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A Systematic Multicriteria-Based Approach to Support Product Portfolio Selection in Microalgae Biorefineries

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Abstract: This work proposes and applies a sequential approach of objective methods to aid the decision-making process for the deployment of microalgae biorefineries. The strategy combines Multicriteria Decision Analysis (MCDA) and weight assignment methods to simultaneously consider technical, economic, and environmental criteria to (1) outrank the best bioproduct options from different biomass fractions present in microalgae biomass at different ratios (namely carbohydrates, lipids, and protein) and (2) define the most suitable biorefining pathways associated with specific pairings of microalgae strains and cultivation conditions. The first part of the assessment identified succinic acid, acrylic acid, and citric acid as the top-ranked bioproducts from carbohydrates, polyurethane from lipids, and thermoplastic extrusion co-feed from protein. The second step of the analysis determined that, when production of a hydrocarbon fuel is desired, the compositional profile of a strain is paramount in defining the biorefining setup that should be pursued. In summary, microalgae lipids should be sent to the production of hydrocarbon fuels if the ratio between neutral lipids and fermentable carbohydrates is higher than roughly 1, with carbohydrates and protein being converted to the higher-value products noted above. Finally, this result was corroborated through process simulations, which indicated superior economic and environmental metrics when strains are paired with suitable conversion pathways identified through MCDA based on their compositional profiles. The outcomes of this work provide clear, objective, guidelines for establishing the best biorefining approach for a large suite of biochemical compositions as a screening method prior to employing detailed process simulations alongside rigorous techno-economic and life-cycle assessments.

Keywords: Multicriteria decision analysis; Decision-making; Microalgae; Biorefinery; Bioproducts

33	No	
34	1,3-PDO	1,3-propanediol
35	1,4-BDO	1,4-butanediol
36	AFDW	ash-free, dry weight
37	AHP	Analytical Hierarchy Process
38	CAP	Combined Algae Processing
39	CRITIC	Criteria Importance through Inter-criteria Correlation
40	DHA	docosahexaenoic acid
41	DISCOVER	Development of Integrated Screening, Cultivar Optimization, and Verification Research
42	EPA	eicosapentaenoic acid
43	ESI	Electronic Supplementary Information
44	EVA	ethylene-vinyl acetate
45	FAME	fatty acid methyl esters
46	GGE	gallon of gasoline equivalent
47	GHG	greenhouse gases
48	LCA	life-cycle assessment
49	LEAPS	Laboratory Environmental Algae Pond Simulator
50	MBSP	minimum biomass selling price
51	MCDA	Multicriteria Decision Analysis
52	PHA	polyhydroxyalkanoates
53	PROMETHEE	Preference Ranking Organization Method for Enrichment Evaluation
54	RFS	Renewable Fuel Standard
55	SMB-IX	simulated moving bed ion exchange
56	TEA	techno-economic assessment
57	TRL	Technology Readiness Level

58

59 1. Introduction

60 Biobased feedstocks such as cellulosic biomass and microalgae, are poised to play a significant role in a
 61 global-scale biobased and carbon-efficient economy. Microalgae, thanks to their high areal and solar yield,

are an innovative novel crop with the advantage of being metabolically plastic, thus being capable of switching compositional profiles between mainly protein, carbohydrate, or lipids in response to cultivation conditions. While one of the central aspirations of large-scale implementation of microalgae biorefineries is the production of biofuels, selling higher-value coproducts appears as an essential precondition to make the industrial facility economically attractive at current algal biomass production costs [1-3]. For that, conversion concepts that enable full biomass utilization are viewed as the most favorable options to help reduce processing costs through the creation of a diversified product portfolio. In this way, the exploitation of microalgae biomass should be designed to maximize the value obtained from any given compositional profile [4-7]. As such, a combination of attractive specific microalgae strains could be preferred to enhance the economic benefits of a large-scale biorefinery [2], which also enables further efforts tied to metabolic engineering and tailoring of species.

As the diversity of microalgae strains and their compositional plasticity yield a wide array of products of industrial interest, ranging from carboxylic acids, alcohols, polyurethane, and protein meal to pigments and biofuels [8-12], the selection of product portfolios for biorefinery design is an important step in the pathway to deploying microalgae-based biorefineries in the future. Until present, most studies focused on detailing process conditions of fixed biorefinery configurations for a given or tailored compositional profile solely from an economic standpoint [13-15] (a valuable approach that could be complemented by other features), while other efforts encompassed economic and environmental metrics to delineate microalgae biorefineries [16-19]. The study presented herein proposes that additional aspects should be considered to select the most advantageous bioproducts obtainable from microalgae biomass, thus blending multiple technical, economic, and life-cycle facets into the analysis. Since it's virtually impossible that a particular product attains the desirable "optimum" outcome for each metric of interest, the selection of options through outranking offers a solution when a traditional optimization procedure is not possible or when a large number of variables prevents the problem from being solved experimentally or computationally. In this way, the effective conversion of microalgae biomass makes for a great test case to examine whether a product suite can be objectively selected. A suitable set of tools for such efforts, Multicriteria Decision Analysis (MCDA) encompasses a series of consolidated methodologies for the outranking of alternatives within the field of operational research - the branch of applied mathematics dedicated to supporting decision-making. MCDA approaches have already been applied to myriad problems in water management, business and financial management, chemistry, logistics and transportation, and social issues, among others [20], with a few studies being centered specifically on the production of renewable fuels and products [21-27]; in the realm of microalgae biofuels, MCDA techniques have been mainly tested on strain selection efforts [28-32], thus not focusing on the design of biorefineries. One specific methodology, named PROMETHEE (Preference Ranking Organization Method for Enrichment Evaluations), appears as a user-friendly option for a finite set of alternatives to be ranked from best to worst and selected among multiple conflicting criteria [20, 33]. In summary, the method carries out a pairwise comparison of the data in the decision-support matrices for all desired criteria, while using an associated weight for each criterion. As the latter denotes the relative importance of each criterion in the broader view of an analysis, assigning the correct weight has a large influence over the final outranking results.

The main objective of this study is to demonstrate for the first time the value of a two-step, MCDA-based approach to define (1) the most preferable bioproducts as may be produced from a pre-defined list for each of the major fractions in microalgae biomass (fermentable carbohydrates, FAME [fatty acid methyl esters] as a proxy for lipids, and protein) and (2) the most suitable portfolio of such products that may be obtained in concert from all three fractions based on the strain's compositional profile and cultivation productivity. Furthermore, selected sensitivities are also performed around the influence of the weight attribution method and the implementation of biases to the methodology. Lastly, the results from the MCDAs were validated through process simulation, techno-economic assessment (TEA), and life-cycle assessment (LCA) of the conversion of algae biomass in a biorefinery context.

2. Materials and Methods

2.1 MCDA: outranking method

The outranking method is comprised of a sequential approach for the determination of rankings based on the data inserted in the decision-making matrices (Figure 1A). As previously introduced, the PROMETHEE method was chosen for this study thanks to its simplicity of implementation in spreadsheets or via coding, and its flexibility towards varying the number of criteria and/or options for outranking. With this methodology, criteria can be evaluated through six different preference functions, labelled types I to VI [33] (Figure 1B). Types are chosen for each criterion following the representativeness of data and the pertinence of each criterion towards assessing the case in question. It is important to note that the threshold values used for pairwise comparison have real-life meaning that can be set by the researcher. The reader is referred to the scientific literature for a full explanation on all types of criteria and their use in PROMETHEE [33].

Please insert Figure 1 here

2.2 MCDA: weight attribution

Assigning a fair weight to each criterion, another critical part of an MCDA effort, can be carried out through several subjective or objective approaches [34, 35]. For comparison purposes, the influence of three distinct weight attribution methods over the outcome of an MCDA is studied in this paper, namely the Analytical Hierarchy Process (AHP) method, the Criteria Importance through Inter-criteria Correlation (CRITIC) method, and the Entropy method. The AHP weighting method requires a matrix for computing the sums of the weights of the criteria, as described elsewhere in the literature [36]. To derive data for it, this study relied on the opinion of individual stakeholders in the field of renewables to build the weights for criteria. For that, a survey was shaped around the perceived importance of different technical, economic, and environmental aspects in decision-making processes and then distributed to professionals in the sector of bioenergy and bioproducts through social media. Participants were encouraged (although not required) to supply additional details, such as field of activity, country of residence, and years of experience in the sector to make sure that the answers were obtained from a diverse group of people and with a significant seniority in the field. The questionnaire was built to provide total weights obtained from a two-layer process: (1) a broad “umbrella” of technical, economic, and environmental aspects that multiplies (2) individual weights for the eight individual criteria outlined and examined in Section 3 (Step #1: Identifying Algae-Derived Products). The main structure of the survey and the 50 respondents’ answers are shown in Sections I and II of the Electronic Supplementary Information (ESI). The CRITIC method, an objective approach to allocate weights among criteria, is based on the interdependence between attributes through employing Pearson product-moment or Spearman rank-order correlations [34], as detailed in Eqs. (1) and (2). Finally, the Entropy method, assigns weights according to the disparity of data within a given dataset (in this case, the decision-support matrix). In weighting efforts, entropy relates to the degree of diversity within an attribute dataset, as shown in Eqs. (3) and (4). When employing this method, the smaller the entropy within the data associated to the criterion, the greater its weight and, therefore, its potential of changing the ranks of alternatives [34].

