



EXPLORING THE ECONOMIC AND ENVIRONMENTAL IMPLICATIONS OF INTEGRATING CARBON CAPTURE IN BIOREFINERY SYSTEMS

Stylianos Fanourakis

ADVERTIMENT. L'accés als continguts d'aquesta tesi doctoral i la seva utilització ha de respectar els drets de la persona autora. Pot ser utilitzada per a consulta o estudi personal, així com en activitats o materials d'investigació i docència en els termes establerts a l'art. 32 del Text Refós de la Llei de Propietat Intel·lectual (RDL 1/1996). Per altres utilitzacions es requereix l'autorització prèvia i expressa de la persona autora. En qualsevol cas, en la utilització dels seus continguts caldrà indicar de forma clara el nom i cognoms de la persona autora i el títol de la tesi doctoral. No s'autoritza la seva reproducció o altres formes d'explotació efectuades amb finalitats de lucre ni la seva comunicació pública des d'un lloc aliè al servei TDX. Tampoc s'autoritza la presentació del seu contingut en una finestra o marc aliè a TDX (framing). Aquesta reserva de drets afecta tant als continguts de la tesi com als seus resums i índexs.

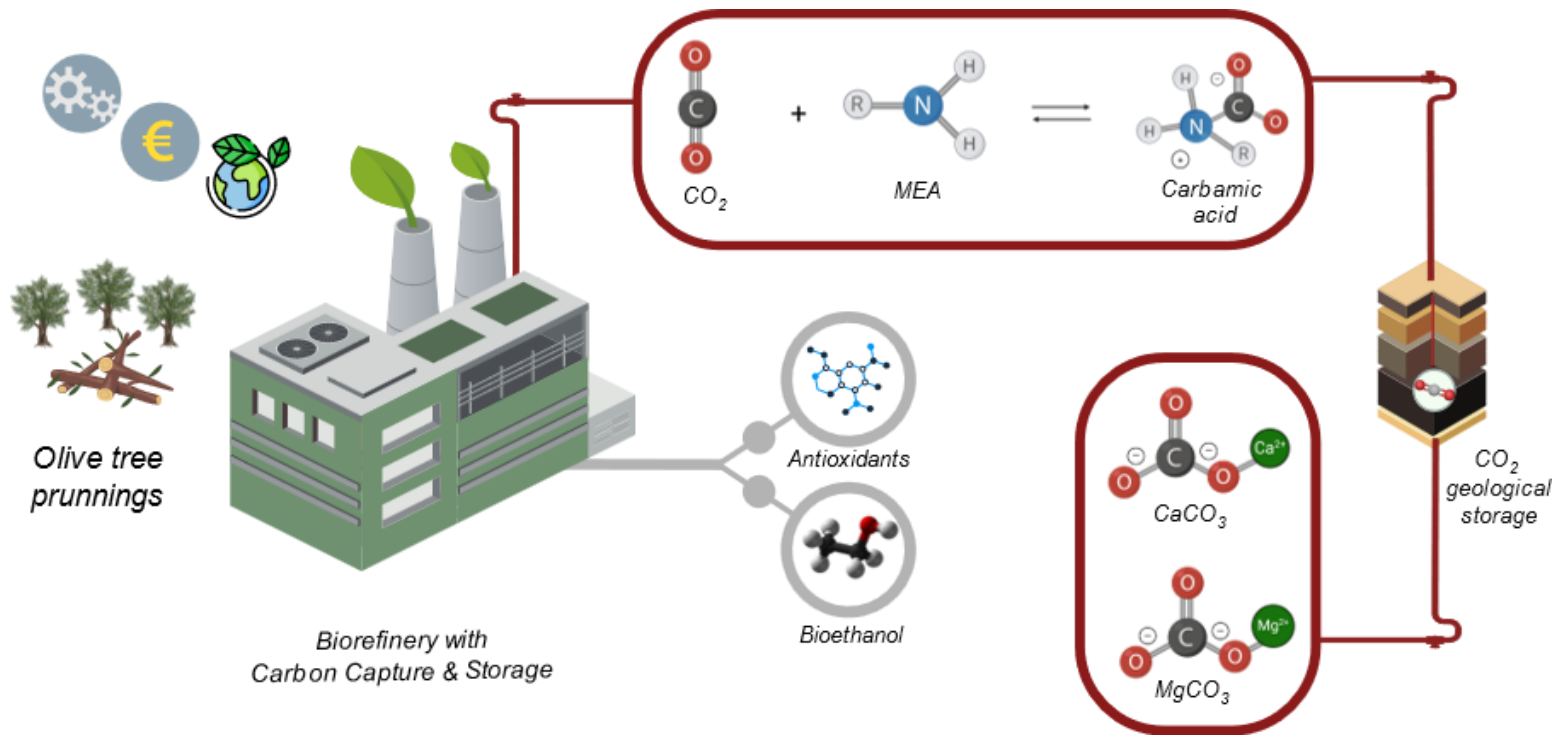
ADVERTENCIA. El acceso a los contenidos de esta tesis doctoral y su utilización debe respetar los derechos de la persona autora. Puede ser utilizada para consulta o estudio personal, así como en actividades o materiales de investigación y docencia en los términos establecidos en el art. 32 del Texto Refundido de la Ley de Propiedad Intelectual (RDL 1/1996). Para otros usos se requiere la autorización previa y expresa de la persona autora. En cualquier caso, en la utilización de sus contenidos se deberá indicar de forma clara el nombre y apellidos de la persona autora y el título de la tesis doctoral. No se autoriza su reproducción u otras formas de explotación efectuadas con fines lucrativos ni su comunicación pública desde un sitio ajeno al servicio TDR. Tampoco se autoriza la presentación de su contenido en una ventana o marco ajeno a TDR (framing). Esta reserva de derechos afecta tanto al contenido de la tesis como a sus resúmenes e índices.

WARNING. Access to the contents of this doctoral thesis and its use must respect the rights of the author. It can be used for reference or private study, as well as research and learning activities or materials in the terms established by the 32nd article of the Spanish Consolidated Copyright Act (RDL 1/1996). Express and previous authorization of the author is required for any other uses. In any case, when using its content, full name of the author and title of the thesis must be clearly indicated. Reproduction or other forms of for profit use or public communication from outside TDX service is not allowed. Presentation of its content in a window or frame external to TDX (framing) is not authorized either. These rights affect both the content of the thesis and its abstracts and indexes.



Exploring the economic and environmental implications of integrating carbon capture in biorefinery systems

STYLIANOS FANOURAKIS



DOCTORAL THESIS

2024

UNIVERSITAT ROVIRA I VIRGILI

EXPLORING THE ECONOMIC AND ENVIRONMENTAL IMPLICATIONS OF INTEGRATING CARBON CAPTURE IN BIOREFINERY SYSTEMS

Stylianos Fanourakis

STYLIANOS FANOURAKIS

Exploring the economic and environmental implications of integrating carbon capture in biorefinery systems

Doctoral Thesis

Supervised by: Dr. Ángel Galán Martín

Dr. Laureano Jiménez Esteller



DEPARTMENT OF CHEMICAL ENGINEERING

SUSCAPE RESEARCH GROUP



UNIVERSITAT ROVIRA I VIRGILI

TARRAGONA

2024



UNIVERSITAT
ROVIRA i VIRGILI

We state that the present study, entitled “Exploring the economic and environmental implications of integrating carbon capture in biorefinery systems”, presented by Stylianos Fanourakis for the award of the degree of Doctor, has been carried out under our supervision at the Department of Chemical Engineering of this University.

Tarragona, 7th June 2024

Doctoral Thesis Supervisors

Dr. Ángel Gálan Martín

Dr. Laureano Jiménez Esteller

Acknowledgments

I would like to express my honest gratitude and appreciation first and foremost to my professors Dr Laureano Jiménez Esteller and Dr Ángel Galán Martín. For prof Laureano allowed me to study for my doctorate under a scholarship scheme which was essential and without it, my PhD would still be a dream and for Dr Ángel who had endless patience to support me with his expertise and supervision throughout this long journey and to this long paper that finally was published in a top tier journal.

