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Valorizing Biodiesel and Bioethanol Side-Streams: Sustainability Potential Assessment through a Multicriteria Decision Analysis Framework and Appraisal of Valuable Compound Recovery Prospects

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Abstract: A framework for assessing, from a sustainability and circular bioeconomy point of view, the best valorization approach for biorefineries side-streams has been developed and validated. Two biorefinery side streams are considered as case-studies for validation: rapeseed meal from biodiesel and corn oil from bioethanol production. Firstly, a methodology to evaluate different valorization scenarios has been developed following a holistic approach that addresses technical aspects, environmental impact, and economic analysis. This way, a framework (inspired by the Battelle Method and using insights from Multicriteria Decision Analysis) has been produced where the sustainability potential of each scenario can be assessed. Such framework has been validated for five valorization scenarios for rapeseed meal and seven scenarios for corn oil. It can be concluded that protein extraction through alkaline (NaOH) hydrolysis is the best approach for rapeseed meal valorization while carotenoids recovery through ion exchange extraction is the most suitable strategy for corn oil. Secondly, for the selected scenarios, an estimation of the maximum recoverable amount of valuable compounds is conducted at the European and country-level. The use of this framework substantially aids in the best choice of the cutting-edge conversion technologies, supporting industry practitioners in the selection of processes to be further scaled-up.

Keywords: sustainability; biorefinery; circular bioeconomy; biomass; biodiesel; bioethanol

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1. Introduction

Concerning sustainability and biorefineries, special attention is paid to biofuels and bioenergy production, as legislation and strategies are aimed at reducing carbon emissions and ensuring energy sustainability. Nowadays, there is an emerging interest worldwide for new valorization approaches of side-streams of biodiesel and bioethanol production, improving their environmental and economic profile, and ensuring greater sustainability of the bioenergy supply chain. These industrial processes usually produce by-products that are currently mostly utilized for energy, animal feed, or other low-value purposes. Specifically, rapeseed meal (RSM) linked to biodiesel production and corn oil (CO) and thin stillage (from bioethanol production) represent excellent sources of bioactive compounds that can be used in different industries such as food supplements [1], specialty chemicals [2], cosmetics [3], and ingredients for detergent market [4]. There are already several attempts of side-stream utilization into other value-added applications (e.g., production of biomethane from thin stillage by anaerobic digestion [5]), but without uncovering and exploiting the full potential residing within these streams. In these scenarios, new valorization processes must be developed and further upgraded.

To have a fully integrated sustainability approach, it is necessary to align the different assessments considering social, environmental, and economic aspects, as well as other set of relevant factors that have also been considered more recently (e.g., technical, human, etc.). Since the idea of sustainable development was identified as distinct from balancing economic wealth growth and environmental deterioration by the end of the sixties, the number of techniques, models, and strategies for measuring sustainability has significantly risen [6]. As a sustainability concept and its evaluation becomes more and more widespread, it is anticipated that the number of instruments for sustainability assessment will rise. Assessment tools already come in over a thousand different varieties. Currently, there is a plethora of sustainability assessment methods that have been extensively reviewed in several publications [6,7], some of them delving deeper into life cycle sustainability assessment [8,9]. These publications conclude that a strategic approach for a coherent and logical framework including pertinent theory and real-world experience, based on a critical study of the state of the art, is needed to design a new evaluation instrument in the field of sustainable development [6]. Practitioners of sustainability assessment have created a growing array of tools, but there is not a tool yet that has been pointed out as the tool of reference, valid for all use-cases.

This aspect becomes especially relevant when circular bioeconomy considerations add up to sustainability assessment exercises. To detect and prevent methods that promote circularity but result in unintended externalities, it is necessary to compare the sustainability of circular bioeconomy techniques to their linear counterparts [10]. Circularity measurements frequently contradict one another, yet operations research techniques like Multicriteria Decision Analysis (MCDA) may be able to resolve this issue. Walzberg et al. [10] noted that this issue makes it necessary to combine several approaches in order to evaluate more accurately the sustainability performance of circular bioeconomy. To maximize each method's benefits and reduce its drawbacks, they have devised hybrid techniques, which integrate various methodologies. Numerous methodologies may be used to examine circularity and have already been integrated in order to address a wide range of research problems. No solution, though, has yet been able to comprehensively address issues regarding the circular bioeconomy. In this scenario, Walzberg et al. [10] conclude that combining techniques from operations research, such as MCDA (as the prevalent inconsistencies between circularity metrics may be resolved by this approach), with techniques from complex systems science and industrial ecology might be an attractive direction for future study.

Life Cycle Sustainability Evaluation is one of the methods frequently employed for sustainability assessment (LCSA). The necessity to preserve the life cycle view while including the three pillars of sustainable development—environmental, economic, and social impacts—led to the creation of this development [8]. The Life Cycle Cost (LCC) approach is employed in LCSA for the examination of economic difficulties. However, it has two major drawbacks: complexity of input–output models and how externalities are handled [9].

It can be drafted that there is still a gap when it comes to industry practitioners making decisions about which technology is the keenest to be scaled-up from a sustainability and circular economy perspective. This is due to the fact that the majority of sustainability assessment methods focus on the three main sustainability pillars (economic, environmental, and social) and require lots of information from the process, but often lack considering technical aspects relevant to easiness and pertinence of the scale-up process that impact sustainability, e.g., need for custom-made vs. off-the-shelf equipment. In this sense, a few publications delve into evaluating the scalability features of technologies while considering some of the three main pillars from sustainability. Piccino et al. [11] focus on life cycle assessment (LCA) studies as a base for developing a framework for scaling up chemical processes. They present a method for simulating industrial scale manufacturing using data at hand without the need for understanding large-scale behavior (process chemistry). Such method is intended to be utilized by LCA practitioners who have no background in chemistry or chemical engineering and can assist in carrying out a scale-up strategy based on a methodical and logical process. Still, it is important to go further and consider not only the environmental dimension of sustainability, but to address the other sustainability dimensions since the application of fully integrated sustainability evaluation methods does not only ensure the comparability of results but also enhances consistency and reduces complexity in data gathering [12].