CRITIC method:

$$C_j = \sigma_j \sum_{k=1}^n (1 - r_{jk}) \quad j = 1, 2, \dots, n \quad (1)$$

$$w_j = \frac{C_j}{\sum_{k=1}^n C_k} \quad j = 1, 2, \dots, n \quad (2)$$

where, σ_j denotes the standard deviation of the j^{th} response, r_{jk} represents the correlation coefficient between two different responses and w_j is the weights of each criterion.

Entropy method:

$$e_j = -\frac{1}{\ln(m)} \sum_{i=1}^m r_{ij} \ln(r_{ij}) \quad j = 1, 2, \dots, n \quad (3)$$

$$w_j = \frac{1 - e_j}{(n - \sum_{j=1}^n e_j)} \quad j = 1, 2, \dots, n \quad (4)$$

where, e_j is the entropy values of the j^{th} response and w_j is the weights of each criterion.

2.3 Data collection

Data in the decision-support matrices was retrieved from multiple sources within the scientific literature, namely market reports, technical reports, and peer-reviewed papers. The numerical values employed in the assessments are further presented and discussed in the main body of the paper and in the ESI. Data for comparison is kept to consistent timeframes and boundaries to a maximum extent while keeping extrapolations to a minimum to avoid unconscious biases. Additionally, whenever needed, data was normalized to avoid disclosing any proprietary information that could be involved. All values are supplied for the common base year of 2018, except when noted.

2.4 Study outline

The main structure of this work is summarized in Figure 2. In Step #1, three independent MCDAs were carried out, each linked to a major class of biomolecules in microalgae biomass (carbohydrates, lipids, and protein). Each individual assessment yields a bioproduct choice that may be produced from each of these

173 biomass constituents after outranking of the options, which consider pre-defined criteria and calculated
174 weights. Step #2 of the study aimed at pairing several microalgae strains with varying compositional
175 profiles to the most suitable product portfolios using the top compounds defined in Step #1. While the AHP
176 method was used as the main weighting approach in Step #1 and CRITIC was employed as the base
177 approach in Step #2, all three methods considered in this study were assessed in Step #1 as a sensitivity
178 analysis. Also, a conscious bias towards either technical, economic, or environmental aspects was applied
179 in Step #1 as another form of a what-if case study. Finally, a suite of process simulations was used to further
180 cross-check the results obtained with the MCDAs of Step #2.

Please insert Figure 2 here

3. Step#1: Identifying Algae-Derived Products

3.1 Rationale

The criteria set employed in Step #1 mixes elements of technical, economic, and environmental nature:

- Technical aspects: estimated maturity level of the main conversion step in the biobased production pathway (more mature technologies are desired); theoretical yield from sugars glucose to product; and perceived complexity of downstream processing for the biobased alternative (simpler pathways are preferred to reduce the already high capital intensity of microalgae systems in industrial scale).
- Economic aspects: estimated U.S. market size (it is desirable to have a strong and well-established industrial demand for the compound); predicted U.S. market growth (the larger the increase in the U.S. market, the higher the possibility for biobased alternatives to penetrate the market and compete with conventionally sourced molecules); and product selling price (averaged over multiple years as many chemical products can experience large price swings depending on market conditions).
- Environmental aspects: average reduction in greenhouse gases (GHG) emission intensity in comparison to a reference compound and cumulative energy demand. Among all the existing environmental impact categories (e.g., water footprint, freshwater ecotoxicity, human toxicity, and others), GHG emission intensity and energy demand were included as the two main criteria of interest in this section because of strong societal pressure to reduce carbon intensity of products and processes.

The pool of products for ranking encompasses compounds traditionally produced in industry, either from fossil-based or renewable sources, with tracked demand in the U.S. The assessment does not consider “promising” chemicals, i.e. those that are expected to become industry staples in the future and without a currently established market (e.g. levulinic acid). It is also limited to those readily obtainable after a one-step conversion from hexoses (e.g. via fermentation or hydrogenation), thus ruling out options that could be synthesized from other biobased compounds in multiple, often catalytic, steps (e.g. butadiene from butanediols or acrylonitrile from 3-hydroxypropionic acid). Chemicals with very large markets (e.g., traditional fossil-based ethylene and propylene) were excluded from the assessment to avoid incurring unfair comparisons, except when all options derived from the same biomass fraction have large markets; in an analogous reasoning, niche compounds with usually low volume markets and very high selling prices were left out (e.g. eicosapentaenoic and docosahexaenoic acids [EPA and DHA, respectively] from lipids or amino acids from protein). Another reason for excluding specialty chemicals is to enhance the scalability of the process, therefore supporting as large a number of microalgae biorefineries as possible (this point is further addressed and assessed in Step #2). The breakdown of assessed products by class of compounds is as follows:

• Carbohydrates: organic acids (lactic acid, succinic acid, propionic acid, acrylic acid, adipic acid [as a surrogate for muconic acid], butyric acid, citric acid, fumaric acid, formic acid, and malic acid), non-fuel alcohols (1,3-propanediol and 1,4-butanediol), sorbitol, and polyhydroxyalkanoates.

• Lipids: fatty acids, fatty alcohols, detergents, and polyurethane.

• Protein: animal feed, methane, and thermoplastic co-extrusion feed [37].

3.2 Outcomes

Using the answers from the 50 respondents of the survey and after a consistency check [38-40], the baseline weights shown in Table 1 were derived for the AHP method. While priorities were fairly evenly distributed, it can be seen that respondents tended to give a preference for environmental aspects in decision-making processes (34.6%), with economic and process aspects being selected at slightly lower levels (33.9% and 31.5%, respectively). Similar results are observed for the eight individual criteria, with some preference towards market growth over market size (38% to 32%) and more markedly towards GHG emission intensity reduction in comparison to total energy demand (55% to 45%). Table 1 also indicates the weights derived using artificially inserted biases towards economic, process, and environmental metrics. Data for all compounds under assessment and the weights associated to the Entropy and CRITIC weighting methods are presented in Section III of the ESI (Tables S1-S5).

237 **Table 1.** Two-layered weighting approach obtained from the results of the survey and final weight for the
238 baseline AHP weighting method.

First-level criteria	Economic aspects			Process aspects			Environmental aspects	
Baseline	33.9%			31.5%			34.6%	
Economic bias	60%			20%			20%	
Process bias	20%			60%			20%	
Environmental bias	20%			20%			60%	
Second-level criteria	U.S. market size	U.S. market growth	Selling price	Theoretical yield	Maturity of conversion step	Complexity of downstream	GHG reduction vs fossil equivalent	Cumulative energy demand
Base weights	32%	38%	30%	39%	21%	39%	55%	45%
Final weights								
Baseline	10.7%	12.8%	10.3%	12.4%	6.7%	12.4%	19.0%	15.6%
Economic bias	19.0%	22.7%	18.2%	7.9%	4.3%	7.9%	11.0%	9.0%
Process bias	6.3%	7.6%	6.1%	23.6%	12.8%	23.6%	11.0%	9.0%
Environmental bias	6.3%	7.6%	6.1%	7.9%	4.3%	7.9%	33.0%	27.0%

When employing the previously described AHP, CRITIC, and Entropy weighting methods to the MCDAs in Step #1, several interesting patterns appear. Figure 3 presents the different outranking outcomes determined for carbohydrate-derived products. Succinic acid appears as the top ranked compound when using the AHP baseline weights calculated with inputs from survey respondents, when applying process or environmental biases, and when applying the CRITIC method. On the other hand, acrylic acid appears as the top result when an economic bias is considered or when the Entropy method is used. Citric acid, while not ranked as the top product in any of the analyses, consistently appeared among the second or third places when using virtually all weighting methods. These three molecules have very distinct characteristics that warrant further scrutiny to fully understand the outranking results.