Following my gratitude recognition, I would also like to extend it to all my previous academic supervisors as they contributed with their patience and persistence to my growth so far and enabled me to pursue doctorate studies. Throughout this long academic journey, many relatives played their roles. All of them helped me in their unique way. Some of them financially and others psychologically. Although, problems arose and better plans could have been made with wiser and more thoughtful plans, still their help was significant even if it seemed not enough at many times. Finally, my gratitude would go to the small and big societies of all the cities I've been to so far. All of them, with their presence and kind efforts, helped me to progress and learn about their culture. Last but not least, I'd like to express my gratitude to public health as this is the paramount and most important agent that allows us to move and exist on this planet. Therefore, the ultimate goal and purpose of my PhD is to contribute to a cleaner environment for generations to come and have a better quality on our lives.

Finally, I'd like to dedicate this thesis to my lovely, warm, and kind grandma who left us during my studies. She has always been supportive of me and never let me down. I will miss her. Last but not least, I'd like to thank the arts and people who have inspired me with their lives, poems, or any other means they provided to help humanity evolve. Also, I'd like to thank people who provided me psychological support.

Summary

This PhD thesis aims to contribute to the EU Green Deal's objective of achieving climate neutrality by 2050. Environmental issues such as climate change, environmental degradation, or resource depletion, are global concerns that could lead to irreversible and unprecedented negative impacts on ecosystem life cycles. Urgent action is needed for action to prevent the risks of public health and climate change-related disasters. The main impact on human and planetary health is related to greenhouse gas (GHG) emissions, which drive the planet's overheating and are responsible for at least a 1.5°C rise in the earth's surface temperature during the last 150 years, primarily due to anthropogenic activities that have accelerated since the Industrial Revolution. Therefore, it is our duty as humanity to foster actions for sustainability, as a response to our engagement with the 17 Sustainable Development Goals (SDGs).

To achieve climate neutrality sustainably, rapid reductions in GHG emissions are crucial, along with the removal of CO₂ from the atmosphere. This thesis sheds light on this direction by performing research on a specific carbon dioxide removal (CDR) technology, aimed at being retrofitted to biomass multiproduct biorefineries. This thesis investigates Bioenergy with carbon capture and storage (BECCS) and its integration into biorefineries to produce high-added value marketable bioproducts and bioenergy while capturing direct CO₂ emissions, thereby potentially reaching a net negative emissions balance. Despite the potential role of BECCS in climate change impact mitigation, it faces still economic and environmental challenges that hamper its large-scale deployment. BECCS systems are currently more expensive than the conventional biorefining methods and can cause collateral environmental impact, a problem that emerges when an environmental problem is solved at the expense of worsening or creating another one (known as burden shifting). Hence, further research is necessary to fully understand the drivers causing the burden-shifting effect and develop strategies to mitigate these adverse effects. This study underscores the potential of integrating BECCS in biorefineries and highlights the importance of governmental financial support to incentivize CDR and BECCS projects through tax reductions, grants, or subsidies. Moreover, a comprehensive evaluation of the broad environmental implications of BECCS projects—including for example eutrophication, acidification, land use, and water consumption—is crucial to fully assess its environmental footprint.

In a nutshell, on the one hand, the techno-economic analysis performed provides answers to determine the cost disparity between BECCS biorefineries and conventional ones, exploring the EU funding schemes to propose financial aid that would render BECCS as financially viable as traditional biorefineries. On the other hand, the Life cycle assessment (LCA) performed gives answers on the environmental impacts beyond climate change, highlighting the BECCS's ability to reduce its carbon footprint (even yielding negative emissions) but also providing insights into the environmental collateral damages that emerge and its magnitude. The comprehensive assessment provided by this thesis serves as a decision-making tool for stakeholders and policymakers, informing measures and technology practices aimed at minimizing environmental impacts.

Resumen

Esta tesis doctoral tiene como objetivo contribuir al objetivo del Pacto Verde de la UE de lograr la neutralidad climática para 2050. Las cuestiones ambientales como el cambio climático, la degradación ambiental o el agotamiento de los recursos son preocupaciones globales que podrían generar impactos negativos irreversibles y sin precedentes en los ciclos de vida de los ecosistemas. Se necesitan medidas urgentes para prevenir los riesgos de desastres relacionados con la salud pública y el cambio climático. El principal impacto en la salud humana y planetaria está relacionado con las emisiones de gases de efecto invernadero (GEI), que impulsan el sobrecalentamiento del planeta y son responsables de un aumento de al menos 1,5° C en la temperatura de la superficie terrestre durante los últimos 150 años, debido principalmente a actividades antropogénicas que se han acelerado desde la Revolución Industrial. Por lo tanto, es nuestro deber como humanidad fomentar acciones para la sostenibilidad, como respuesta a nuestro compromiso con los 17 Objetivos de Desarrollo Sostenible (ODS).

Para lograr la neutralidad climática de manera sostenible, es crucial reducir rápidamente las emisiones de GEI, junto con la eliminación de CO₂ de la atmósfera. Esta tesis arroja luz en esta dirección mediante la investigación de una tecnología específica de eliminación de dióxido de carbono (CDR), destinada a ser adaptada a biorrefinerías multiproducto de biomasa. En particular, esta tesis investiga la bioenergía con captura y almacenamiento de carbono (BECCS) y su integración en biorrefinerías para producir bioproductos y bioenergía comercializables de alto valor agregado mientras se capturan emisiones directas de CO₂, alcanzando así potencialmente un balance neto de emisiones negativo. A pesar del papel potencial de BECCS en la mitigación del impacto del cambio climático, aún enfrenta desafíos económicos y ambientales que obstaculizan su despliegue a gran escala. Los sistemas BECCS son actualmente más caros que los métodos convencionales de biorrefinería y pueden causar un impacto ambiental colateral, un problema que surge cuando un problema ambiental se resuelve a expensas de empeorar o crear otro (lo que se conoce como transferencia de carga). Por lo tanto, es necesaria más investigación para comprender completamente los factores que causan el efecto de transferencia de carga y desarrollar estrategias para mitigar estos efectos adversos. Este estudio subraya el potencial de integrar BECCS en biorrefinerías y destaca la importancia del apoyo financiero gubernamental para incentivar proyectos CDR y BECCS a través de reducciones de impuestos, donaciones o subsidios. Además, una evaluación integral de las amplias implicaciones ambientales de los proyectos BECCS (incluyendo, por ejemplo, la eutrofización, la acidificación, el uso de la tierra y el consumo de agua) es crucial para evaluar plenamente su huella ambiental.

En pocas palabras, por un lado, el análisis tecnoeconómico realizado proporciona respuestas para determinar la disparidad de costos entre las biorrefinerías de BECCS y las convencionales, explorando los esquemas de financiación de la UE para proponer ayudas financieras que harían que BECCS fuera tan financieramente viable como las biorrefinerías tradicionales. Por otro lado,

el análisis del ciclo de vida realizado da respuestas sobre los impactos ambientales más allá del cambio climático, destacando la capacidad de la BECCS para reducir su huella de carbono (incluso produciendo emisiones negativas), pero también brinda información sobre los daños colaterales ambientales que surgen y su magnitud. La evaluación integral proporcionada por esta tesis sirve como una herramienta de toma de decisiones para las partes interesadas y los formuladores de políticas, informando medidas y prácticas tecnológicas destinadas a minimizar los impactos ambientales.