To the best of this publication authors' knowledge, a decision-making support framework that has a holistic approach for sustainability and scalability assessment has not been developed nor validated for biomass valorization options selection. Within this context, the research presented herein focuses on MCDA due to its potential to address several aspects at the same time, providing the holistic feature. The three components that make up the MCDA's strength are: (1) the information found in the criteria that were chosen; (2) the weights assigned to each criterion; and (3) consensus among the stakeholders over the weights assigned to each criterion [6]. It was also considered very important to include in the framework to be developed normalization, aggregation, and weighting. If weighting and aggregation are not conducted explicitly, each reader will ascribe weighting to the data based on their own value system, which will result in varying interpretations [9]. The way to tackle this and to ensure that the framework can be easily used and replicated for other processes is thanks to the transference functions.

Specifically, the method developed by the Battelle-Columbus Institute [13], the so-called Battelle Method (BM), is the main quantitative method that has been developed for the evaluation of environmental impacts. Its objective is the systematic evaluation of the impacts of a project using homogeneous indicators, which are defined through different parameters demonstrating the representativeness of the environmental impact derived from the actions considered. The parameters are arranged in different components grouped in multiple environmental categories with their corresponding values being transformed into commensurable units to assure subsequent comparison by means of transformation techniques.

This way, in the frame of the present investigation, a BM inspired framework based in MCDA principles has been developed and validated for assessment of sustainability potential for innovative valorization approaches for biodiesel and bioethanol side-streams. Accordingly, the following research questions (RQ) have been addressed:

- RQ1. How can a methodology for side-streams valorization scale-up selection be developed from the sustainability perspective that is easy to use and that does not require extensive knowledge or specific software deployment?
- RQ2. What is the most suitable approach to support a holistic assessment?
- RQ3. Which aspects from a technological process are linked to sustainability (from the environmental, technical, and economic fields)?
- RQ4. Which is the most suitable approach for valorizing rapeseed meal and corn oil as biorefinery side-streams?
- RQ5. What is the maximum quantity of valuable compounds that Europe could produce if the selected side-streams would be fully valorized?

The research presented is structured as follows: An overview of the selected side-streams and valorization approaches as well as how the framework has been shaped is provided in Section 2. Here, the selected biorefineries (biodiesel and bioethanol productions) are presented, together with the selected side-streams and their characterization. The collection of data used for the recovery potential estimation and the way that the BM approach has been used as the key idea for the framework development are explained (answers to RQ1 and RQ2), delving into the technical, economic, and environmental assessment techniques so as to define the Sustainability Potential Index (SPI, answer to RQ3). Section 3 starts presenting the results from the validation exercise as the framework is used to assess five scenarios for RSM and seven scenarios for CO valorization (answer to RQ4). Then, the estimation of the quantity of valuable compounds that could be recovered through the selected scenarios in European countries is provided (answer to RQ5). Section 4 discusses the results and Section 5 concludes by summarizing the key findings, highlighting the research's shortcomings, and outlining any possibilities and future development prospects.

2. Materials and Methods

Steps followed towards the development of the sustainability potential assessment framework and the subsequent valuable compounds recovery prospect evaluation are described next. Case studies used for validating the proposed framework are presented here as well.

2.1. Sustainability Potential Assessment Framework Development

The rationale for the sustainability potential assessment is based on an MCDA approach. Specifically, the Analytic Hierarchical Process (AHP) approach has been followed as a trade-off solution between the reliability of the solution, amount of information needed, and ease of use. According to Vaidya et al. [14], the unique quality of AHP is its adaptability to be coupled with other strategies, allowing the user to gain advantages from all the combined ways and thus better accomplish the intended aim. This is why the authors have deemed this MCDA approach as the most suitable one to be combined with BM. AHP is a precise method for calculating the relative importance of the various decision-making factors. Through pair-wise comparisons, the experiences of individual experts are used to assess the relative magnitudes of different aspects.

The BM dimension is considered since such method is identified as quantitative and reliable as it can consider different measurements from an objective point of view as it converts different measurements into common units by means of a scalar or "value function". Following the goal of developing a framework that is easy to be implemented and used by all kinds of stakeholders, the decision matrix has been created in an Excel file.

Steps followed during the development of the framework are presented next. Most of them are the usual ones for MCDA frameworks development while some of them have been added due to the BM consideration:

1. Goal and scope definition: the MCDA will use, for the environmental and technical aspects assessment, the same system boundaries and functional unit, focusing on the process itself, i.e., the same system boundaries and functional unit as the LCA will be considered, as this will be the methodology used for environmental impact assessment. As for the economic aspects, the equipment costs and maintenance are considered as well. It is important to notice that, while the LCA does not consider local conditions, organizational issues or local regulatory issues, the MCDA could consider these aspects in the decision making at a later stage.
2. Selection of systems for comparison: scenarios to be assessed and compared need to be fully defined. It is very important that, for each scenario, the following aspects are clearly identified: feedstock, main technology and expected final products.
3. Definition of criteria and sub-criteria: here is where the application of BM principles starts to be considered. BM names the main criteria as categories and the sub-criteria as components. Therefore, for each of the selected categories (environmental, technical, and economic), components need to be defined.
4. Rating: to be able to rank the different systems, and to capture local interests and conditions, each set of categories and components (criteria and sub-criteria in the developed framework) need to be rated in accordance with their relative importance. Hence, a total of 1000 sustainability potential units are allocated to each component (similar to BM where 1000 units of measurement are distributed among the different components).
5. Definition of the transformation functions: for each component, a transformation function is defined, making it possible to conduct the assessment process unequivocally and objectively.

The fourth and fifth steps are presented in Section 3, since they are developed ad hoc for the biodiesel and bioethanol side-streams valorization approaches assessed.