Succinic acid has a significant edge in several categories, such as selling price, theoretical yield, and maturity of the conversion step, as attested in several recent studies [41-46], albeit with a very limited current market size and projected market growth for this specific product (exclusive of potential derivative products that may be made from it, such as tetrahydrofuran or 1,4-butanediol; Table S1, Section III of the ESI).

Acrylic acid, on the other hand, shows the highest market size and growth among the bioproducts in question, which positions it as a competitive molecule depending on what the decision-maker chooses to prioritize. However, it is noteworthy that the direct conversion of mixed sugars to acrylic acid via fermentation is still in its infancy [47], thus meriting the lowest score in the category that assesses the maturity of the conversion step. Also, although this work mainly focuses on direct routes from the major fractions in algae biomass – carbohydrates, lipids, and protein – to several end products, a brief exercise was carried out to demonstrate the robustness of the obtained results and to point out possible ramifications moving forward. If it is considered that acrylic acid can be produced via 3-hydroxypropionic acid [48] (or other feedstocks such as glycerol [49, 50] or lactides [51]) at an estimated Technology Readiness Level (TRL) of 3, at lower overall process yields, and at a slightly higher downstream complexity, the molecule would still remain at the top positions of this outranking independently of the weighting method of choice.

Finally, citric acid appears as a secure option in view of a relatively high market size and projected market growth, a high theoretical yield from mixed sugars, and a highly mature conversion step coupled with a simple downstream process. It should be emphasized that the molecules presented in Figure 3 are based on end-use as chemical products; some of these molecules may alternatively be converted into hydrocarbon fuels, which is not accounted for in here but is separately considered as an alternative scenario subsequently.

Please insert Figure 3 here

For products derived from lipids or protein, varying the weighting method or applying conscious, pre-determined biases to the analyses did not influence the results. For any case study, the top molecule derived from lipids is polyurethane while the preferred product from protein is the thermoplastic extrusion co-feed. For lipid conversion, polyurethane was determined to be the best choice across the various weighting methods as it combines a set of technical, economic, and environmental parameters that surpasses its competitors in nearly all categories under assessment – a similar reasoning can be applied to explain thermoplastic extrusion co-feed as the protein-derived compound of choice as well. For detailed data on the outranking of bioproducts from lipids and protein, the reader is referred to Tables S2 and S3 in Section III of the ESI.

3.3 Sensitivity analyses

It is noteworthy that a limitation of the results presented herein is that, if a single category is essential to product adoption (e.g., meeting a minimum market size), this may be lost within the MCDA if the other categories are sufficiently preferable. To help reduce the uncertainty around the results obtained with an MCDA-based outranking of algae-derived bioproducts, selected sensitivity analyses were then carried out, with its main results presented in this section.

Incorporating uncertainty aspects. A stochastic procedure using Latin Hypercube sampling-based simulations with 10,000 interactions helped to demonstrate the stability of the outranking results obtained using either AHP or CRITIC weighting methods. Figure 4 presents the distribution of probability for the placement of each of the 14 compounds under scrutiny when applying variation ranges to their selling price, U.S. market growth, and downstream process complexity. When using the AHP method, the positions of the top four compounds in the outranking have a probability of at least 68% of corresponding to the ones verified with deterministic values, reaching 100% for succinic acid being ranked as the top compound. For the CRITIC weighting method, the top two chemicals (succinic acid and citric acid) appear with a probability of being at first and second positions of 82% and 77%, respectively.

Please insert Figure 4 here

Production of hydrocarbon fuels. Although not among the options of bioproducts assessed in Step #1, hydrocarbon fuels are a highly sought-after component in algae-based biorefineries [52, 53]. In this regard, an exercise towards the effect of converting two previously mentioned compounds, namely butyric acid and propionic acid, into hydrocarbon fuels was carried out. When assigning parameters for the production of hydrocarbons via either propionic acid or butyric acid through the extrapolation of recent available data for butyric acid catalytic upgrading [54, 55], these drop-in fuels would be ranked at the top of the list for two different weighting methods: Entropy and AHP with an artificially-applied economic bias. This result shows the possibility of carbohydrate-derived fuels to be competitive even with other high-value molecules, such as succinic acid. In comparison to their acid precursors, these fuel derivatives would be able to attain a larger market (i.e., that of commodity fuels) with a higher market growth and provide further reductions in GHG emission intensity in comparison to their fossil counterparts; however, the low yields and increased downstream complexity of these products incur additional challenges when considered alongside the relatively low value of fuel products. More specific analyses to outrank fuel options could be further carried out using data in the literature [56, 57].

4. Step #2: Selecting Biorefining Portfolios

4.1 Rationale

The second part of this study targets the identification of the most suitable product mix among a series of product portfolios built with the top compounds defined in Step #1 for several microalgae strains with distinct compositional profiles. A different set of criteria is employed in this set of assessments:

• Economic potential. Defined according to Eq. (5), this metric represents the sum of potential revenues obtained with the commercialization of the biocompounds synthesized from carbohydrates, protein, and lipids from 1,000 kg of ash-free, dry weight (AFDW) biomass. The estimates are based on theoretical yields from each of these three fractions to the molecules of interest and on their full recovery from the respective reactional mixtures, thus not being inclusive of the associated processing and capital costs.

$$EP = \sum_{i=1}^3 (Fraction_i * Yield_i * Selling\ price_i) \quad (5)$$

where i refers to each main class of biomolecules in microalgae (1 = lipids; 2 = carbohydrates; 3 = protein) and the economic potential EP is given in \$.

• Potential of GHG emission intensity reduction. Similar to the economic potential, this metric considers the potential for reduction in GHG emission intensity offered by the full product portfolio of the biorefinery in comparison to emissions for the reference compounds produced through conventional methods, as represented by Eq. (6). This is also estimated using theoretical yields from each of the three main fractions in microalgae biomass to the molecules of interest and on their full, unburdened recovery from the production process.

$$GEIR = \sum_{i=1}^3 (Fraction_i * Yield_i * (1 - GHG\ reduction) * GHG_{reference,i}) \quad (6)$$

where i refers to each main class of biomolecules in microalgae (1 = lipids; 2 = carbohydrates; 3 = protein) and the GHG emission intensity reduction $GEIR$ is given in kg CO₂eq/kg algae.

• Maximum supported number of biorefineries. The number of identical microalgae biorefineries that could be deployed in the U.S. is determined so as the total amount of the limiting compound in terms of market size in the product portfolio (i.e., the one derived from carbohydrates) does not exceed 30% of its current estimated U.S. apparent consumption. Each biorefinery is considered to be coupled to a microalgae biomass output of 170,000 thousand tonnes per year, obtained in a 5,000-acre algae plant [58].

• Complexity of the biorefining process. This criterion is assessed as a discrete, quantitative scale based on the individual downstream processing complexities associated with each of the products in the biorefining portfolio. This category can be thought of as a preliminary indicative of the capital intensity for the process,

354 something that would require in-depth TEA to be determined by considering the fully burdened processing
 355 costs for each individual option (which isn't otherwise captured here).

356

357 Eleven distinct product portfolios were then built using the top product from lipids, the top product from
 358 protein, the top three products derived from carbohydrates, and, alternatively, hydrocarbon fuels
 359 synthesized from carbohydrates and lipids, as detailed in Table 2. All three main carbohydrate-derived
 360 molecules from Step #1 (succinic acid, acrylic acid, and citric acid) were included in the analyses for a
 361 broader perspective moving forward. The product portfolios in all biorefineries were based on a Combined
 362 Algae Processing (CAP) approach previously defined and published elsewhere [1, 59], in essence a
 363 fractionation approach to isolate and subsequently separately upgrade lipids, protein, and carbohydrate
 364 biomass constituents, as a means to selectively add value to all biomass fractions in microalgae biomass.
 365 These product portfolios were individually paired with productivity and compositional data from 13
 366 different, high-productivity summer strains cultivated either under nutrient-replete or nutrient-deplete
 367 conditions. This dataset was generated under the DISCOVER (Development of Integrated Screening,
 368 Cultivar Optimization, and Verification Research) consortium, where researchers have developed a strain
 369 selection pipeline using different cultivation scales aiming at finding suitable candidates for deployment in
 370 outdoor facilities [60-62]. The productivity and compositional data for the 13 strains employed in this study
 371 was generated using nutrient-replete and nutrient-deplete cultivations in Laboratory Environmental Algae
 372 Pond Simulator (LEAPS) reactors, which simulate outdoor cultivations conditions in 1-L indoor
 373 photobioreactors [4, 62]. Microalgae cultivations with high and low nutrient levels (i.e., at nitrogen
 374 concentration above 10 ppm until biomass harvest for nutrient-replete cultivations and below 1 ppm for
 375 nutrient-deplete runs [62]) usually lead to distinct outcomes in terms of growth rates and compositional
 376 profiles: while the former allows for high productivities and yields biomass with a high protein content, the
 377 latter reduces areal productivities but enriches microalgae biomass in carbohydrates and lipids. Tradeoffs
 378 between these two parameters are also discussed later in this study. It is worth highlighting that the analysis
 379 presented herein is constrained to the dataset for the 13 summer strains evaluated using the LEAPS reactors,
 380 as the original experimental work by Huesemann et al. [62] also presents (incomplete) productivity and
 381 compositional data for several other top-performing winter strains.

