of the hot stream h and cold stream c with their respective external utilities; and α_1 and α_2 are parameters corresponding to capital cost correlations. Furthermore, global heat transfer coefficients, $U_{h,c}$, U_h^{CU} , U_c^{HU} have been calculated based on Ulrich and Vasudevan (2004) for all the potential process stream matches, taking into account their composition. They are reported in the Supplementary Material.

Thus, the heat exchanger network capital cost (*HENC*) is calculated as shown in Eq. (13), while the total utility cost is given by Eq. (14), as follows,

$$HENC = \sum_{k \in ST} \sum_{c \in C} \sum_{h \in H} \left(\alpha_0 z_{h,c,k} + H X_{h,c,k} \right) + \sum_{h \in H} \left(\alpha_0 z_h^{CU} + H X_h^{CU} \right)$$
$$+ \sum_{c \in C} \left(\alpha_0 z_c^{HU} + H X_c^{HU} \right)$$
(13)

$$TUC = \beta_{CU} \sum_{h \in H} q_h^{CU} + \beta_{HU} \sum_{c \in C} q_c^{HU} + \sum_{k \in ST} \sum_{c \in C} \sum_{h \in H^U} \beta_h q_{h,c,k}$$
$$+ \sum_{k \in ST} \sum_{c \in C^U} \sum_{h \in H} \beta_c q_{h,c,k}$$
(14)

where α_0 corresponds to fixed cost associated with heat exchanger units; β_{CU} and β_{HU} stand for the coldest cooling and the hottest heating utility costs, respectively; β_h and β_c are the heating utility *h* and the cooling utility *c* costs, respectively.

5. Results and discussion

5.1. Experimental results: macroalgae hydrolysis and TGA

Although *M. pyrifera* and *L. vadosa* hydrolysis produced several monosaccharides, sorbitol was the most abundant in both cases. Relative percentages, determined through GC-MS, are shown in Table 1. Experimental conversion was around 70 % wt. with both species.

Sorbitol was quantified by means of a calibration curve in GC-MS following the same silylation protocol. Sorbitol concentrations of 0.45 g sorbitol/g DW and 0.39 g sorbitol/g DW were obtained from *M. pyrifera* and *L. vadosa* hydrolysis, respectively.

When performing Thermo Gravimetric Analysis (TGA), it was determined that *M. pyrifera* hydrolyzate had 0.643 g VS/g DW and 0.357 g NVS/g DW while *L. vadosa* hydrolyzate had 0.756 g VS/g DW and 0.244 g NVS/g DW. These values are incorporated as parameters in the biorefinery model proposed in this work.

Table	I			
Main	mono	saccharides	produced	from
brown	algae	hydrolysis in	n Area %.	

	M. pyrifera	L. vadosa
Sorbitol	76.3	70.9
Fucose	8.5	7.4
Mannose	2.6	16.1
Xylose	3.4	-
Glucose	9.1	-
Galactose	-	1.1
Talose	-	2.4

5.2. Numerical results

In this case study we consider a fixed production of 920 t/y of sorbitol, taking into account current market demand. The model is implemented in a personal computer with an Intel® Core[™] i7-4700 K processor, operating at a CPU frequency of 3.6 GHz, and with 8 Gb RAM. The model is formulated in GAMS 35.2.0 (McCarl et al., 2016) and solved using DICOPT, with CONOPT and CPLEX as nonlinear and linear sub solvers, respectively (Grossmann et al., 2003). SBB solver was also used to solve the model; nevertheless, no solution was found in one hour of CPU time. The MINLP model corresponding to the simultaneous process and heat exchanger network design has 50,482 constraints, 49,530 continuous variables and 10,640 binary variables. The problem size increases significantly when the equations for HENs are included, i.e., the initial process design problem has around 5337 constraints, 5399 continuous variables and 13 binary variables. There are 23 potential streams of each kind, hot and cold, and 20 stages were considered for heat integration. This fact largely increases the number of binary variables. It should be noted that we cannot guarantee a global optimal solution due to the problem non convexity, but we obtained a high-quality local solution as it is discussed in the following sections.