Concerning the goal and scope definition, the study has been conducted in the frame of the Bio-Based Industries Joint Undertaking funded EXCornsEED project, an innovation project devoted to valorization of biorefinery side-streams through a combination of innovative extraction, concentration, and purification technologies. The case study for this project has been the Envien Group, based in the Central and Eastern Europe region (Slovakia, Czech Republic, Hungary, Croatia, and Poland, being one of the largest and most significant groups of companies in such area) active in the production of biofuels.

As for the selection of systems for comparison, the side-streams considered in the frame of the present research are RSM and CO. RSM is a free-flowing material resulting from the production of crude rapeseed oil, obtained by the subsequent extraction of rape seeds after the pressing process, being a very valuable nutritional side-stream full of proteins (min. 33% in weight), minerals, and other very interesting compounds, e.g., sinapic acids and polyphenols. CO is a liquid side-stream of bioethanol production, isolated from corn thin stillage and is rich in lipophilic bioactive substances such as carotenoids, phytosterols, tocopherols, and omega 6. The main composition of RSM and CO streams mentioned has been published elsewhere [14].

Regarding the valorization scenarios to be assessed in order to validate the proposed framework, twelve scenarios have been selected for the valorization of the selected side-streams. For each one, the following aspects have been identified: (1) feedstock; (2) main technology; and (3) expected final products. These 12 scenarios are 12 different valorization technologies developed in the frame of the aforementioned EXCornsEED project (Table 1).

Table 1. Scenarios from the selected case studies (rapeseed meal and corn oil valorization) used for validating the proposed sustainability potential assessment framework.

Scenario	Feed	Product	Technology
R1	RSM	Proteins	Alkaline hydrolysis (NaOH)
R2	RSM	Polyphenols	Ion extraction
R3	RSM	Polyphenols	Enzymatic extraction
R4	RSM	Proteins	Enzymatic extraction
R5	RSM	Proteins	Alkaline hydrolysis (Na_2CO_3)
C1	CO	Carotenoids	Ion extraction
C2	CO	Triglycerides	Liquid-liquid extraction
C3	CO	Bioactives (mix)	Supercritical extraction with alumina
C4	CO	Bioactives (mix)	Supercritical extraction with silica gel
C5	CO	Triglycerides	Ionic liquid extraction
C6	CO	Bioactives (mix)	Solid extraction (bind and elute)
C7	CO	Triglycerides	Solid extraction (fractioning)

With respect to the definition of categories and components, this has been done following a holistic approach concerning sustainability. In order to properly address and assess all aspects and dimensions that conform sustainability, circular bioeconomy and scale-up target, environmental, economic, and technical issues have been considered. This approach is aligned with recent publications about sustainability assessment [15,16].

This way, categories have been sorted into three main sustainability criteria: addressing technical performance, environmental aspects, and economic aspects. As for the environmental aspects, the LCA is considered. For the economic aspects, different ratios and economic information are examined, while process characteristics evaluation is related to the technical aspect. In order to define the set of components and subsequent rating, i.e., sustainability potential units allocated to each component, a DELPHI Method [17] inspired workshop was organized where partners from the EXCornsEED project participated. Expertise among this group ranges from circular bioeconomy, biorefineries, process development, process scale-up and optimization to environmental impact assessment, economics, etc. As a first output of this workshop, the following set of components was defined as follows and as depicted in Figure 1.

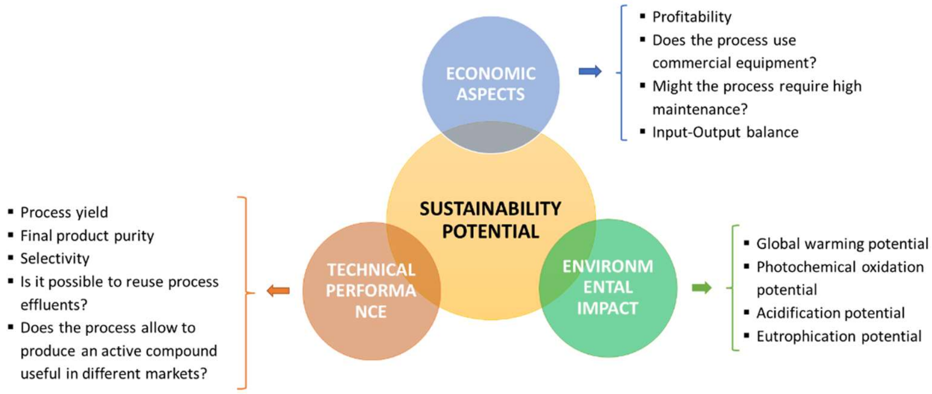

Figure 1. Set of categories and components defined as a result of the DELPHI Method inspired workshop.

- Technical Performance: Process yield, Final product purity, Selectivity; Is it possible to reuse process effluents? and Does the process allow for producing an active compound useful in different markets?
- Environmental Impact: Global warming potential, Photochemical oxidation potential, Acidification potential, and Eutrophication potential.
- Economic Aspects: Profitability; Does the process use commercial equipment? Might the process, at a theoretical commercial side, require any high maintenance? and Input–Output balance.

The second conclusion from this workshop was the rating and transference function definition. For each component, the different qualitative and quantitative values (e.g., yield in % for technical category, global warming potential for environmental category or OPEX in € for economic category, among others) are converted to normalized commensurable units (from 0 to 1) through transference functions (or scalar functions). This commensurable unit that results from the transference function is called Sustainability Value in the proposed framework.

Once sustainability potential points are allocated to the different components and the normalized transference functions are defined, it is possible to calculate the Sustainability Values for each defined scenario together with the corresponding SPI. Calculations are done according to Equation (1):

$$\text{Sustainability Potential Index (SPI)} = \sum_{i=1}^{12} (X_i \cdot W_{xi}) \tag{1}$$

where X_i are the Sustainable Potential units for every 'i' component, and W_{xi} are the Sustainable values for every 'i' component calculated using the aforementioned transference functions (values between 0 and 1).