382 All base parameters to carry out the MCDAs in Step #2 for the 26 pairings of strains and cultivation
 383 conditions are shown in Table 3. All data employed in the MCDAs of Step #2 are shown in Section IV of
 384 the ESI (Table S6 for strains, Klein et al. (2023) [4] for productivity and compositional profile data, and
 385 Tables S7-S31 for the values used to populate the decision-making matrices).

386

387 **Table 2.** Composition of product portfolios for assessment in Step #2.

Fraction	Compound	Product portfolio										
		P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11
Lipids	Hydrocarbon		✓	✓	✓							

	Hydrocarbon fuel with policy incentives						✓	✓	✓			
	Polyurethane	✓				✓				✓	✓	✓
Carbohydrates	Hydrocarbon	✓										
	Hydrocarbon fuel with policy incentives					✓						
	Succinic acid		✓				✓			✓		
	Acrylic acid			✓				✓			✓	
	Citric acid				✓				✓			✓
Protein	Thermoplastic co-feed	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Fraction	Compound	Yield (g/g)	Selling price (\$/t)	Theoretical potential reduction in GHG emission intensity	GHG emission intensity of the reference compound (kg CO ₂ eq/kg product)	Market size (kty)	Biorefining complexity ^u
Lipids	Hydrocarbon	0.92 ^a	887 ^h	50% ^l	4.14 ^p	-	2
	Hydrocarbon fuel with policy incentives	0.92 ^a	1,419 ⁱ	50% ^l	4.14 ^p	-	2
	Polyurethane	1.36 ^b	4,500 ^j	55% [63]	3.33 ^q	614 [64]	3
Carbohydrates	Hydrocarbon	0.30 ^c	887 ^h	50% ^l	4.14 ^p	-	4
	Hydrocarbon fuel with policy incentives	0.30 ^c	1,419 ⁱ	50% ^l	4.14 ^p	-	4
	Succinic acid	1.01 ^d	2,940 [65]	54% [66]	1.89 [66]	1.5 [64]	3
	Acrylic acid	0.72 ^e	1,350 [64]	25% ^m	6.89 ^r	367 [64]	3
	Citric acid	1.01 ^f	1,250 [64, 67]	0% ⁿ	4.70 ^s	146 [64]	1
Protein	Thermoplastic co-feed	0.60 ^g	2,250 ^k	35% ^o	2.57 ^t	-	1

391 ^a Yield for the CAP conversion of neutral lipids [68].

392 ^b Yield for the conversion of 75% of neutral lipids to polyurethane [68].

393 ^c Yield for sugar conversion to hydrocarbon fuels via butyric acid [69].

394 ^d Assumed a 90% fermentation yield of the theoretical maximum of 1.12 g/g [70].

395 ^e Assumed a 90% fermentation yield of the theoretical maximum of 0.80 g/g [71].

396 ^f Assumed a 90% fermentation yield of the theoretical maximum of 1.12 g/g [72].

397 ^g Considers a 40% protein solubilization during microalgal biomass pretreatment.

398 ^h Estimated from a fuel selling price of \$2.50/gallon of gasoline equivalent (GGE) based on the density of gasoline.

399 ⁱ Estimated from a fuel selling price of \$4.00/gallon of gasoline equivalent (GGE) based on the density of gasoline (policy incentives of \$1.50/GGE).

400 ^j Rigid foam price estimated from multiple sources [64, 73, 74].

401 ^k Estimated from a thermoplastic extrusion co-feed price of \$0.90/kg and a 40% protein content in the final product [53].

402 ^l Minimum required GHG emissions reduction for biomass-based diesel in the Renewable Fuel Standard (RFS) [75].

403 ^m Due to lack of data in the literature for processes using direct fermentation to acrylic acid, reduction in GHG emission intensity is considered to be the same as that for
404 propionic acid [76].

405 ⁿ No expected reductions in GHG emission intensity as the current market competitor is already biobased. A case-by-case assessment could show differences in GHG
406 emission intensities depending on variations in feedstock or processing options, which is outside the scope of this study.

407 ^o Due to lack of data in the literature, reduction in GHG emission intensity for this compound is considered to be the same as that for PHA [77].

408 ^p Estimated for an energy density of 45.5 MJ/kg of diesel and a base emission of 91 gCO₂eq/MJ.

409 ^q Average GHG emission intensity of rigid and flexible foams [78].

410 ^r GHG emission intensity of acrylic acid from fossil energy [78].

411 ^s GHG emission intensity of citric acid recovered with calcium precipitation [67].

412 ^t GHG emission intensity set equal to that of ethylene-vinyl acetate (EVA) [79].

413 ^u Rationale and outcomes detailed in Table S5 of the ESI.

All pairings of microalgae/cultivation conditions are mostly favored when portfolio P10 is chosen, which is exclusively comprised of high-value products: acrylic acid from carbohydrates, polyurethane from lipids, and thermoplastic co-feed from protein. On the assumption that a biorefinery targeting a hydrocarbon fuel is required, P5 and P7 appear as the top choices for most microalgae strains, as indicated in Figure 5 for each combination of microalgae strains and cultivation conditions (nutrient-replete or nutrient-deplete). P5 comprises the production of a hydrocarbon fuel from carbohydrates, polyurethane from lipids, and thermoplastic extrusion co-feed from protein, while P7 obtains acrylic acid from carbohydrates, a hydrocarbon fuel from lipids, and the same thermoplastic co-feed from protein. Additionally, Figure 5 shows that the cultivation condition (either nutrient-replete or nutrient-deplete) highly influences the portfolio choice for six strains, favoring either P5 or P7 as the proportion between their major fractions change.

It is also interesting to note that, despite succinic acid being consistently ranked as the top product from carbohydrates in Step #1, it does not appear in the product portfolios for the conversion of microalgae biomass through Step #2. This can be explained by the very low volume of the succinic acid market in the U.S., which only amounts to less than ten thousand tonnes per year [64]. In this way, when calculating the maximum number of biorefineries supported for product portfolios P2, P6, and P9 (all of them producing succinic acid), the result is essentially zero, thus largely jeopardizing the chances of such portfolios to emerge in the top positions of the assessment. While this criterion ultimately hinders the adoption of biorefineries with succinic acid production in Step #2 of the study, the current market volume for this molecule does not prevent it from being among the first positions in Step #1 as the influence of other categories ultimately outweighs the importance of this economic parameter. This panorama could change if the demand for succinic acid increases in the coming years due to the development of new applications or expanding into downstream derivative products for this potential platform molecule. On the other hand, the feasibility of deploying biorefineries with the production of acrylic acid at competitive prices has already been demonstrated in other studies [80, 81].

Moreover, it should be noted that changing the criteria for the assessment or structuring the existing criteria in a different manner could have implications for the results of the MCDAs. For instance, redefining the economic potential criterion in a similar style to that of other studies in the literature [4, 82], i.e., in which part of the operational cost (usually the cost with feedstock) are subtracted from the total revenue obtained with the commercialization of products, would have diverse results depending on the weighting method. An assessment showed that, if the minimum biomass selling price (MBSP) was to be included in the economic potential equation, this would not change the outcomes of the MCDAs of Step #2 for the CRITIC weighting method. For the Entropy method, results could somewhat vary – and resemble more the ones derived using the CRITIC method as the Entropy method structure would assign a higher weight to the economic potential criterion due to a change in the data used to populate the decision-making matrix. In this way, for this specific purpose, omitting the cost incurred with algae biomass is a valid simplification of the economic potential equation and a good proxy for the economic performance tied to a given product portfolio, especially when the MBSP is not known or can't be easily estimated with the available data.