Contents

List of figures	13
List of tables	15
List of abbreviations	16
1. Introduction	17
1.1 Background and motivation.....	17
1.1.1 Climate change and sustainability.....	17
1.1.2. Carbon dioxide removal	19
1.1.3 Bioenergy with carbon capture and storage	22
1.1.4 Technical, economic, and environmental implications of BECCS at industrial scale.....	25
1.1.5 The olive sector in Spain and olive-derived biomasses	27
1.2 Objectives of this thesis	28
1.3 Scientific contribution and structure of the thesis	29
2. Methodological framework: Integrated environmental and techno-economic assessment.....	29
2.1 Process simulation.....	30
2.1.1 Chemical process simulators.....	30
2.2.2 Sequential modular or simultaneous.....	31
2.2.3 Sizing and rating unit operations	32
2.2.4 Simulation results	33
2.2 Economic analysis.....	34
2.3 Life cycle assessment	36
2.3.1 Goal and scope definition.....	37
2.3.2 Life cycle inventory analysis	38
2.3.3 Life cycle impact assessment.....	40
2.3.4 Life cycle interpretation	42
2.3.5 Environmental databases, methods and software tools	43
3. Case study: Olive-tree pruning biorefinery	48
3.1 Summary	48
3.2 Introduction.....	48
3.2.2 Olive pruning tree biomass-based biorefinery. Scenario definition.	51
3.2.3 Methods description.....	52
3.3 Results and Discussion.....	58
3.3.1 Economic performance	58

3.4 Conclusion case study	65
4. General conclusions.....	66
5. Future work.....	67
6 References	68
7. Appendix	84

List of figures

Figure 1: Contribution of different sectors to greenhouse gas emissions (GHG) globally, 2019 (IPCC, 2022).	18
Figure 2: Carbon Dioxide Removal (CDR) technologies.....	21
Figure 3: The greenhouse gas emissions gap between the nationally determined contributions and the climate goals.....	22
Figure 4: Simplified life cycle assessment scenarios.....	37
Figure 5: Integration of background and foreground systems in life cycle inventory analysis. ...	40
Figure 6: ReCiPe 2016 model to visually indicate the transformation from mid-point to endpoint indicators.	47
Figure 7: Graphical overview of the two scenarios for the olive pruning tree biomass-based biorefinery. On the left, the fossil BIOR NG scenario, which relies on natural gas to power the biorefinery. On the right, the alternative scenario BIOR CCS shows the integration of bioenergy with carbon capture and storage subsystem.....	52
Figure 8: Schematic flowsheet of the olive pruning tree biomass biorefinery system comprising five subsystems: SS1: Feedstock subsystem, SS2: Antioxidant subsystem, SS3: Bioethanol subsystem, SS4: Wastewater treatment subsystem, SS5: Cogeneration subsystem.....	55
Figure 9: Costs breakdown of the two scenarios. The column on the left BIOR CCS integrates bioenergy with carbon capture and storage (BECCS) within the biorefinery. The column on the right corresponds to the BIOR NG scenario, which relies on natural gas to power the biorefinery. Error bars depict the pessimistic and optimistic cost estimates according to the sensitivity analysis conducted.	59
Figure 10: Breakdown of the carbon footprint for the BIOR NG and BIOR CCS scenarios for the production of 1 kg of bioethanol and 0.15 kg of antioxidants.....	62
Figure 11: Comparative environmental implications of the two biorefinery scenarios. The column on the left BIOR CCS scenario integrates bioenergy with carbon capture and storage within the biorefinery. The column on the right corresponds to the BIOR NG scenario, which relies on natural gas to power the biorefinery. SOD: stratospheric ozone depletion, IR: Ionizing radiation, OF, HH: ozone formation, human health, FPMF: Fine particulate matter formation, OF, TE: ozone formation, terrestrial ecosystems, TA: terrestrial acidification, FER: freshwater eutrophication, MER: marine eutrophication, TE: terrestrial ecotoxicity, FE: freshwater ecotoxicity, ME: marine ecotoxicity, HCT: human carcinogenic toxicity, HNCT: human non-carcinogenic toxicity, LU: land use, MRS: mineral resource scarcity, FRS: fossil resource scarcity and WC: water consumption.	64
Figure 12A Flowsheet of the antioxidant plant [SS2 in Figure 8 in the main manuscript].	85
Figure 13A. Flowsheets for the bioethanol plant [SS3 in Figure 8 in the main manuscript].	86
Figure 14A Flowsheet for the wastewater treatment plant [SS4 in Figure 8 in the main manuscript].	88

Figure 15A Simplified flowsheet for the cogeneration plant [SS5 in Figure 8 in the main manuscript]89

List of tables

Table 1: List of LCA-related methods, tools, and databases.....	42
Table 2: ReCiPe 2016 impact categories and their units.....	46
Table A1: Heating/cooling demands for the biorefinery.....	91
Table A2: Contingencies and correction factors employed in the economic calculations.....	93
Table A3: Material factors.....	94
Table A4: Cost parameters for utilities, raw materials and operating labors.....	95
Table A5: Uncertainty ranges of inputs for the sensitivity analysis of main cost parameters.....	96
Table A6: Inventory of 1 kg on olive tree pruning biomass.....	97
Table A7: Inventory of the biorefinery for the production of 1 kg of bioethanol and 0.15 kg of antioxidants (functional unit).....	98
Table A8: Absolute values for the 18 ReCiPe 2016 midpoint categories.....	101

List of abbreviations

GHG	Greenhouse gas
CDR	Carbon dioxide removal
DACCS	Direct air carbon capture and storage
BECCS	Bioenergy with carbon capture and storage
NET	Negative emissions
NDC	Nationally determined contributions
CCS	Carbon capture and storage
MEA	Monoethanolamines
DEA	Diethanolamines
DMEA	Dimethylethanolamines
OPTB	Olive pruning tree biomass
LCA	Life cycle assessment
CO ₂ eq	Carbon dioxide equivalent
ETEA	Environmental and techno-economic analysis
CPS	Chemical process simulation
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
CAPEX	Capital expenditure
OPEX	Operational expenditure
NPV	Net present value
PBT	Payback time
IRR	Internal rate of return
TAC	Total annual cost
AF	Annualized factor
ROI	Return on investment
TAP	Total annual production
LCOB, NG	Levelized cost of BECCS or natural gas
EIA	Environmental impact assessment
ERA	Environmental risk assessment
CBA	Cost benefit analysis
MFA	Material flow analysis
UNEP	United nations environment program
FU	Functional unit
APOS	Allocation at the point of substitution
CFCs	Chlorofluorocarbons

1. Introduction

1.1 Background and motivation

1.1.1 Climate change and sustainability

Climate change poses significant challenges to global communities today, necessitating urgent attention from nations, governments, and stakeholders due to its potential for unprecedented consequences if left unchecked (European Commission, 2024). At its core, climate change is driven by the greenhouse effect, where certain atmospheric gases trap heat that would otherwise escape into space. While natural phenomena also contribute to climate variability, scientific consensus underscores that anthropogenic activities since the Industrial Revolution have exerted a far more pronounced impact.

The concentration of greenhouse gases (GHGs) such as carbon dioxide (CO₂), methane, and nitrous oxide has surged dramatically over the past 170 years, primarily due to the combustion of fossil fuels and changes in land use after the Industrial Revolution. For instance, CO₂ levels have risen from 280 ppm in 1850 to over 410 ppm today, exacerbated by industrial activities and the reliance on fossil-based energy sources in all economic sectors (Siegert Martin et al., 2020).