2.2. Literature Review and Data Gathering for Recovery Prospects Appraisal

Firstly, a literature review [18] was done to gather the numerical data needed for the recovery potential estimation. Data were collected from both scholarly journals and non-academic organizations. The rationale behind this approach is that sometimes this kind of information (production data, business information) can be found not only in peer-reviewed material but also in publications from the professional domain. Moreover, as the data to be retrieved are linked to circular bioeconomy, this decision was backed by conclusions from Geissdoerfer et al. [19]: "The inclusion of non-peer-reviewed articles is appropriate since circular economy is a new area of research and (. . .) has not been extensively addressed by peer reviewed articles".

As a result, publications from business organizations, Eurostat datasets and website, project reports, Science Direct, Web of Science, MDPI, Springer, Taylor & Francis, Google Scholar, and others have been vetted as data sources. The key words used in the data search were (i) "bioethanol" AND "side-stream" OR "side-stream" AND "production" OR "availability"; (ii) "biodiesel" AND "side-stream" OR "side-stream" AND "production" OR "availability"; (iii) the various names of selected side-streams (RSM and CO) were also searched separately next to AND "production". Based on scanning the identified documents, data that were considered not reliable, outdated or not representative were discarded.

Content of valuable compounds in the selected side-streams was gathered from literature [20,21]. Valuable compounds product prices were checked with market suppliers.

3. Results

3.1. Sustainability Potential Assessment Framework Development and Validation

Following the main principles of BM and through the DELPHI-inspired workshop already described, a total of 1000 Sustainability Potential units were allocated among the different components (sub-criteria) for each of the categories (main criteria, namely environmental, economic, and technical). The allocation of this units is represented in Figure 2.

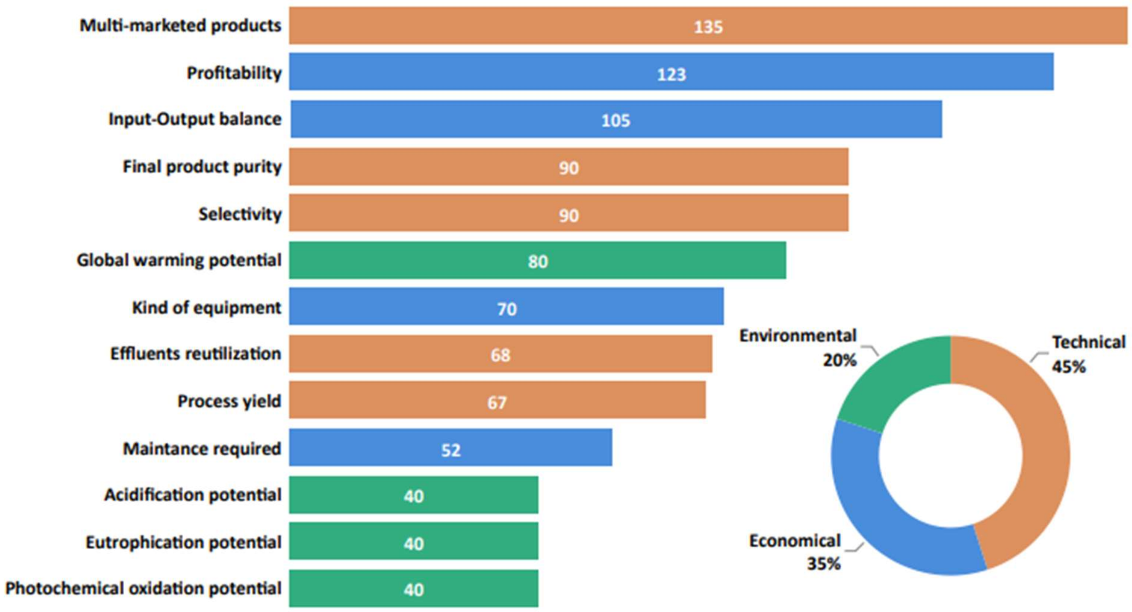

Figure 2. Sustainability Potential Units distribution among the different categories and components.

After allocating the Sustainability Potential Units, the transference functions were defined. The next paragraphs describe how the transference functions for technical performance components have been defined:

- Process yield, final product purity, and selectivity: the value is linearly extrapolated according to the corresponding ratio where 0 is for 50% and 1 for 100%.
- Effluents reutilization: the value is extrapolated according to the corresponding reuse ratio where 0 is for 0% reuse and 1 is for 100% reuse.
- For Products useful in different markets, 4 target markets: food (elders), food (toddlers), cosmetics and chemicals were identified, and a discrete function was defined as follows: for 1 market, factor = 0.25; for 2 markets, factor = 0.5; for 3 markets, factor = 0.75; and for 4 markets, factor = 1.

In the case of environmental impact components, transference functions are as follows:

- Global warming potential, Photochemical oxidation potential, Acidification potential, Eutrophication potential rate from 0 to 1 according to the results of the LCA carried out to the different scenarios. The rating will be 0 for the highest amount (kg CO_2 eq/kg–kg C_2H_4 eq/kg–kg SO_2 eq/kg–kg $PO_{4-}{}^{3}$ eq/kg, respectively), and 1 to the lowest amount, and rates for the intermediate values will be extrapolated.