Please insert Figure 5 here

4.3 Identifying the space of application of microalgae biomass

While Figure 5 presents a snapshot of the strain/biorefinery pairing outcomes of Step #2 using the CRITIC weighting method, more comprehensive conclusions on the application of MCDA on microalgae biorefining options can be drawn with the implementation of a sensitivity analysis. For this, more than 100 distinct fictional compositional profiles spanning various ratios of fermentable carbohydrates, nonpolar (FAME-like) lipids, and protein have been derived and used as inputs to the methodology employed in Step #2. These simulated compositions were then paired with the top-ranked biorefining approaches as identified through MCDA. Figure 6 shows the general spaces of application of microalgae biomass as determined by two different criteria weighting approaches: Entropy and CRITIC methods.

The Entropy method, because of its mathematical formulation [34] and the data inputs for assessment, tends to assign large weights to some criteria in detriment of others. In this study, the criterion linked to the maximum number of supported biorefineries for increased scalability consistently harnessed more than 80% of the total weight, with the remainder 20% or less being divided among the three remaining criteria. In this way, Figure 6A indicates that the best biomass processing approach can be identified simply by the lipids-to-carbohydrates ratio found in algae biomass, with a proportion below 0.94 favoring the processing of carbohydrates to fuels or above this value supporting the conversion of lipids to fuels. On the other hand, the CRITIC method, through the utilization of Pearson correlations [34], allocates more evenly distributed weights among the four criteria under scrutiny – which hover around an average value of 25% each. Figure 6B identifies a narrower region for which the conversion of carbohydrates to fuels is favored, i.e., between lipids-to-carbohydrates ratios of 0.26 and 1. Biomass processing options that favor lipids to fuels are desired for compositional profiles with lipids-to-carbohydrates ratios below 0.26 and above 1. Biomass productivity, although not a factor that influences the outranking of biorefining options in this sensitivity analysis, should definitely be considered in estimating the economic feasibility of any biomass production-conversion system in view of its determinant role in defining the cost of biomass production [58].

Please insert Figure 6 here

Finally, the 26 pairings between strains and cultivation conditions considered in this work were subjected to process simulations using a combination of electronic spreadsheets and correlations for both mass and energy balances derived from the commercial software Aspen Plus V10 (AspenTech, Bedford, MA). The simplified block diagram in Figure 6C shows the general process layout for the chosen biorefinery, which fractionates algae biomass for the production of succinic acid from sugars, hydrocarbon fuels from lipids, and thermoplastic extrusion co-feed from protein in residual biomass (a more complete process flow diagram is shown in Section V of the ESI, alongside a description of the various sub-processes considered in the simulations). The outputs from the process simulation were then used to inform both TEA and LCA to determine the pertinent economic and environmental metrics associated with the biorefining of algae biomass with varying compositional profiles (main TEA and LCA parameters also shown in Section V of the ESI). The objective of this effort was to assess whether the conversion of algae biomass through a biorefining setup centered on lipid-to-fuel conversion is more favorable to the algae strains and cultivation conditions previously identified through the MCDAs of Step #2 as being advantaged by such a conversion process (application space indicated in blue in Figures 6A and 6B). Figure 6D combines the total revenue of the biorefinery with the reduction in GHG emissions attained by the product portfolio in comparison to their fossil-based counterparts, as assessed by process simulation, TEA, and LCA. The plot indicates that the conversion of biomass from algae strains with lipids-to-carbohydrates ratio above 1 or below 0.26 (represented by blue dots, as identified by the CRITIC method), present, in general, superior economic performance in the form of larger revenue associated with higher mitigation of GHG emissions in comparison to the strains marked in orange – which could likely yield better economic and environmental results in biorefineries based around the production of fuels from carbohydrates.

It is noteworthy that, while the plot in Figure 6D illustrates only two metrics associated with the biorefining of algae biomass, the findings from the process simulation effort help supporting the results from the MCDA work even if the latter considers parameters beyond economic and environmental metrics for decision-making purposes. Additionally, it should be pointed out that varying several of the inputs considered in this analysis could alter some of the results presented herein, such as technical parameters (efficiencies for biomass pretreatment, sugar fermentation, lipid extraction and conversion, among others), economic assumptions (prices of inputs, selling price of products, compatibility and price of policy credits), and environmental considerations (LCA boundaries and life-cycle database, for example). To minimize this risk, all possible parameters were kept consistent with those employed in Steps #1 and #2 of the MCDAs, as well as with those used in previous process simulation and TEA of algae biorefineries (detailed in Section V of the ESI). In a similar way, the choice of downstream purification of succinic acid alone could have significant impacts towards both the economic and environmental performance of the biorefineries. The process considered herein assumes a simulated moving bed ion exchange (SMB-IX) system: since it requires significant quantities of external inputs for operation, namely sulfuric acid, sodium hydroxide, process steam, and electricity [83], its use helps explaining the relatively low total reduction in GHG emissions obtained in each biorefinery. Switching to other downstream processing possibilities with lower environmental impact, such as direct crystallization from low-pH fermentations or electrodialysis powered by renewable electrons, could help reduce the overall carbon footprint of succinic acid production [84-86]. Lastly, since the main goal of this validation effort was to evaluate the suitability of a lipid-to-fuel biorefinery for the conversion of algae biomass, it is expected that exchanging succinic acid for other molecules such as either acrylic acid or citric acid as the high-value co-product from sugars could potentially yield equivalent conclusions from the TEA and LCA work – although this should be confirmed by specific process simulations.

5. Conclusions

The first part of this study presents clear winners when outranking bioproducts from different biomass fractions, namely succinic acid, acrylic acid, and citric acid from carbohydrates, polyurethane from lipids, and thermoplastic extrusion co-feed from protein. Such results, especially for carbohydrates, contrast with those that would be obtained if a fully “human-biased” assessment was carried out or if only one dimension of the analysis (often the economic one) was considered – e.g., molecules such as citric acid would be less likely to be part of product portfolios from microalgae processing in biorefineries. Later, when applying a similar methodology to identify the best product portfolios based on microalgae composition and other broad economic and environmental aspects, some interesting patterns also appear. Initially, a portfolio comprised only of high-value products (acrylic acid, polyurethane, and thermoplastic extrusion co-feed) would be the best option for any of the 13 strains in consideration, while adding more constraints in the form of the production of hydrocarbon fuels would lead to a more diverse landscape of microalgae-based biorefineries. Another finding of this work is the clear role of compositional profile in defining the core biorefining strategy of algae biomass, with lipid-to-carbohydrate ratios higher than roughly 1 warranting the preferential processing of lipids into fuels with the remainder of the algae biomass compounds being sent to higher-value applications. Finally, the process simulation, TEA, and LCA effort carried out as the final stage of this work corroborated the analysis stemming from the sequential MCDAs.

The application of MCDA methods to a multitude of problems with different scopes is what makes them an attractive yet simple tool for decision-making processes. This study is the first demonstration of an objective, MCDA-guided effort to provide guidelines towards biorefining of microalgae biomass from multiple perspectives (though it is noteworthy that this is an academic exercise demonstrating the application of MCDA methods, and other factors dictating commercialization or research directions may not be reflected here). While this methodology is developed and applied on algal biomass with accessible

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compositional profiles, it could also be easily transferable to other feedstock types and/or product portfolios of interest. Additionally, the option of minimizing the introduction of biases in the weighting of criteria is a safer way to approach such decision-making processes. The main challenge remains in choosing appropriate criteria and obtaining reliable data to populate the decision-making matrices. In the future, ramifications of this analysis could lean towards more specific factors of interest, such as prioritizing the production of certain compounds with limited domestic availability or adding value to microalgae biorefineries through the selection of niche markets to be explored. Other products of high industrial interest could be targeted for production from microalgae biomass as well. Adding different criteria to the assessment, such as the water footprint involved with the production of biobased compounds [87], would enrich the analysis, and provide an extra dimension to the outranking process.

Conflicts of Interest

None to declare.