As a first step, we solve the optimal design problem for both process and heat exchanger network, maximizing the project net present value (NPV). To get further insights on the environmental and social aspects, we next solve the problem maximizing RePSIM.

5.2.1. Net present value (NPV) maximization

In the first case, optimization results provide an objective function value (NPV) of 44.6 MM\$ in a CPU time of 67 s, and the optimal scheme includes sorbitol production from *M. pyrifera* and its further valorization through the conversion to dimethyl-isosorbide (DMI), the biosolvent for pharmaceutical and personal care industries (Fig. 3). These results are in agreement with previously reported results (Casoni et al., 2020).

As it has recently been mentioned in literature (Ding et al., 2020; Kumar et al., 2021), macroalgae could be an efficient source for hydrogen production. However, this process is not selected in the optimal scheme, as shown in Fig. 3. This result is associated with the low hydrogen productivity from biomass (0.004 g H_2/g VS), while it represents additional equipment units. Numerical results indicate that energy obtained from AD through methane provides 48 % of the required electric energy and 94 % of the required thermal energy for the integrated DMI production plant.

To assess the impact of simultaneous heat exchanger network synthesis in process design, we carry out a comparison with an optimal base case that does not include the optimal design of the heat exchanger network, and the one that includes it. It must be pointed out that the base case only uses external utilities to satisfy heating or cooling requirements. Table 2 shows the corresponding results. Although the reduction in the NPV objective function is only around 1 %, significant utility savings are achieved since its corresponding annual cost decreases by 70.7 %. Furthermore, it

Table 2

Comparison of numerical results for optimal biorefinery scheme with simultaneous HEN design and without HEN design for NPV maximization.

	Without HEN	With HEN	Difference
NPV (MM\$)	44.2	44.6	0.9 %
Utilities (\$/y)	97596	28626	-70.7 %
Capital cost (\$)	4,58,485	452026	-1.4 %
N° of matches	19	19	0.0 %
Utilities matches	19	9	-52.6 %

is important to note that the optimal scheme including the HEN synthesis provides a decrease in capital cost of the heat exchanger network of 1.4 %. The number of heat exchangers in the network is the same in both cases, however, when including HENS, the number of matches with utilities decreases in 52.6 %. Thus, the optimal solution can improve both fixed and variable costs related to the heat exchanger network.

Fig. 4 shows the heat exchanger network corresponding to the optimal scheme. From the 23 potential streams of each kind, it includes ten hot streams and nine cold streams. It should be noted that stream splitting is not taken into account since this operation is not always attractive from the practical point of view (Biegler et al., 1997). Although intermediate utilities such as low and medium pressure steam are considered as available, only high-pressure steam (HPS) is selected as hot utility in the optimal configuration. In this case study, HPS cost is 10 % higher than the low-pressure steam (LPS) cost, the least expensive hot utility (see Supplementary Material). It should be noted that LPS could be used in units such as HX1, HX2, HX37, HX38 and HX43 (due to minimum temperature difference).

The selection of HPS is associated with its high temperature, which allows for reducing the heat exchanger area in the corresponding matches, and consequently, the capital cost. This result indicates that the formulated model can find suitable trade-off solutions between the capital and operating cost. On the contrary, sequential approaches based on the heuristic rule of minimizing the utility cost first, could not find this process design. For instance, using LPS in the heat exchangers HX1, HX2, HX37, HX38 and HX43 reduces the utility cost in 20.4 %, but the capital cost associated with the HEN increases in 8.3 %, and consequently, the NPV values reduces in 0.4 %.

Even though utility savings allow for a reduction of 70.7 % in the corresponding annual cost, its impact over the NPV is low (see Table 2). This outcome is related to raw material costs, which constitute the main contribution to direct expenses (87 %); whereas total utility costs are around 1.5 % of direct expenses. Particularly, cooling and heating utilities represent 0.8 % of direct expenses.