The transference functions for economic aspects are presented next:

- Profitability: Prices from final products per kg or per L were considered. The lower price would be equivalent to 0.2 and the higher price would be equivalent to 1, extrapolating for the rest of scenarios values. In case of a scenario providing several final products, the price of the different products would be summed up;
- Kind of equipment: Since ad-hoc equipment could affect process economics by increasing the CAPEX, the following rating considerations could be used (having in mind a full commercial scale): All the process equipment needs to be tailor-made: 0; Only one piece of equipment (the one related to the core of the proposed process) and one piece of auxiliary equipment need to be tailor-made: 0.2; Only one piece of equipment (the one related to the core of the proposed process) needs to be tailor-made: 0.4; Several auxiliary equipment need to be tailor-made: 0.6; Only one piece of auxiliary equipment needs to be tailor-made: 0.8; Both main and auxiliary equipment can be acquired from commercial catalogues: 1;
- Scale-up potential: Rating was defined after the answer of the following two main questions: (1) is the business easy to scale up: is the possibility to multiply incomes based on sustainable investments?, and (2) Does the scalability of production mean an optimization of costs production?

  For (1) no; and (2) no; the factor is 0.
  For (1) no; and (2) yes; the factor is 0.33.
  For (1) yes; and (2) no; the factor is 0.67.
  For (1) yes; and (2) yes; the factor is 1.

- Maintenance of the process: High maintenance (e.g., replacement of at least one main equipment, all auxiliaries, membranes, sensors, etc. once per year) ~0; High-medium maintenance (e.g., replacement of all auxiliaries, membranes, sensors, etc. once per year) ~0.25; Medium maintenance (e.g., replacement of all auxiliaries, membranes, sensors, etc. every two years) ~0.5; Medium-low maintenance (e.g., replacement of membranes every two years) ~0.75; Low maintenance (no major replacement of main equipment, nor auxiliaries, etc. is expected within 3 years of operation) ~1;
- Input–Output balance: This component is related to OPEX and the income from selling process of produced bioactive compounds. The input-output balance needs to be calculated per each scenario and then a rating allocation and extrapolation would need to be done as in the case of profitability.

The above presented framework was used to rank the different developed technologies. Firstly, transference functions were used to calculate the Sustainability Values for each component. The results for the different categories are provided in Tables 2 and 3.

Table 2. Calculated Sustainability values for the defined components. Case study: rapeseed meal valorization.

Component	R1	R2	R3	R4	R5
Process yield	0.30	0.00	0.00	0.00	0.00
Product purity	0.82	0.60	0.00	0.85	0.00
Selectivity	0.90	0.40	0.80	0.70	0.60
Effluents reutilization	0.00	0.00	1.00	0.00	0.00
Multi-marketed products	1.00	1.00	0.50	0.50	0.50
Global warming potential	0.95	0.96	0.90	0.81	0.00
POP *	0.95	0.96	0.83	0.72	0.00
Acidification potential	0.94	0.96	0.91	0.82	0.00
Eutrophication potential	0.91	0.93	0.87	0.71	0.00
Profitability	0.80	0.80	0.80	1.00	0.60
Kind of equipment	1.00	1.00	1.00	0.80	0.80
Maintenance required	0.75	0.75	1.00	0.50	0.75
Input-Output balance	0.70	0.70	0.80	0.60	0.60

* POP: Photochemical Oxidation Potential.

Table 3. Calculated Sustainability values for the defined components. Case study: corn oil valorization.

Component	C1	C2	C3	C4	C5	C6	C7
Process yield	0.40	0.00	0.00	0.00	0.00	0.00	0.00
Product purity	0.80	0.05	0.05	0.10	0.05	0.05	0.00
Selectivity	0.80	0.35	0.35	0.10	0.05	0.05	0.00
Effluents reutilization	0.00	0.90	0.50	0.90	0.90	0.90	0.00
Multi-marketed products	1.00	0.50	0.50	0.15	0.00	0.00	0.25
Global warming potential	0.34	0.94	1.00	0.98	0.85	0.63	0.96
POP *	0.41	0.95	1.00	0.97	0.90	0.74	0.96
Acidification potential	0.29	0.95	1.00	0.98	0.85	0.64	0.96
Eutrophication potential	0.28	0.92	1.00	0.99	0.77	0.43	0.93
Profitability	1.00	0.15	0.15	0.15	0.15	0.15	0.00
Kind of equipment	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Maintenance required	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Input-Output balance	0.80	0.70	0.70	0.70	0.70	0.70	0.20

* POP: Photochemical Oxidation Potential.

It is worth noticing that, when a scenario has 0 points, it means that the assessed component has the worst value compared with the rest of assessed scenarios (as it is the case of the environmental components for R5) or that obtains 0 according to the transference function (as it is the case for C7 in most of the technical components).

Then, it was possible to obtain the SPI for each scenario and rank them accordingly. Calculations were done according to Equation (1). Results are provided in Figure 3.

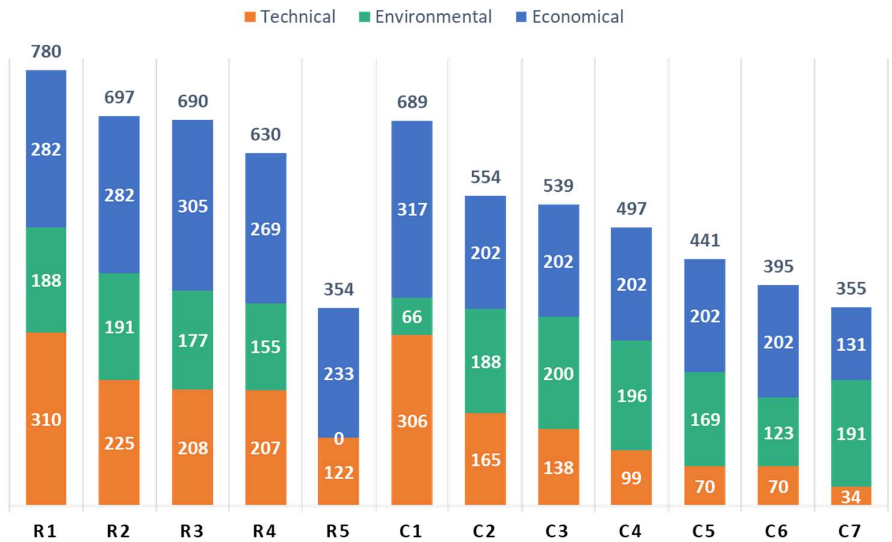

Figure 3. Sustainability Potential Indexes for the assessed scenarios.