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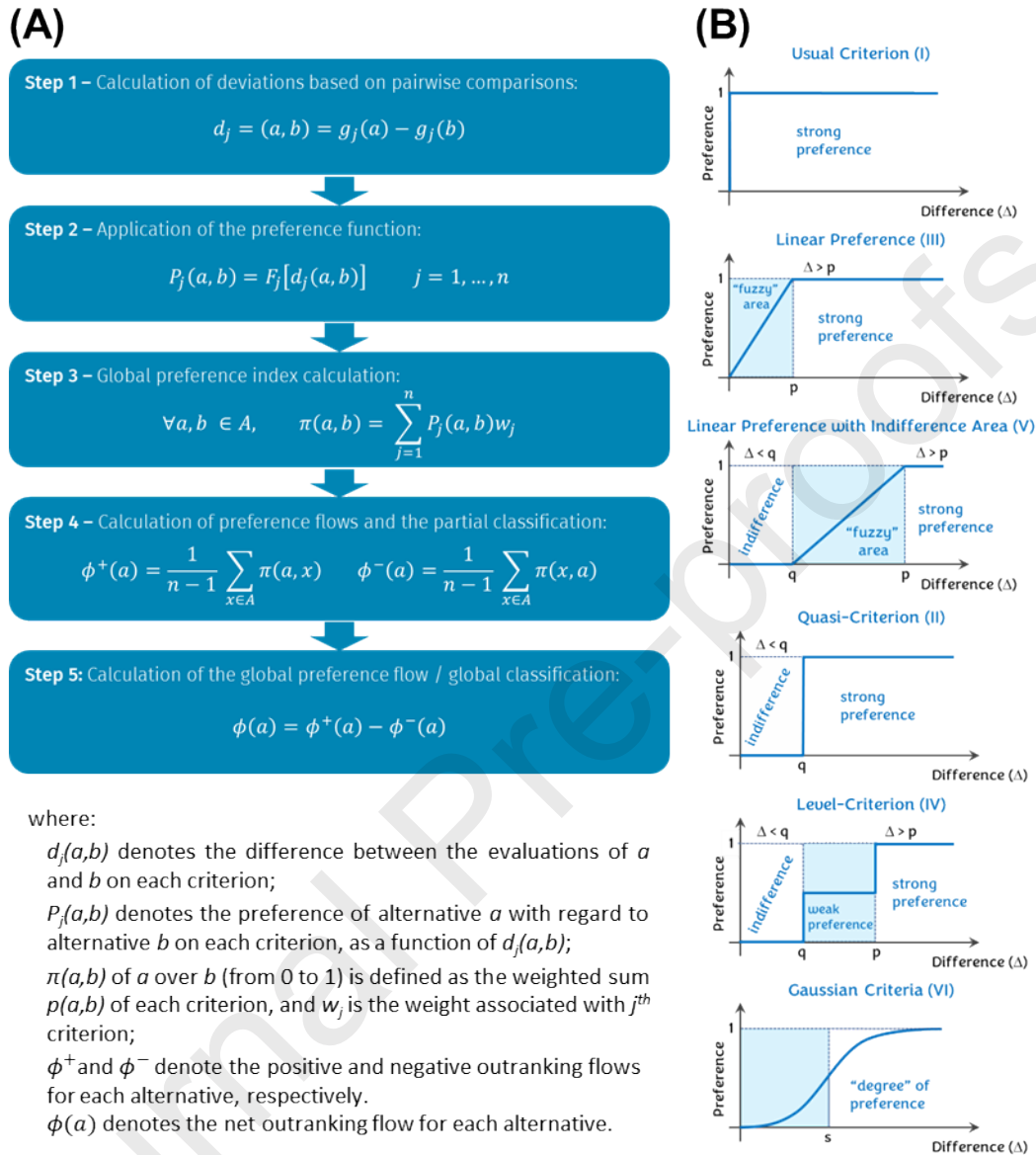


Figure 1. Main aspects for the definition of an MCDA problem. (A) Stepwise procedure for the implementation of PROMETHEE II. (B) Preference functions and thresholds determine the desired alternative based on its impact on the problem, with the aim of either minimizing or maximizing its contribution to a given criterion.