5.2.2. Renewable process synthesis index metric (RePSIM) maximization

As a second step, considering RePSIM as the objective function, optimization results provide a value of -4.25 MM\$/y in 137 s, selecting *M. pyrifera* as raw material for sorbitol production, and its further conversion into isosorbide dinitrate (ISDN), the vasodilator drug. These results are also in accordance with previous work (Casoni et al., 2020). It is worth mentioning that the RePSIM metric is developed aiming at positive values for sustainable processes. Therefore, the present process has a satisfactory performance with a RePSIM value close to zero (Martín, 2016).

Hydrogen production via dark fermentation (DF) is, again, not selected. Although this byproduct improves the environmental pillar of RePSIM, numerical results indicate that this improvement does not offset the worsening of the economic pillar, mainly due to the increase in investment cost. Results show that 49 % and 100



Fig. 3. Integrated biorefinery optimal configuration for NPV maximization.

% of electric and thermal energy, respectively, are produced in the combined heat and power cycle (CHP) through methane from biogas. It is important to note that not only does the incorporation of AD allow for obtaining green energy, but it is also a way to recycle biomass nutrients from the digestate (mainly phosphorus and nitrogen).

We also assess the influence of simultaneous process and HEN design in RePSIM maximization through a comparison with a base case without heat integration. Table 3 shows that the objective function value increases 2.3 % in the case with simultaneous biore-finery and HEN design. Utility requirement reduction is quite important (79.6 %), nearly 9 percentage points higher, as compared to NPV maximization. At the same time, capital cost increases by 18.1 % with respect to the base case. Due to the tradeoff between

Table 3

Comparison of numerical results for optimal biorefinery scheme with simultaneous HEN design and without HEN design with ReP-SIM objective function.

	Without HEN	With HEN	Difference
RePSIM (MM\$/y)	-4.35 1 14 780	-4.25 23422	2.3 %
Capital cost (\$)	311410	367707	18.1 %
N° of matches Utilities matches	16 16	16 10	0.0 % -37.5 %

capital and variable costs, numerical results show that utilities are more relevant in the objective function than capital cost. It should be noted that both the production costs (P) and the consumed energy (E) increase as external utilities do, and these variables are



Fig. 4. Heat exchanger network for simultaneous biorefinery and HEN design (Objective function: NPV). Hot streams: red arrows moving from right to left. Cold streams: blue arrows moving from left to right. HPS: high pressure steam. CW: cooling water. RU: refrigeration utility.

Table 4RePSIM pillars comparison.

	Without HEN	With HEN	Difference
Economic (MM\$/y)	-6.47	-6.48	-0.2 %
Environmental (MM\$/y)	-0.217	-0.179	17.5 %
Social (MM\$/y)	2.336	2.41	3.2 %

important factors for the economic and the environmental pillars of the RePSIM function, respectively. Regarding the number of heat exchangers, the same number (16) is obtained with and without HENS, however, the former case can reduce matches with utilities in 37.5 %.

Considering that the objective function RePSIM has three pillars, we analyze the contribution of each one, and compare the results of the base case in which the macroalgae biorefinery is designed without its HEN and the case with simultaneous design of process and HEN, as shown in Table 4. It can be seen that the economic pillar is the most important factor. These results are in agreement with Casoni et al. (2020), where we suggest that economics overly weights, at the expense of the environmental and social terms. Its contribution is always negative since it includes production and investment costs. Consequently, RePSIM value is usually negative. Nonetheless, it is worth mentioning that the present process design is also profitable as its NPV is positive with a value of 27.8 MM\$.

Regarding the comparison with the optimal base case, there is a negligible difference in the economic pillar. On the contrary, there is a significant improvement in the environmental performance, mainly due to consumed energy savings. The social pillar also improves when the HEN is simultaneously designed with the integrated macroalgae biorefinery. The analysis of utility savings over RePSIM improvement is similar to the case of using NPV objective function. For the ReP-SIM optimization problem, utility cost represents 1.9 % of direct expenses, whereas cooling and heating utilities represent 0.97 % of direct expenses, so the actual impact on the objective function is positive. This fact is important because energy savings continue to be a challenge that macroalgae integrated biorefineries must face in order to reduce utility costs, to improve energy recovery and to augment the process sustainability. HENS has been performed on other biorefinery optimal designs producing a higher impact over the selected objective function (Belletante et al., 2020; Yuan et al., 2013). A similar reduction in heating and cooling utilities requirement (about 63 %) was reported by other authors that applied sequential heat integration techniques to an integrated biodiesel refinery (Kastritis et al., 2012).