Several sectors are contributing to the GHG that directly drives climate change's adverse effects. Transportation and energy production are the most relevant, with the transportation sector alone responsible for nearly 15% of the total annual GHG emissions globally (IPCC, 2022). Industrial activities, particularly from coal and natural gas combustion, contribute an additional 24% of GHG (IPCC, 2022). Many of the manufactured products are energy-intensive such as chemicals, iron, steel, cement, concrete, aluminum, glass, and paper. In addition to them, emissions resulting from agriculture, forestry, and other land use activities account for 22%, and electricity or heat generation accounts for 34% of the total GHG emissions worldwide. The agriculture sector is known to emit large amounts of methane and nitrous oxides, which are responsible for global warming (United Nations Environment, 2022). The wide adoption of chemical fertilizers combined with various crop-management practices that focus on maximizing yields over soil health means that this sector accounts for nearly three-quarters of the nitrous oxide found in the stratosphere (Pan et al., 2022). Also, livestock production is the major contributor to atmospheric methane, which is emitted during the digestive processes of cattle and other ruminants (Palangi and Lackner, 2022). The extraction of oil and gas, as well as the consumption of fossil fuels that are produced by them, emits a great amount of greenhouse gases too. Drilling, fracking, transporting, and refining are the most significant sources of carbon dioxide and among the most relevant for methane. While methane may not be as prevalent as CO₂, it is around 30 times more effective in trapping heat into the atmosphere (Environmental Protection Agency, 2024).

The building sector emits a great amount of greenhouse emissions. Heating, cooling, cooking, operating appliances, and maintenance tasks accounted for 9% of Spanish overall emissions in

2021. Additionally, an average of 40% of the energy used in the buildings ends up as waste (Bellapart R&D, 2023). This expenditure might be attributed to inefficient construction materials (e.g., old windows), poor insulation, and outdated machinery (e.g., old lighting technologies, old air-conditioning, etc.) (Kilpatrick Kerry, 2014). Nowadays, there are a lot of initiatives, to employ high-efficiency standards, and retrofit them with the most state-of-the-art technologies to reduce emissions (European Commission, 2020). In Fig.1, an overview of all sectors contributing to the total GHG in Spain is shown (Burgueño Salas, 2023).

Deforestation is another way to generate greenhouse gases. By cutting down the trees for logging or digging up vegetative biomass all the existential carbon that is captured at ground or underground level is released back into the atmosphere. Well and long-known side effects of deforestation go far beyond this issue: desertification, soil erosion, fewer crops, flooding, and a host of problems for local people.

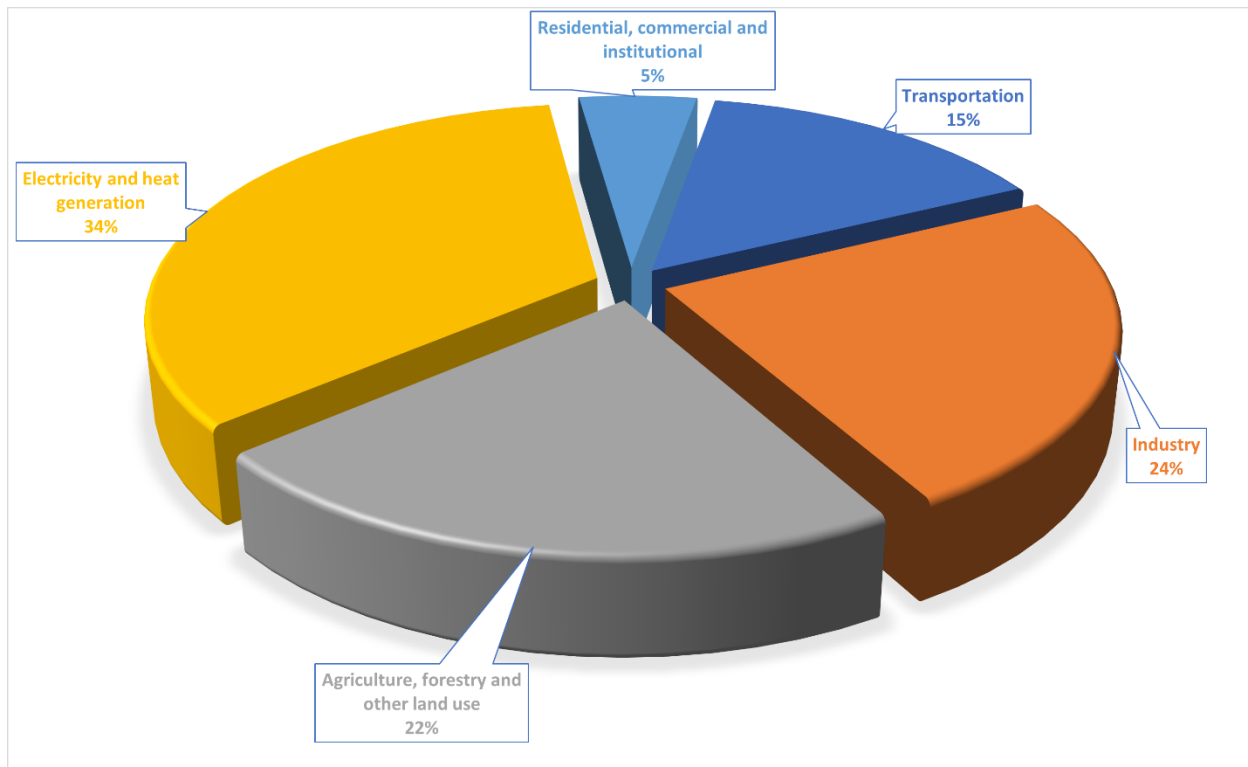


Figure 1: Contribution of different sectors to greenhouse gas emissions (GHG) globally, 2019 (IPCC, 2022).

The situation is alarming as global GHG emissions continue to rise. The latest IPCC report underscores the mounting risks associated with ongoing global warming, projecting an increase in the frequency and severity of extreme weather events. These include more frequent and intense heatwaves that exacerbate heat-related illnesses and strain on infrastructure, prolonged droughts that threaten agricultural productivity and water security, and rising sea levels that heighten the

risk of coastal flooding, endangering coastal communities and ecosystems (Blackett Matthew, 2023; Directorate-General for Climate Action, 2023). Furthermore, intensified storms, such as hurricanes and typhoons, are expected to become more frequent and destructive, posing significant threats to vulnerable regions worldwide. These potentially devastating phenomena collectively define the impacts of climate change, demonstrating the urgent need for global action. The findings from the IPCC underscore the imperative not only to reduce greenhouse gas (GHG) emissions but also to actively pursue strategies for carbon dioxide removal. These efforts are crucial for mitigating the adverse impacts of climate change and for transitioning towards a sustainable future that ensures the resilience of communities and ecosystems worldwide.

1.1.2. Carbon dioxide removal

One of the European Union's commitments aimed at dealing with climate change is the EU Green Deal policy (Calvin et al., 2023), which sets goals for climate neutrality by 2050, or GHG reductions of at least 55% by 2030. One of the ways to achieve these goals is by adhering to the triptych of fundamental pillars: fostering energy efficiency, promoting renewable energy, and incorporating mobility clean systems (Bello et al., 2020). Although this is a promising route, it still, may appear as a very complex task as it leads to complex multi-stakeholder problems and troubles in decision-making. Prioritization needs to be given to aims that address present and emerging sustainability problems and simultaneously benefit society and the environment.

Minimizing the risks associated with global warming requires a comprehensive strategy that combines robust reductions in GHG emissions with the widespread implementation of Carbon Dioxide Removal (CDR) technologies and practices (Calvin et al., 2023) As the world confronts increasingly severe climate impacts such as rising temperatures, intensified storms, and rising sea levels, simply cutting emissions alone may not sufficiently mitigate these threats. Therefore, integrating CDR measures becomes essential to actively draw down carbon dioxide levels from the atmosphere, thereby stabilizing climate patterns and mitigating the long-term consequences of climate change.

CDR consists of practices and technologies aimed at removing carbon dioxide from the atmosphere, thereby, compensating for emissions exceeding the carbon budget and those that are difficult to decarbonize. The amount of CDR that will be needed is heavily dependent on the final residual emissions, the pace of emission reductions, the natural carbon sinks, and technological advances (Galán-Martín et al., 2021b), as delayed reductions in emissions can amount to hundreds of billions of up to several trillions of metric tons of carbon dioxide. Regardless of the CDR required to meet the climate goals, this poses a significant engineering challenge due to the immense scale needed compared to current emission levels and because the CDR industry is still in its nascent stages of development.