It can be pointed out, from analyzing the chart provided in Figure 3, that the scenario with highest SPI for RSM valorization is R1 (protein production through alkaline (NaOH) hydrolysis). In the case of CO valorization, the highest SPI is the one for carotenoids production through ion extraction.

3.2. *Appraisal of Recovery Prospects*

Once the different valorization alternatives have been evaluated, the recovery prospects of the valuable compounds to be extracted through the most advantageous options (proteins from RSM and carotenoids from CO) have been quantified for European countries. This has been carried out by conducting the corresponding calculations, using as a starting point the data retrieved through the literature review exercise that has been performed (previously described in Section 2.2 Literature review and data gathering for recovery prospects appraisal).

Table 4 presents the total production of the side-streams considered in the present research (RSM and CO). There was a lack of data for some countries for side-stream volumes since they are sometimes classified as waste and therefore production data are not quantified and/or made public. For these cases, the total production in 2020 for biodiesel and bioethanol [22,23] has been used as calculation basis and side-stream volumes have been estimated accordingly. In line with the ePure report [23], around 51% *w*/*w* from all bioethanol produced in Europe comes from corn, while Duren et al. [24] report that 79% from European biodiesel comes from rapeseed. Additionally, the RSM amount generated during biodiesel accounts, on average, for 0.6579 tons of RSM being produced per each t of biodiesel [25]. The distribution of products and side-streams obtained when processing 1 bushel of corn for bioethanol production is: 18.2 lbs of ethanol, 15.5 lbs of DDGs, 0.7 lbs of technical CO [26]. Then, these calculations were extended in order to consider dry weight figures. According to [26], dry weight RSM without impurities equals 90.46% w. while dry weight CO without impurities amounts to 99.5% w [21]. Figure 4 provides qualitative information of the RSM and CO production.

Table 4. Estimated corn oil and rapeseed meal generated in Europe in 2020 and potential production of proteins from rapeseed meal and carotenoids from corn oil in European countries.

Country	Rapeseed Meal * (kt)	Proteins (kt)	Corn Oil * (kt)	Carotenoids (t)
Austria	335	121	8.8	3.9
Belgium	234	84	19.2	8.4
Bulgaria	52	19	3.5	1.5
Czech Republic	218	79	8.2	3.6
Finland	260	94	6.0	2.4
France	1198	432	73.5	32.2
Germany	1971	711	40.5	17.7
Hungary	52	19	28.2	12.3
Ireland	30	11	0.3	0.1
Italy	1150	415	14.4	6.3
Latvia	90	32	0.8	0.4
Lithuania	101	37	1.0	0.4
Netherlands	1113	401	20.8	9.1
Poland	813	295	35.1	15.4
Portugal	375	135	0.1	0.0
Romania	156	56	0.4	0.2
Slovakia	70	25	6.4	2.8
Spain	2020	794	20.3	8.9
Sweden	234	84	14.0	8.9
United Kingdom	319	115	18.1	7.9
Total	10,978	3958	320.5	142.5

* Dry without impurities.

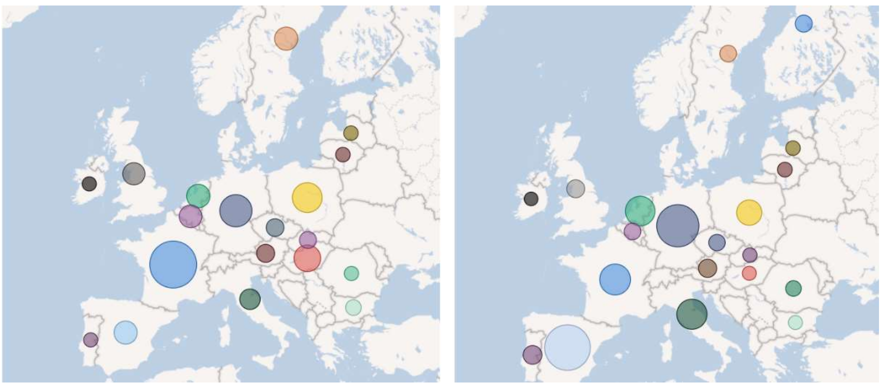

Figure 4. Qualitative representation of the production of CO (**left**) and RSM (**right**).

Data for the studied valuable compounds per country as well as other substances of interest with high market potential (phenolic and sinapic acids for RSM and tocopherols and phytosterols for CO) can be found in Supplementary Materials where an interactive map for the different European countries has been included.

4. Discussion

Concerning the developed and validated framework, it could be pointed out that the three components that make up the MCDA's strength are: (1) the information found in the criteria that were chosen; (2) the weights assigned to each criterion; and (3) consensus among the stakeholders over the weights assigned to each criterion.

The framework validation exercise (assessment of the 12 selected scenarios) provided interesting information about the SPI and how this differs between scenarios. The evaluated processes obtained SPI ranging 354–780, being the greatest variations in technical and environmental aspects. It is worth noticing that, among RSM and CO scenarios, the ones related to RSM valorization achieved the highest SPI.

As for RSM valorization, the top three scenarios were: (1) protein extraction by alkaline hydrolysis (NaOH) and acidic precipitation; (2) polyphenols extraction using ionic resin; and (3) polyphenols enzymatic extraction. Both first- and second-ranked scenarios obtained same marks for economic aspects, but the first scenario ranked better for technical aspects (more than 300 Sustainability Potential Units). This is due to the fact that the alkaline protein extraction requires off-the-shelf equipment and provides higher process yield, final product purity, and selectivity. Protein extraction also provides the possibility of obtaining different products, so this adds up to the technical aspects linked Sustainability Potential Units. Although the second scenario obtained better environmental marks, the difference was only three Sustainability Potential Units vs. the first scenario. This slightly better environmental performance is mainly due to the lower energy intensive consumption and the amount of effluents to be processed that the ion extraction and enzymatic extraction represent. It is worth pointing out that both alkaline extraction and ion exchange extraction obtain similar Sustainability values for environmental and economic categories, but alkaline extraction obtains better values for purity and selectivity. The third scenario is quite like the second one, with worse technical and environmental performance but better economical behavior due to having the highest effluent reutilization (but the positive issue mentioned does not counter the not so good punctuation in the rest of the aspects).