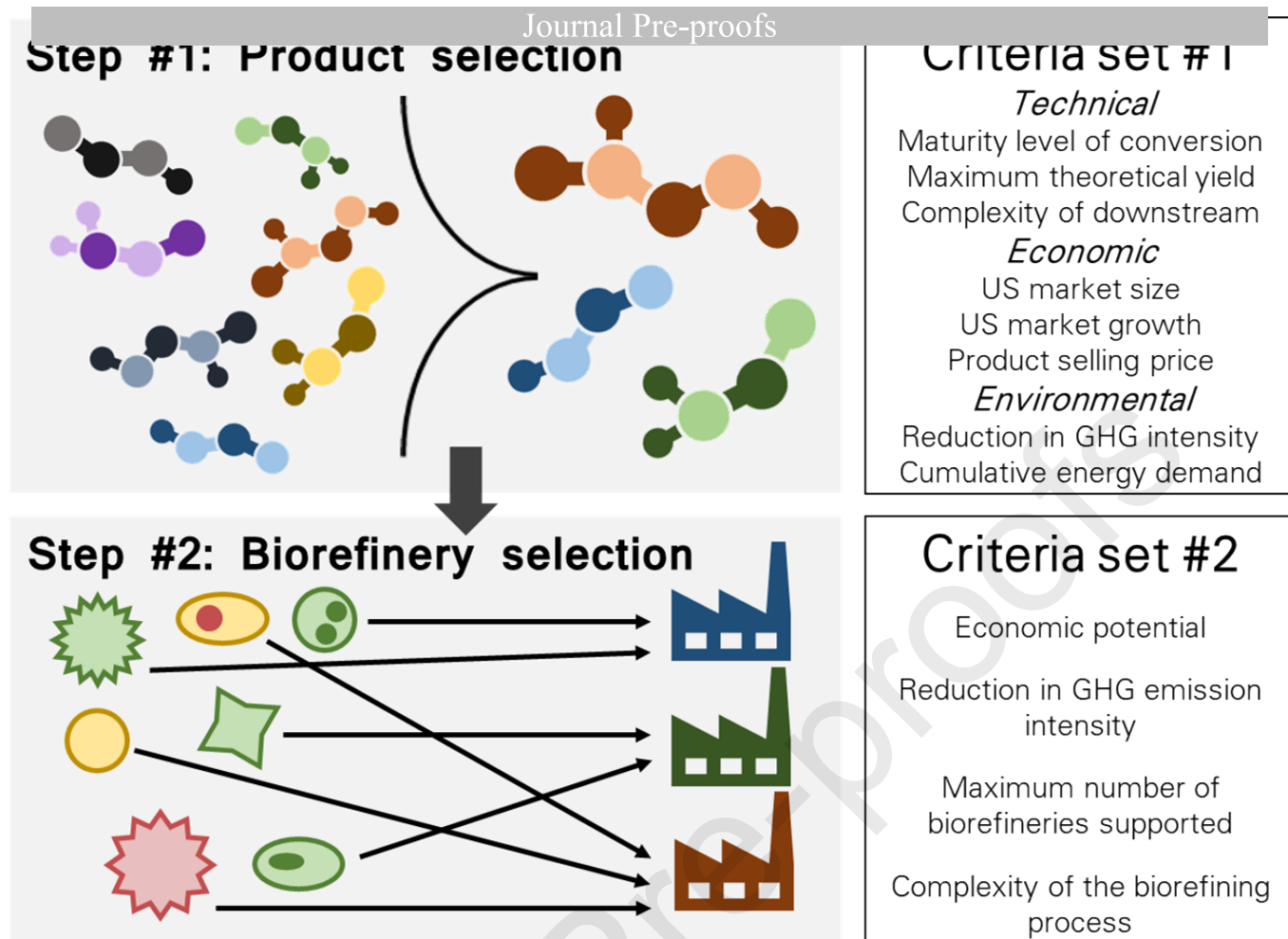


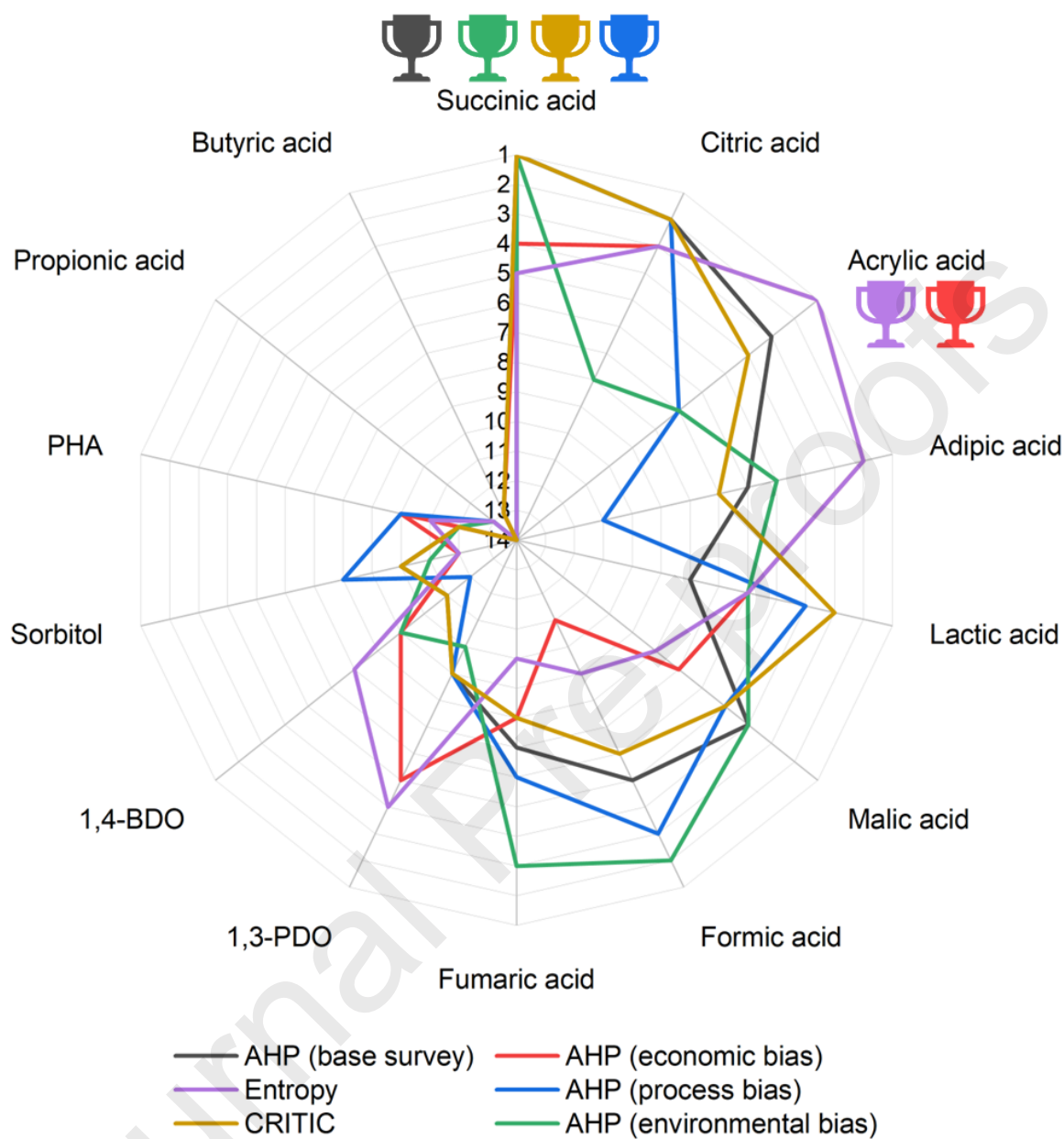
Figure 2. Outline of the study presented in this paper: MCDA-based selection of products derived from microalgae biomass (Step #1) and assignment of biorefining portfolios to different microalgae strains (Step #2).

GHG:

greenhouse

gases

779



780

781 **Figure 3. Outranking of carbohydrate-derived products using several weighting methods: AHP (base**
782 **data from survey, economic bias, process bias, and environmental bias), Entropy, and CRITIC.**
783 Choosing lipid- and protein-derived products yielded unchanging outcomes independently of the weighting
784 method: polyurethanes and thermoplastic extrusion co-feed, respectively.

785 AHP: Analytical Hierarchy Process; CRITIC: Criteria Importance through Inter-criteria Correlation.

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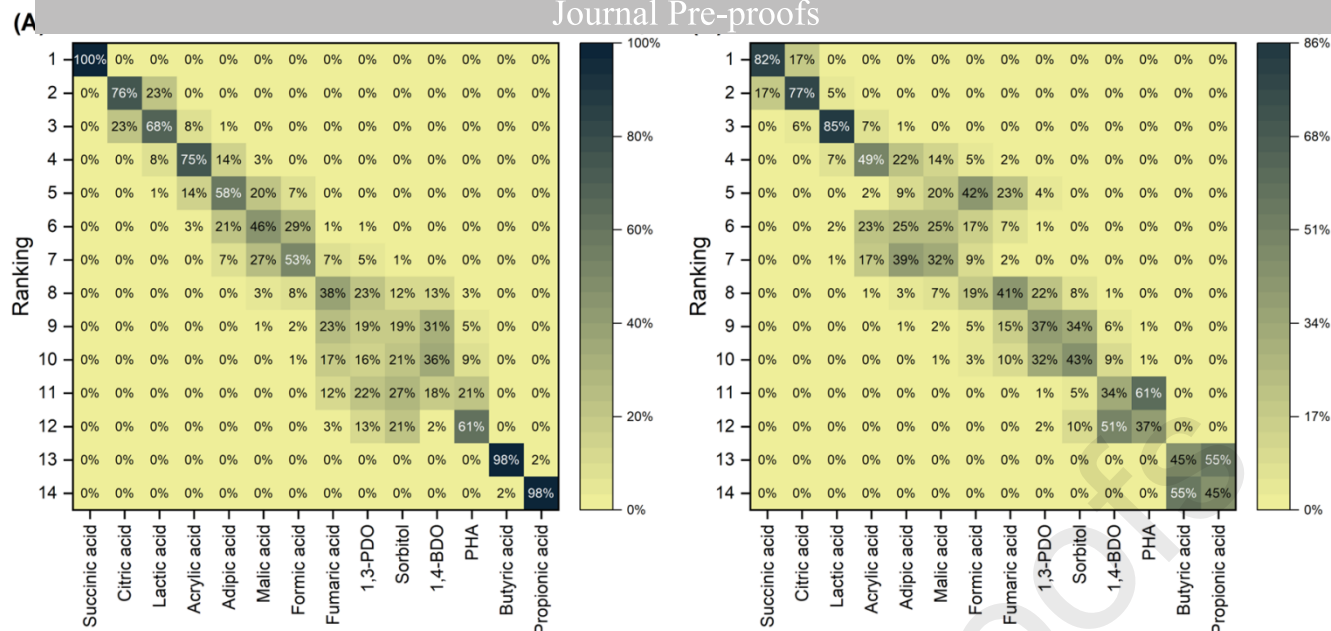


Figure 4. Effect of variations in selling price ($\pm 30\%$), U.S. market growth ($\pm 30\%$), and complexity of downstream (± 1 on normalized data) over the outranking placement of the assessed molecules using the (A) AHP and (B) CRITIC weighting methods.

AHP: Analytical Hierarchy Process; CRITIC: Criteria Importance through Inter-criteria Correlation; 1,3-PDO: 1,3-propanediol; 1,4-BDO: 1,4-butanediol; PHA: polyhydroxyalkanoates.