It is also important to note that the algorithm proposed in the present work allows for the simultaneous process and heat exchanger network synthesis, and this approach has been proven to have a better performance than the sequential one (Escobar and Trierweiler, 2013; Quirante et al. 2018).

We also analyze the breakdown of the environmental pillar, which considers both CO2 mitigation and emissions, for the macroalgae refinery plant producing ISDN. As we described in Section 4.1, this pillar includes CO₂ mitigation of the main product (M) and by-products (B), CO_2 emissions due to fertilizer use (F), CO₂ emissions of raw materials (RM), CO₂ emissions due to energy consumption (E), and water consumption (W). In order to define a base case for comparison purposes, Fig. 6 also shows CO₂ mitigation and emissions related to the corn-based ISDN production since the conventional route to produce sorbitol is from this raw material. It is observed that CO₂ mitigation due to the main product of the algae-based biorefinery is 80 % higher than the value corresponding to the corn-based biorefinery. Even more, the macroalgae based-plant has CO2 mitigation due to by-products and macroalgae production does not require fertilizers, which has CO₂ emissions associated with it. The CO₂ emissions of raw material increase in 4 % for the macroalgae-based biorefinery, but its CO2 emissions of energy consumption are reduced in 72 %, as compared to the corn-based plant. As an advantage of the conventional route, its CO₂ emissions due to water consumption are negligible. As a global result, not only does macroalgae feedstock prevent the use of food as raw material, but it also provides a reduction of 7 % in carbon dioxide emissions, as compared to the conventional route.

5.2.3. Cost breakdown of DMI and ISDN production plants

In this section we present a revenue and cost breakdown for both chemical production plants described previously. The main products of the biorefinery plants are DMI and ISDN corresponding to the results from NPV and RePSIM maximization cases, respectively.

Table 5 shows the breakdown of revenues and costs associated with the optimal process design of DMI and ISDN production plants. Revenues from DMI biorefinery is higher than the one obtained by the optimal scheme if RePSIM is employed as an objective function (ISDN production). Despite ISDN production level overtake in 22 % the one achieved by the DMI plant (803 t/y vs 656 t/y), the DMI international selling price is 92 % higher with respect to the ISDN selling price. It is also observed that fertilizer's profit is the same for both cases since its production mass flowrate is directly linked to the macroalgae flowrate that enters the anaerobic digester (AD). It should be noted that sorbitol production capacity is fixed at 920 t/y and *Macrocystis pyrifera* strain is selected for both biorefinery designs, then the fertilizers production is the same in both plants.

Regarding the costs, numerical results of Table 5 show that DMI biorefinery manufacturing expenses are approximately 1 MM\$/y

Table 5

Revenues and	costs bi	reakdown i	for	both	chemical	production	plants.
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	Values for NPV maximization $(\$/y)$	Values for RePSIM maximization (\$/y)
1. Revenues	17409281	11432000
1.1. DMI	16418430	0
1.2. ISDN	0	10440960
1.3. Fertilizers	953181	953181
2. Manufacturing expenses	3841000	2777000
2.1. Direct expenses	3342000	2411000
2.1.1. Raw materials	2698000	1901000
2.1.2. Supervisory labor	29000	25000
2.1.3. Maintenance and repairs	228000	153000
2.1.4. Operating supplies	23000	15000
2.1.5. Laboratory charges	29000	25000
2.1.6. Utilities	51242	44756
2.1.7. Operating labor	285000	247000
2.2. Indirect expenses	499000	366000
3. General expenses	711000	511000
3.1. Administrative cost	68000	53000
3.2. Distribution and selling	433000	308000
3.3. Research and development	211000	150000
4.4. Income taxes	3515000	2213000



Fig. 5. (a) Raw materials cost breakdown for DMI optimal production from *M. pyrifera* (process and heat exchanger network simultaneous design). (b) Raw materials breakdown for ISDN production from *M. pyrifera* (process and heat exchanger network simultaneous design).