For the top ranked scenario, concerning the implications from the operational point of view, the process is a solid–liquid extraction step that is done at room temperature and using commercial equipment. Therefore, it could be concluded that it is not an energy intensive process except for the protein drying stage. Using off-the-shelf equipment is a positive aspect as well. As for the environmental costs, the most relevant aspect here is the reuse of the discarded liquid effluent that is left after separating the extracted solid from the alkali dilution. Process efficiency would be directly linked to the optimization of the solid/liquid ratio and the amount and number of times that the separation resulting effluent could be recirculated to the process, i.e., used as feedstock again. Although the alkali solution would not imply high waste management costs as it is not a very dangerous solvent (NaOH concentration is rather low), large volumes (produced in the case of not being possible to re-use the effluent under a high soli/liquid ratio) would imply relevant waste management costs.

Regarding the valorization of RSM and the assessment of several alternatives, only one peer reviewed publication has been identified so far as relevant to the results presented herein. This publication by Beaubier et al. [27] describes how Multiobjective Decision Making strategies built upon the Rough Set approach can be used for selective albumin extraction from RSM. On three process performance indicators (albumin extraction yield, albumin content in the extract, and phytic acid content in the residual solid residue), the effects of pH and NaCl concentration during the extraction step were examined. Hence, rather than assessing different valorization scenarios, the publication focuses on assessing different process parameters, i.e., evaluating different process parameters for process optimization. Briefly, most RSM valorization papers found describe a particular process that has been developed, not focusing on the comparison among different scenarios. There are two research works worth mentioning concerning the protein extraction from RSM. One is the work from Rodrigues et al. [28] that delves into the different methods, limitations, and potential of protein production using oilseed plants as feedstock. The other one is the publication from Baker et al. [29], which compares protein production using four different crop residues. Nevertheless, in any of these publications, a quantitative analysis of the different approaches for valorizing RSM is provided.

In the case of CO, the top three scenarios were: (1) carotenoids production by ion extraction; (2) triglycerides production through liquid–liquid extraction; and (3) mix of bioactive compounds production by supercritical extraction with alumina. While the second and third scenarios obtained rather similar SPI, the first scenario ranked more than 140 Sustainability Potential Units of difference vs. the second one. The most relevant issue that can be noticed when comparing the top three scenarios is that, by focusing only on environmental aspects, the carotenoids production would be discarded as it has less than a third of the points that the other scenarios have. However, when other categories are analyzed, carotenoids production duplicates the technical linked Sustainability Potential units of the other two alternatives and goes more than 100 points higher for economic issues. Providing a closer look at the Sustainability Values of the top three scenarios, it can be seen that, from the technical point of view, process yield, purity, and selectivity are much higher for the carotenoid's extraction. Only in the component Effluents reutilization do the other two scenarios obtain higher scores. As for environmental impact, scenarios 2 and 3 obtain almost the same values, with the first one being considerably lower. For economic issues, the Sustainability value for carotenoids is 1 (the maximum), while scenarios 2 and 3 mark only 0.15. This is due to higher market prices for carotenoids.

For the top ranked scenario, and from an operational point of view, the ion extraction based on the use of ionic resins requires a careful optimization in order to identify the operational parameters that enhance resin lifetime without compromising process performance. Moreover, the resin regeneration process is a key step in the scenario. These aspects would be linked to process operational costs as the resin replacement costs can become a relevant cost if this is needed very often. In addition, ethanol is used as eluent, being evaporated after. It is important therefore to optimize as well the amount of ethanol to be used in order to minimize the costs linked to the evaporation step. From an environmental cost point of view, ion extraction would generate a certain amount of waste (spent effluent and spent resin) so the waste management costs need to be carefully evaluated as well.

Regarding the CO valorization and the assessment of different alternatives, no publication specifically devoted to this has been identified so far (there are just several peer reviewed publications presenting particular approaches).

As it can be drafted from both analyses, RSM and CO scenarios, the variability in points from the different categories provides evidence about how the selection of a process based on separate analyses of these categories would lead to incomplete conclusions since other relevant aspects might be overlooked.

Delving into the results from the recovery prospects' appraisal exercise, the amounts of RSM and CO that can be produced in Europe reach 11 million tons and 320 ktons, respectively. The countries that produce the largest quantity are Spain and Germany in the case of RSM and France and Germany in the case of CO. Considering the SPI obtained for the processes evaluated, the most interesting options are the recovery of crude proteins from RSM, which could amount a total of 3985kt in Europe, with Spain, France, and Italy as the top three countries (794, 432, and 415 kt, respectively). In the case of CO and carotenoids recovery, there is a potential of 142.5 t for carotenoids recovery in Europe, with France (32.2 t) and then at a wider distance Germany and Poland (17.7 and 15.4 t, respectively). Going a step further than evaluating just the recovery potential (amount) of these valuable compounds, the market potential in terms of economic benefit can be estimated as well.

Market prices for proteins from RSM and carotenoids form a CO amount 3–8 €/kg (research to market-3BCAR) for protein and 30–80 €/kg for carotenoids [30,31].