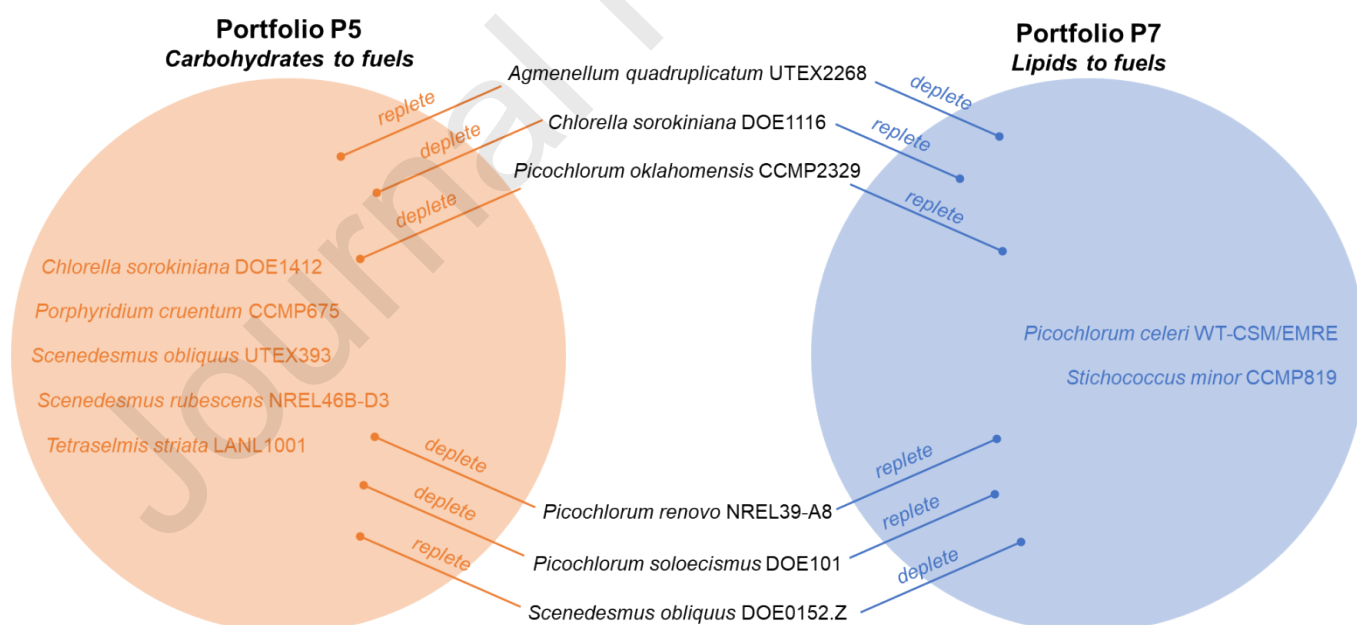
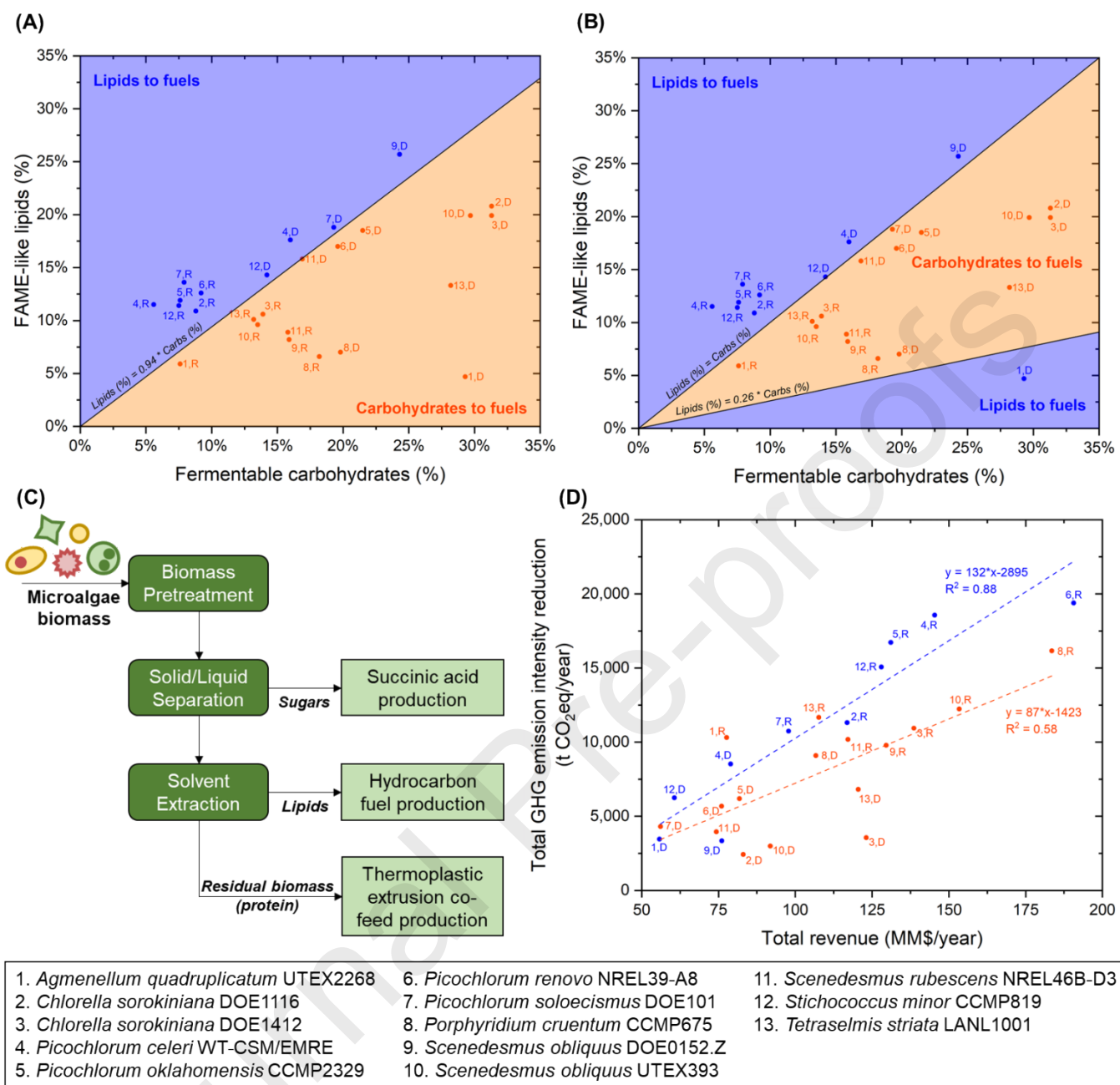


Figure 5. Preferred product mix choices determined in Step #2 using the CRITIC weighting method for biorefining strategies that yield a hydrocarbon fuel. Portfolio P5 yields polyurethane from lipids, while portfolio P7 yields acrylic acid from fermentable carbohydrates; both portfolios synthesize a thermoplastic extrusion co-feed from proteins.



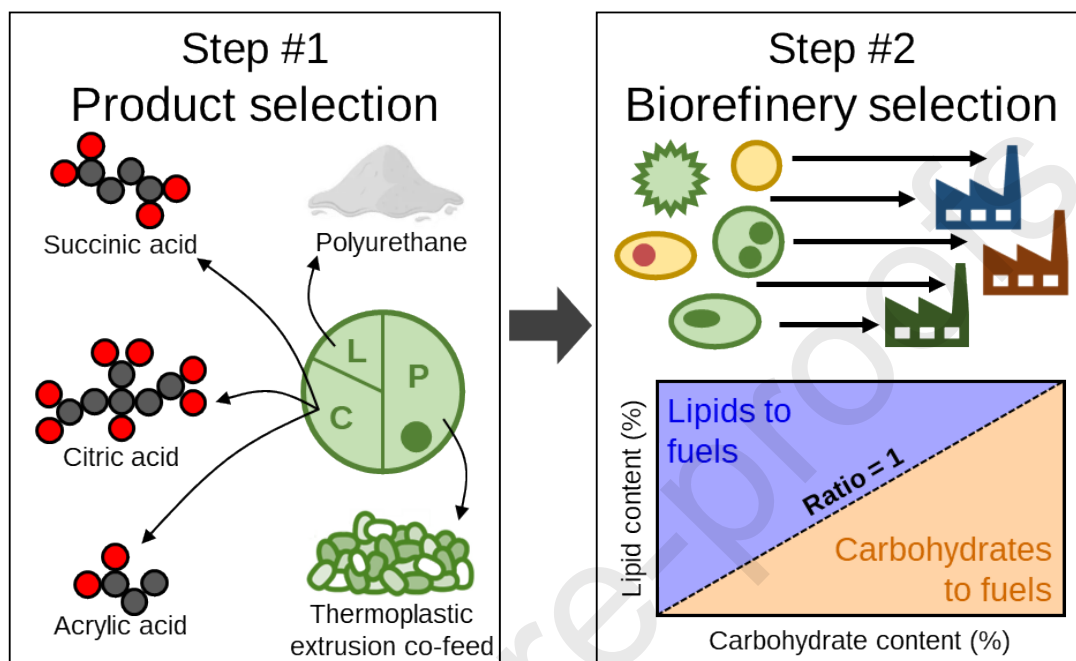
801

802 **Figure 1. General space of application of microalgae biomass as a function of the compositional**
803 **profile of fermentable carbohydrates and FAME-like (nonpolar) lipids using (A) Entropy and (B)**
804 **CRITIC weighting methods.** Shading indicates favorability to convert either lipids or carbohydrates to
805 hydrocarbon fuels with the alternate constituent routed to higher-value products when fuel production from
806 at least one fraction is a necessity. Plot labels ‘R’ and ‘D’ stand for nutrient-replete and nutrient-deplete
807 cultivations, respectively, while numbers 1-13 refer to the 13 strains assessed in this study - as shown in
808 the box. Process simulations of algae biomass conversion in biorefineries followed the general diagram
809 shown in (C), with the main economic and environmental outcomes of the 26 simulations presented in (D).
810 The color-code used for the pairings between strains and cultivation conditions shown in (D) is the same
811 as that determined using the CRITIC weighting method.

812 CRITIC: Criteria Importance through Inter-criteria Correlation; FAME: fatty acid methyl esters.

Graphical Abstract

Multicriteria Decision Analysis (MCDA)



Highlights

- First application of an objective method to outrank bioproducts and biorefineries.
- Decision-making process with technical, economic, and environmental criteria.
- Case study for the methodology: selecting microalgae-derived product portfolios.
- Succinic, citric, and acrylic acids ranked as the top carbohydrate-derived products.
- Lipid-to-carbohydrate ratios $> \sim 1$ should be converted in lipid-to-fuel biorefineries.