The CDR portfolio of options available encompasses various technological solutions and practices, including afforestation, reforestation, soil carbon sequestration, biochar production, direct air

capture and sequestration (DACCS), enhanced weathering, ocean fertilization, and bioenergy with carbon capture and sequestration (BECCS). In Fig. 2, a graphical representation of the various CDR methods is shown.

Overall, the CDR technologies spectrum varies regarding its eco-friendliness. Some of the methodologies seen in Fig. 2 are based on natural solutions, such as the ones of soil CO₂ sequestration, afforestation, ocean fertilization, and the blue carbon techniques. Trees absorb CO₂ during their photosynthesis to trade it with pure oxygen back to the atmosphere. Carbon dioxide dissolves in the soil and carbon forms stable bonds with minerals through mineralization and gets sequestered in the soil (Riedl et al., 2023). Additionally, in the blue carbon technique, the existing underwater flora (mainly of plankton and other species) absorb atmospheric CO₂ during their natural process of photosynthesis and return oxygen (Hilmi et al., 2021).

Another CDR technique, ocean fertilization, is a deliberate or accidental action to shed fertilizers or other sorts of nutrients to water bodies such as oceans, for the microorganisms and bacteria to feed and grow, so absorb more CO₂ during their daily functions. The fertilizers and nutrient effluents may be a result of agricultural activities too, while trying to stimulate phytoplankton activity and it also has similarities with the blue carbon technique (Gattuso et al., 2021). The uncontrolled influx of those, however, may cause water the negative effect of eutrophication, therefore this CDR method must be audited and practiced with caution. An additional benefit of this method is that fertilizers and nutrients contain calcium oxide (CaO), and with their addition to the water, slaked lime is formed (calcium hydroxide, Ca(OH)₂), an element that reacts with atmospheric CO₂ to form calcium carbonate (CaCO₃). Calcium carbonate finds many uses, mainly as a pH regulator (Rodriguez-Stanley et al., 2004). Calcium carbonate is an insoluble salt, that hardens the water and adjusts its pH by increasing water's alkalinity (James M. Omernik et al., 2018). Ocean fertilization possesses the features of an eco-friendly CDR technique, but, unfortunately, the adverse effects of fertilizers, pesticides, and nutrients can have in eutrophication and acidification of the water, as well as the soil degradation and the potential damage to flora and fauna may not render it as the safest option for carbon removal (Lampitt et al., 2008).

Another CDR method is the utilization of biochar. Biochar is a carbon-rich residue stemming from biomass pyrolysis and is characterized by its stable carbon composition. This material is used as a soil amendment and can perform carbon sequestration for a limited time. In agricultural practices, it is used as a soil fertilizer but since it is a byproduct of a thermochemical conversion under limited oxygen conditions, energy is required to be produced, therefore it has an impact on the environment. It also needs a prior modification to improve its physicochemical properties, such as surface area, porosity, and surface functional groups before its use as a carbon adsorbent, as by default exhibits poor adsorption performance (Guo et al., 2022).

However, the CDR options receiving the most attention are BECCS and DACCS which are expected to play crucial roles in the suite of technologies aimed at achieving negative emissions and combating climate change by reducing atmospheric CO₂ levels. Both methods utilize a

chemical reaction strategy to capture CO_2 from the atmosphere, then compress and store it permanently, achieving the known negative emissions (NET) balance. DACCS technologies commonly utilize a sorbent such as sodium hydroxide (NaOH) to react and capture CO_2 from the air, precipitate it into stable sodium carbonate (Na_2CO_3) which subsequently will be heated to produce a pure gaseous CO_2 stream, and later the solid material will be recycled to the process (Gambhir and Tavoni, 2019). DACCS entails carbon footprint impact as it requires high energy demands to operate (Günther and Ekaradt, 2022). A similar case is with the BECCS system, which utilizes biomass resources to generate bioenergy or bioproducts through combustion or conversion processes (fermentation, gasification). In BECCS, the CO_2 emitted during these processes is captured and stored underground (carbon capture and storage or CCS), effectively removing CO_2 from the atmosphere. BECCS not only generates energy but also achieves negative emissions by offsetting CO_2 emissions produced from biomass combustion (Günther and Ekaradt, 2022).

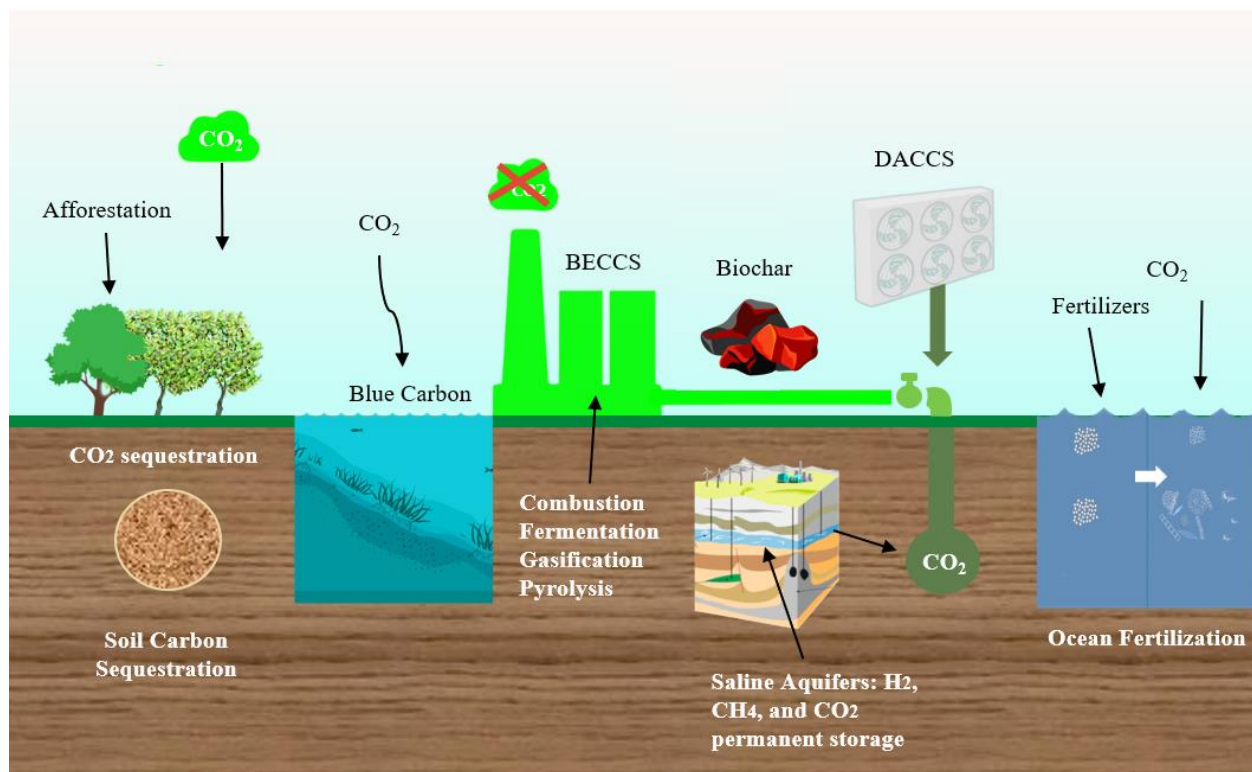


Figure 2: Carbon Dioxide Removal (CDR) technologies.

Despite the unavoidable necessity of CDR technologies to achieve global climate neutrality goals and net-zero targets committed to by countries worldwide, many Nationally Determined Contributions (NDCs) do not currently include plans to scale up BECCS or other CDR technologies and practices.

CDR technologies, such as BECCS, is increasingly recognized as essential tools to offset residual emissions and achieve negative emissions necessary for stabilizing global temperatures. However, while international agreements and national climate strategies emphasize the urgency of reducing emissions, there remains a gap in specific plans and investments dedicated to scaling up CDR technologies within existing policy frameworks (Fig.3) (Lamb et al., 2024).