Fig. 6. RePSIM metric environmental pillar breakdown for ISDN optimal production from *M. pyrifera* and from corn starch. See Section 4.1 for terms description. Green arrows: CO_2 mitigation. Red arrows: CO_2 emissions.

higher than the ones corresponding to ISDN plant. This major difference is mainly attributed to raw material costs, which are 42 % higher for the DMI production plant (NPV maximization). General expenses of the DMI production plant, which are calculated as a percentage of the total cost (Ulrich and Vasudevan, 2004), are approximately 0.1 MM\$/y higher than the general expenses of the ISDN biorefinery. Those results are in agreement with selection of ISDN production for RePSIM maximization case study since the economic pillar of this objective function considers the production cost and is the most important contributor (see Table 4).

Finally, income taxes (calculated as a function of the net profit) are 59 % higher for DMI biorefinery, as compared to ISDN biorefinery. Despite DMI costs are higher than ISDN ones (38 %), revenue differences are substantially larger for DMI production (52 %), resulting in higher income taxes for the biorefinery scheme obtained for NPV maximization case study.

It is also worth mentioning that DMI production cost is 6.92 \$/kg for the optimal pathway simultaneously optimizing process and HEN. The international selling price for DMI is 25 \$/kg (Alibaba, 2021). The production costs breakdown indicates that raw materials constitute the main contribution to production costs with 59.4 %. The raw materials cost breakdown is presented in Fig. 5 (a) and shows that DMC contributes in 50 %. ISDN production cost is 4.09 \$/kg for the optimal configuration considering simultaneous process and HEN design, while the international selling price for ISDN is 13 \$/kg (Alibaba, 2021). For this pathway, the production cost breakdown shows that raw materials represent 58 %. Furthermore, raw materials cost breakdown shown in Fig. 5 (b) indicates that HNO₃ contributes 67 %.

6. Conclusions

The present work proposes MINLP models for addressing the sustainable production of chemicals, materials, biofuels and fertilizers from macroalgae using NPV and RePSIM, respectively, as objective functions. The superstructure includes the integrated biorefinery and its heat exchanger network. To the best of our knowledge, this is the first-time simultaneous optimal design of a macroalgae biorefinery and its HEN is carried out in a challenging problem, with more than 50,000 continuous and 10,000 binary variables and more than 500 potential stream matches, with variable stream flowrates.

Dimethyl-isosorbide (DMI) and isosorbide dinitrate (ISDN) are the optimal alternatives when solving MINLPs with NPV and ReP-SIM objective functions, respectively. International selling prices for both chemicals produced from corn starch (food-based production) are significantly higher than our optimal production costs, which highlights this project profitability, as well as its sustainability. The simultaneous process and heat exchanger network design through superstructure optimization allowed for energy savings of 70.7 % and 79.6 % when considering NPV and RePSIM objective functions respectively. Thus, the simultaneous approach has demonstrated to be efficient and robust. Furthermore, when analyzing the impact over RePSIM, environmental and social pillars improve in 17.5 % and 3.2 % respectively. The total plant energy (thermal and electrical) obtained from the anaerobic digestion are 70 % and 74 % for NPV and RePSIM cases, respectively. Not only do these results reflect the potential of brown macroalgae as feedstock for green energy production, but they pave the way to an integrated biorefinery with zero waste. In both plants, fertilizers are produced in the same way as nature recycles nutrients. These fertilizers will be available to be used in algae or higher plant cultures, allowing for the replacement of industrial ones which are less sustainable.

Current work focuses on formulating a water network design problem involving wastewater treatment and volatile solid valorization from dark fermentation to address hydrogen production in this scenario.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

H. Alejandro Pedrozo: Software. Andrés I. Casoni: Software, Investigation, Writing – original draft, Writing – review & editing. Fernando D. Ramos: Software, Investigation, Writing – original draft, Writing – review & editing. Vanina Estrada: Software, Investigation, Writing – original draft, Writing – review & editing. Maria Soledad Diaz: Conceptualization, Investigation, Methodology, Supervision, Funding acquisition, Project administration, Writing – review & editing.

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Supplementary materials

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