Aside from the market potential and economic benefit that Europe could find in the protein and carotenoids production from side-streams, it is worth considering as well how this could affect the scenarios and targets for 2050 in terms in potential land use and climate impacts. Röös et al. [32] calculated the minimal amount of agricultural land necessary for Western Europe to feed itself from its own land base in 2050, as well as the resulting GHG emissions. A variety of food eating pattern-based scenarios were modeled, each based on various "protein futures". The scenarios included artificial meat and dairy, livestock on "ecological leftovers" (livestock reared only on land unsuited to cropping, agricultural residues and food waste, with consumption capped at that level of availability), intensive and efficient livestock production using today's species mix, intensive efficient poultry–dairy production, intensive efficient aquaculture–dairy production, and a "plant-based eating" scenario. "Projected diet" and "healthy diet" variations were simulated for each scenario. The new possibility brought by having plant-based protein coming from RSM could be added now to these assessments since, as it has been pointed out by the recovery prospect appraisal, there is a considerable amount that could be produced by valorizing biodiesel side-streams. Specifically, the Smart Protein project concluded that, in Europe, consumption of plant-based foods has surged by 49% in just two years [33].

Concerning carotenoids, according to Yaqoob et al. [34], the greatest market for them being used as a natural coloring agent is predicted to be Western Europe, followed by the US, in 2024, when consumption of natural carotenoids is projected to reach 2699.8 Mt. Together, the following compounds account for over 90% of the market's value: capsanthin, astaxanthin, beta-carotene, lutein, annatto, lycopene, and canthaxanthin. The two most well-known carotenoids, astaxanthin and beta-carotene, account for over half of the worldwide carotenoid market. In fact, nowadays, Germany already leads the European market for carotenoids [28], i.e., the country has the needed infrastructure and organizational issues needed to harness their second place as a European country in the recovery prospects' appraisal exercise conducted.

It is worth mentioning that the appraisal exercise has been done considering a hypothetical situation where all the side-streams volumes are valorized to their full extent. This is fulfilled if 100% of the available side-stream is processed, and 100% of the valuable compound is recovered. The aim of this hypothesis is to trigger discussions among policy makers and industry, creating awareness of the potential that Europe poses and that could bring the region to the forefront of the circular bioeconomy scene. Actually, not all of the side-streams available volume is valorized, as in some cases it is still not profitable due to the lack of a proper scale-up process, value chain, etc. Moreover, in the case of CO, this stream is sometimes recirculated to the bioethanol production process in order to increase process yield. The primary limitations of the present research are linked to the non-inclusion of societal aspects in the framework. This occurred because the main aim was to focus on the scale-up process and on providing a quick, easy method for practitioners. Information about societal implications is sometimes hard to obtain or unknown, especially when developments are still at an early Technology Readiness Level. In addition, limitations are linked to challenges encountered when searching for information as a result of the inherent difficulty in quantifying by-products, co-products, and side-streams due to formal designations as waste or residue and End-of-life state consideration as it is described in different European and national regulations pose (e.g., the Waste Framework Directive [35]).

Concerning future research to be carried out, the developed framework could be expanded so it can assess the full commercial scale and all dimensions from sustainability by including social aspects as a new category. It would also be interesting to explore whether other dimensions being recently considered in sustainability discussions (such as institutional or cultural) are applicable and/or relevant in the circular bioeconomy context [36]. In addition, further validation using other biomass sources would allow for ensuring that the developed transference functions remain valid and consistent, allowing an objective assessment. As for recovery prospects appraisal, it would be extremely helpful to broaden the study to include the North and South American, as well as the Asian areas, as the data offered in this article focus only on European nations.

Lastly, regarding the impact of the research presented herein and how this could support the development of the science, the proposed and validated framework could be used by researchers that usually use only BM based methodologies in order to expand their current tools portfolio when facing the problem of analyzing different valorization scenarios under technical and economic perspectives (aside from just the environmental perspective considered in the BM). Industry practitioners could also benefit from the proposed framework as it does not require specific software (it can be easily implemented in an MsOffice Excel sheet) or deep knowledge about chemistry or process parameters. As for the recovery prospects' appraisal results, this information would be very valuable for both policy makers and stakeholders looking for investing in circular bioeconomy related processes. Knowing the regional potential for valuable compounds would allow for drafting better ad-hoc policy measures (such as incentives to certain technologies or products) and would also allow for private sector and investors to make better decisions on where to build biorefineries.

5. Conclusions

There is a growing pressure on biorefineries for them to increase their sustainability, when the valorization of side-streams represents the possibility to lower their environmental impact while increasing their economic performance due to the additional incomes that the marketing of additional by-products provides. In this context, many new valorization approaches are being investigated, it being difficult for practitioners to make decisions about which one is the most suitable one for further scale-up due to the lack of tools that are easy to use, require a limited amount of data, and provide a holistic dimension for sustainability assessment while considering circular bioeconomy dimension at the same time.

In order to address this issue, a multicriteria decision analysis has been developed and validated for two main side-streams: rapeseed meal from biodiesel production and corn oil from bioethanol manufacturing. During the development, the categories and components rating as well as the transference functions were defined in order to perform an objective and unequivocally assessment process. For the validation, seven and five scenarios were considered for rapeseed meal and corn oil valorization, respectively. For each scenario, the feedstock, main technology and final product were defined, and the Sustainability Potential Index was calculated. The most relevant scenarios in terms of sustainability potential towards scale-up are protein recovery from rapeseed meal through alkaline (NaOH) extraction and carotenoids recovery from corn oil through ion extraction. The analysis of the different categories shows how choosing a method based on individual assessments (only one of these categories) would result in incomplete results since other important factors can be neglected.

For both valuable compounds, a recovery prospects appraisal exercise was conducted to identify, in a theoretical scenario, where all side-streams are valorized, the potential amount per European country. There is a potential recovery of 3985kt of crude protein from rapeseed meal and 7644 t of carotenoids form corn oil for Europe. This is relevant information to be considered in the assessment of future scenarios of European consumption and manufacturing targets.

Finally, it is important to point out that this framework is relevant to stakeholders involved in biomass, as it has been designed primarily to support technology developers in their decision process, significantly supporting the selection of the optimal conversion technologies in the case of the biomass sustainability and circular bioeconomy.

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