As countries continue to refine their climate action plans and enhance their commitments under the Paris Agreement, integrating robust strategies for CDR deployment will be critical. This includes incentivizing research and development, establishing regulatory frameworks, and mobilizing financial resources to accelerate the deployment and scaling of CDR technologies. Addressing this gap in NDCs is pivotal to ensuring comprehensive and effective climate action that aligns with global climate goals and safeguards the future of our planet.

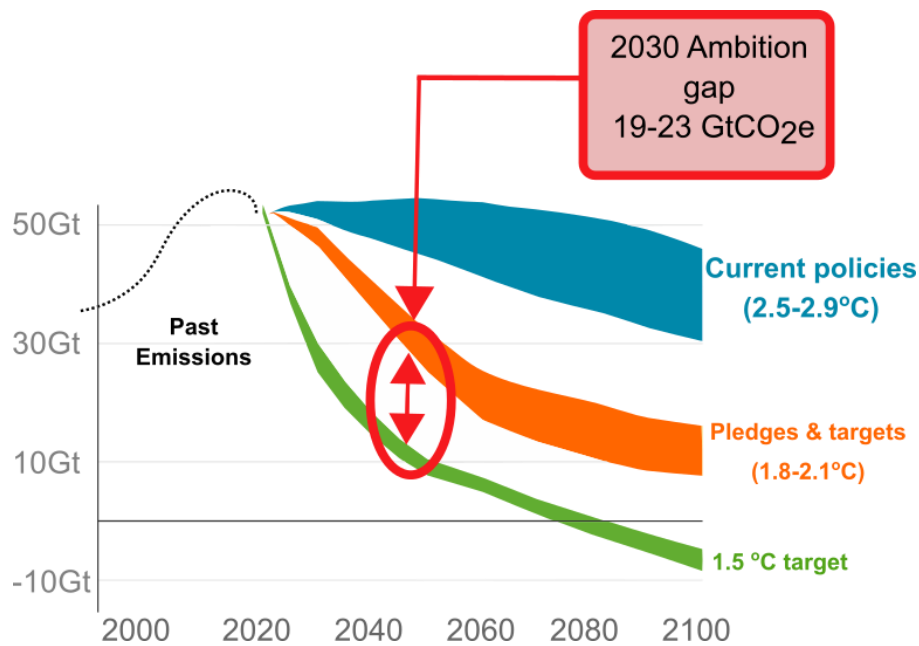


Figure 3: The greenhouse gas emissions gap between the nationally determined contributions and the climate goals.

1.1.3 Bioenergy with carbon capture and storage

The BECCS concept lies at the heart of biorefineries, which are plants that employ biomass feedstocks (as agricultural residues, forestry residues, energy crops, and organic wastes) to produce a range of valuable products, including bioenergy, biofuels, biochemicals, and biomaterials. In essence, Carbon Capture and Storage (CCS) systems can be integrated into existing and new biorefinery plants to capture and store carbon dioxide (CO₂) emissions generated during bioenergy production processes. The unique and compelling feature of BECCS is that if the amount of CO₂ physically removed from the atmosphere exceeds the emissions released over its life cycle, it

allows renewable resources to be efficiently converted into a variety of products but also actively removes CO₂ from the atmosphere, thereby contributing significantly to CDR efforts.

BECCS holds significant promise, particularly when applied to energy generation. By utilizing biomass materials, BECCS facilities generate bioenergy in the form of heat and electricity through combustion. This bioenergy can be used to power various industrial processes, providing a renewable, sustainable, and carbon-negative energy alternative to fossil fuels.

Therefore, a BECCS system, in essence, is a cogeneration unit, combusting biomass instead of fossil fuels, making it an eco-friendly alternative and introducing it among the pillars of the bioeconomy (Dees et al., 2023). It is considered a CDR technique and is among the incentivized projects related to the EU Green Deal policy (Tamme and Beck, 2021). BECCS takes advantage of the natural process of photosynthesis, where plants, trees, and flora capture inorganic CO₂ from the atmosphere and through the carbon fixation process, convert it into organic carbon for their growth in exchange for pure oxygen (Alberts et al., 2002). This CO₂ gets stored in the form of organic carbon inside the biomass and is released during chemical conversions in a biorefinery context (Ataeian et al., 2019). To overcome this vicious cycle, of capturing and releasing back into the atmosphere, BECCS comes as a novel prominent tool to capture it and permanently store it so it never goes back. BECCS shows prominence among CDR options as it allows for decarbonization while providing marketable bioproducts and bioenergy at the same time and is the only CDR technique that does that (Mathilde Fajardy and Carl Greenfield, 2024).

The process begins with the collection and preparation of biomass feedstocks. During combustion, the biomass releases carbon dioxide (CO₂) into the atmosphere. However, the unique advantage of BECCS lies in its ability to capture and store this CO₂ using carbon capture technology. One of the most used is the chemisorption CO₂ technology, which is based on amines in the form of monoethanolamines (MEA), diethanolamines (DEA), or dimethylethanolamines (DMEA) (Ling et al., 2019). When CO₂ reacts with amines it forms carbamate ion, a negatively charged molecule that can interact with water to form carbamic acid through the liquefaction process, it can be cooled and compressed to a liquid state making it easier for storage and transportation (Peter Baldwin, 2009). In essence, the goal of compression is to reach a supercritical state where CO₂ behaves both as a liquid and as a gas.

Alternative methods for CO₂ capture have been proposed in studies such as (Dubey and Arora, 2022). Mainly, technologies of post-combustion capture, pre-combustion capture, or oxyfuel combustion exist for this purpose. The most common approach that our case study also uses is the post-combustion capture one with amines. Amines will also undergo a process called stripping to release the captured CO₂ from the amine solution, which can then be stored or utilized. The stripping process, however, is energy-intensive, requiring heat to release the captured CO₂, and can have an impact on the performance of the BECCS system (Almena et al., 2022). As technologies and research advance, a minimization of this stripping energy will be feasible, so climate change impact is reduced. In the oxyfuel combustion process, biomass is burnt in a mixture

of oxygen and recycled flue gases, instead of air. The flue gases containing CO₂ are separated from nitrogen using a filter and then condensed, resulting in a concentrated stream of CO₂ that can be stored. The remaining flue gases can be recycled back into the system for energy preservation. Oxyfuel combustion technology also enables BECCS negative emissions helping to the reduction of carbon footprint (Ling et al., 2023). Finally, in the pre-combustion technology, biomass is first converted into gas (syngas) through a gasification process. During this process, syngas passes through a filter or solvent that captures CO₂ separating from the other gases in the stream. The carbon dioxide then is compressed and stored while the other gases are combusted to produce electricity and heat. Advantage of this process is that it is more efficient in capturing CO₂ from other processes, but a disadvantage is that it requires additional equipment and infrastructure that makes it more expensive and complex for BECCS systems (Restrepo-Valencia and Walter, 2023).

Regardless of the capture technology, the captured CO₂ can be transported and stored underground (or utilized in industrial applications), effectively reducing net greenhouse gas emissions. After capture, the CO₂ is compressed to a supercritical state for efficient transportation. Compression increases the density of CO₂, reducing its volume and facilitating economical transport via pipelines, trucks, or ships to suitable storage sites. The storage sites include geological formations deep underground, where CO₂ can be securely trapped for long periods. Common storage sites include depleted oil and gas reservoirs, deep saline aquifers, or unmineable coal seams. These geological formations provide stable and impermeable conditions that prevent CO₂ from escaping back into the atmosphere (long-term storage).

The deployment of BECCS projects at a large scale is still scarce but the efforts so far are not merely theoretical (Olsson et al., 2022; Steyn et al., 2022) Only one large-scale pilot BECCS industrial plant is currently operating worldwide, in Illinois, USA, producing bioethanol from corn fermentation, and has the potential to capture 1 million tons of CO₂ per year (Global CCS Institute Ltd, 2019). They are demonstration projects in operation today that span small-scale pilots to ambitious commercial projects. For instance, in Europe, particularly in Nordic countries and the United Kingdom, operational BECCS facilities within biorefineries and power plants are demonstrating the practical viability of integrating biomass energy production with CCS. These projects serve as test beds, showcasing how bioenergy derived from agricultural and forestry residues, can be harnessed to generate heat and electricity while concurrently capturing and securely storing carbon dioxide underground. The total current deduction amounts to 2 million tons CO₂/year and is expected to rise to 60 million tonnes CO₂/year by 2030 (Mathilde Fajardy and Carl Greenfield, 2024) considering biogenic sources worldwide, which falls short of the approximately 185 Mt CO₂/year as per Net Zero Emissions by 2050 (NZE) scenario predictions (Mathilde Fajardy and Carl Greenfield, 2024).

Although, around 2 Mt CO₂/year is captured from biogenic sources, less than 1 Mt of CO₂ is stored in dedicated space (Mathilde Fajardy and Carl Greenfield, 2024). The remaining is reutilized in products as a feedstock, sold as oil recovery enhancement, and as a greenhouse yield booster (Mathilde Fajardy and Carl Greenfield, 2024) but that means that it will eventually return to the

atmosphere and never get permanently stored. Bioethanol-based BECCS biorefineries, are the most economic of all the BECCS-type biorefineries and entail a rich CO₂ gaseous stream. Currently, there are plans to expand BECCS facilities in other sectors too, such as BECCS for the power sector industry, fuel transformation sector, and cement industry. Combining all of the above BECCS plants, it is estimated a total reduction of CO₂ three times higher than the initial predictions by 2030 (Mathilde Fajardy and Carl Greenfield, 2024).

There are still many ongoing challenges that represent important obstacles to the widespread adoption of BECCS solutions. High upfront costs, technological refinements, ensuring sustainable biomass sourcing, and a deep understanding of the broad environmental implications of its industrial scale are critical hurdles that must be addressed. Yet, supportive policy frameworks and incentives are emerging worldwide and the momentum behind BECCS continues to grow. Governments and industry stakeholders alike are recognizing the pivotal role that BECCS can play in achieving global carbon dioxide removal targets and advancing towards a carbon-neutral future. BECCS moves closer to becoming a transformative solution in the fight against climate change, offering hope for a sustainable tomorrow built on innovation, resilience, and collective action.

1.1.4 Technical, economic, and environmental implications of BECCS at industrial scale

Understanding the technical feasibility, economic viability, and environmental implications of the large-scale deployment of BECCS will be crucial for overcoming existing challenges and unlocking its full potential as a sustainable energy solution. By addressing these multifaceted considerations, stakeholders can pave the way for BECCS to play a transformative role in global efforts to mitigate climate change and achieve carbon neutrality.

Technical assessments are essential to optimize the efficiency and reliability of BECCS technologies, ensuring they can operate effectively at scale. This involves refining the logistics for the biomass acquisition, and biomass conversion processes, enhancing carbon capture efficiency, and integrating storage methods that guarantee long-term stability and safety. Despite the maturity of CO₂ capture technologies, the transportation and storage value chain add significant technical complexity to BECCS projects. Transporting captured CO₂ involves advanced infrastructure, including compression units, pipelines, and specialized transport networks, which can be costly to build and maintain. Additionally, the secure transportation and storage of CO₂ over long distances poses engineering and logistical challenges, especially when crossing different jurisdictions with varying regulatory frameworks.

Economic assessments are crucial for determining the financial feasibility and competitiveness of BECCS compared to conventional energy sources. BECCS systems require significant amounts of additional biomass to generate the necessary heat and electricity for the entire biorefinery. Additionally, the construction and maintenance of carbon capture and storage (CCS) infrastructure, coupled with the energy-intensive nature of the capture process, contribute to

increased operational costs (Mohammed B Alqaragully et al., 2015). Assessing these costs involves analysing the economic implications of sourcing and transporting large quantities of biomass, the expenses associated with capturing and compressing CO₂, and the investment required for secure CO₂ transportation and storage infrastructure. Strategies to reduce costs, such as scaling up production and streamlining operational processes, need to be explored to attract investment and incentivize commercial deployment.

Furthermore, the complexity of BECCS value chains also entails environmental implications that must be fully understood. Therefore, environmental assessments that evaluate the lifecycle of the whole BECCS system play a pivotal role in evaluating the overall sustainability of projects. One of the primary environmental concerns is the extensive land use required for biomass production, particularly when dedicated energy crops are considered. Large-scale deployment of BECCS could lead to permanent deforestation, extinction of flora, and soil degradation (Babin et al., 2021). Additionally, sustaining the necessary agricultural practices for biomass can result in eutrophication, acidification, and increased water consumption. Moreover, the operation of CCS units often requires certain quantities of monoethanolamine, a chemical used in capturing CO₂ which entails nitrogen bonds and might contribute to environmental acidification (Mohammad Abu Zahra and Erik Gjernes, 2010). The transportation and storage phases also contribute to its environmental footprint, attributed to the infrastructure and the equipment needed to inject it into geological sites, such as saline aquifers, and because other activities across the value chains still rely on fossil fuels. By understanding and mitigating all the potential environmental risks, stakeholders can develop strategies to minimize the adverse effects of BECCS, thereby enhancing its sustainability and effectiveness as a climate mitigation solution.

Given all the implications of BECCS in the different domains, it is imperative to conduct comprehensive technical, economic, and environmental assessments to evaluate the feasibility and sustainability of BECCS projects. Technical assessments are needed to optimize each stage of the CO₂ value chain, ensuring that transportation and storage processes are reliable and efficient. economic assessments help identify potential cost-reduction strategies, such as optimizing biomass supply chains, improving process efficiencies, and exploring financial incentives or subsidies that could enhance the overall viability of BECCS projects. Environmental assessments ensure that the entire BECCS process minimizes adverse impacts on ecosystems and complies with environmental regulations of CO₂ reduction targets. Overall, an integrated approach encompassing technical, economic and environmental dimensions is crucial to ensure technical feasibility, economic viability, and maximizing the environmental benefits and ultimately realizing the full potential of BECCS in contributing to global carbon dioxide removal efforts and achieving climate neutrality goals.

1.1.5 The olive sector in Spain and olive-derived biomasses

In Europe alone, approximately 70% of the world's olive oil production can be found. Tunisia and Morocco also contribute 10% of the global production. In total, around 7.7 million hectares are accounted for olive groves in the Mediterranean basin alone. That makes clear, that the cultivation of olive trees is the backbone of the socio-economic and cultural life of many regions of the Mediterranean regions (SustainOlive, 2024). It is a leading economic agent, accounting for millions of employment opportunities, making it an economic livelihood hub in large areas of the agricultural world, by averting rural depopulation. From ancient times, Mediterranean people used to rely on olive fruit for their daily nutritional fat intake (Loumou and Giourga, 2003). Even now, olive fruit is one of the multiple important and valuable export products, linked with the culture of that area. It requires low-fertility soils, can grow even in inclined and shallow land surfaces, demands low watering, and acts as a carbon sequestration method, due to its biomass nature.

Spain stands as the world's leading producer and exporter of olives, supported by its Mediterranean climate and fertile soils, particularly in regions like Andalusia. The olive sector in Spain occupies a prominent position within the nation's agricultural landscape, characterized by extensive cultivation and a rich cultural heritage. Within the realm of olive production, various biomasses derived from olives play a crucial yet underutilized role. These biomasses include olive pomace, olive stones, and residues from the olive oil extraction process. Only the province of Jaén accounts for more than 20% of global olive oil production, so that large amount of olive-derived biomasses are generated every year making it an appealing setting for establishing biorefineries (Romero-García et al., 2016).

Despite their abundance, these biomasses often do not receive adequate attention in sustainable resource management strategies (Galán-Martín et al., 2022a). One significant biomass resource within the olive sector is derived from olive tree biomass pruning. Olive pruning tree biomass (OPTB) is essential for maintaining tree health and productivity, resulting in biomass composed of branches, leaves, and small wood pieces. This biomass is rich in cellulose, lignin, and other organic compounds. However, it is frequently left in fields as an organic soil amendment, inefficiently burned, or underutilized, representing missed opportunities for economic and environmental benefits.

Efforts are increasingly focused on harnessing the potential of olive pruning biomass across multiple sectors. Firstly, it is a valuable source for bioenergy production through processes like pyrolysis, gasification, and combustion (Fanourakis et al., 2024; Maggiotto et al., 2023) These biofuels offer renewable alternatives to fossil fuels, contributing to energy security and reducing greenhouse gas emissions. More, recently other valorization pathways for OPTB are being explored for the production of fine and specialty chemicals, cosmetics, and other bioproducts due to its natural compounds and sustainable sourcing. Biorefineries require olive pruning tree biomass (OPTB) as input for them to process; in Jaén, 585,000 hectares (ha) produce over 1 million tons of OPTB per year (Romero-García et al., 2016). OPTB is often collected during the winter season

after harvesting and air-drying leaving a moisture of approximately 7% w (Romero-García et al., 2016). Moreover, proximity to the land groves of no more than 100 km distance is crucial to guarantee continuous and uninterrupted supply from the groves to the establishments under rational costs.

Additionally, various regional policies and incentives are emerging to support the sustainable management and utilization of agricultural residues, including olive pruning biomass. For example, the Andalusian government has implemented the Andalusian Bioeconomy Strategy (Koch, 2023) aimed at promoting the use of biomass for energy production and encouraging investments in biomass valorization projects. At the national level, the Spanish Renewable Energy Plan also includes measures to support the integration of biomass into the energy market, ensuring a stable demand for biomass-derived products (Government of Spain, 2020) All these instruments collectively facilitate market integration and encourage investments in biomass valorization, turning OTPB from an underutilized resource into a significant economic and environmental asset.

In conclusion, the olive sector not only sustains agricultural and economic prosperity but also holds considerable untapped potential in its biomass resources. Maximizing the utilization of olive tree pruning biomass (OTPB) through innovative technologies and biorefineries is essential to harness the potential environmental and economic benefits. From an environmental perspective, utilizing OTPB mitigates greenhouse gas emissions associated with open burning or landfill disposal. Moreover, it promotes a circular economy where agricultural residues are transformed into valuable resources, enhancing overall environmental sustainability. Economically, valorizing OTPB creates new revenue streams for farmers and rural communities and supports job creation in biomass collection, processing, and conversion industries (development of biorefineries), contributing to regional economic development. Hence, ongoing research and innovation are essential to optimize the utilization of OTPB. This PhD thesis precisely focuses on researching biorefinery processes to unlock and maximize the value of OTPB, driving both environmental and economic advancements in its sustainable valorization.

1.2 Objectives of this thesis

This thesis aims to contribute to the fight against climate change by facilitating and supporting the EU Green Deal's goals for climate neutrality by 2050. To achieve this, the research focuses on the deployment of sustainable environmental practices, specifically bioenergy with carbon capture and storage (BECCS) identified as a crucial technology for reducing atmospheric carbon dioxide levels. To this end, one of the main objectives is to provide a comprehensive assessment of the benefits and drawbacks of implementing BECCS in an olive tree pruning-based biorefinery using advanced tools such as life cycle assessment (LCA) and techno-economic analysis (TEA). The study aims to foster public engagement and inform stakeholders and policymakers about the successful implementation of BECCS in the broader context of climate change mitigation.

The overarching objective will be accomplished through the following secondary objectives:

- Conduct a comprehensive review of previous studies and literature on BECCS, focusing on technological advancements, environmental impacts, economic feasibility, and policy considerations.
- Perform a detailed assessment of integrating BECCS technology into an OPTB biorefinery to produce antioxidants and bioethanol, focusing on evaluating its technical, environmental, and economic implications by performing an integrated life cycle analysis (LCA) and techno-economic assessment (ETEA).
- Compare the BECCS proposal with a conventional biorefinery and assess strengths and weaknesses in both environmental and economic dimensions.
- Foster public engagement and inform policy and decision-making about the burden shift effect that appeared in BECCS systems and suggest ways to mitigate it.

1.3 Scientific contribution and structure of the thesis

This thesis aims to contribute to the body of research on biorefinery and in particular to shed light on the scalability challenges and implications towards unlocking the BECCS potential. The thesis consists of one scientific peer-reviewed journal publication and its derived peer-reviewed conference publications. The publication is entitled “Economic and environmental implications of carbon capture in an olive pruning tree biomass biorefinery” and was published in the Journal of Cleaner Production (Volume 456, 1 June 2024, 142361).

The thesis is structured as follows. Chapter 1 includes the introduction and motivation of this work. Chapter 2 introduces the methodological framework of the research by presenting the integrated environmental and techno-economic assessment based on simulation as basic tools to perform the economic analysis and the LCA assessment. Chapter 3 presents the case study that explores the integration of BECCS into a biorefinery system that converts olive tree prunings into bioethanol and antioxidants. Finally, the general conclusions of the thesis are presented in Chapter 4, and the future work in Chapter 5. Chapters 6 and 7 include the references and the Appendix.

2. Methodological framework: Integrated environmental and techno-economic assessment

In this chapter, the methodological framework employed in this thesis is presented. The methodology revolved around an integrated approach combining techno-economic analysis with environmental assessment. This methodological framework is designed to provide a comprehensive evaluation of the case study presented in section 3.

The industrial-scaled deployment of biorefineries faces major challenges and hinders in establishing biomass resources routes, problems of economic viability, and dubiety in their

environmental impacts. No matter the type of the biorefinery and its output products, modern biorefineries should operate environmentally sustainable and advance the economic growth of their societies. Understanding the interconnections and trade-offs between economic and environmental performance is crucial for designing and scaling sustainable biorefinery processes.

The integrated Environmental and Techno-Economic Assessment (ETEA) methodology provides a comprehensive framework to evaluate the feasibility and sustainability of biorefinery technologies. An in-depth review of the last decade of research applying the integrated ETEA approach to biorefinery systems can be found in (Almada Pérez Deborah et al., 2023). ETEA provides a robust framework for evaluating biorefinery technologies from technical, economic, and environmental perspectives by combining process simulation, economic assessment, and Life Cycle Assessment (LCA) which enables stakeholders to optimize biorefinery operations, achieve economic profitability, and mitigate environmental impacts.

This section explores the application of ETEA through process simulation, economic assessment, and Life Cycle Assessment (LCA). First, the biorefinery plant is simulated at scale using process simulation models and tools. Those models represent the scale-up problem of the facilities and are often built relying on basic principles for every unit operation (thermodynamic data and energy and raw materials balances) that can be retrieved from experimental results, literature data or databases (e.g., National Renewable Energy Laboratory, NREL) (Smith, 2002). The process simulation results (see section 2.1) provide the mass and energy flows entering and leaving the system that eventually will help to estimate the economic indicators (see section 2.2) and necessary to perform the LCA study (section 2.3).

2. Process simulation

2.1 Chemical process simulators

Chemical process simulators (CPS) are software applications designated to model process plants, like biorefineries, large-scale manufacturing industries that produce commodities, or small high-added-value products. CPS are extremely important, as they predict the behavior of systems before their development, which can guarantee that the unit will perform as expected. The validation of the prediction of these units is the key aspect of CPS. Their performance has been validated with pilot plants of plant data. In a CPS, an industrial process can be simulated using discrete unit operations, where the physical and chemical transformations take place. Common processes such as heat exchangers, pumps, and distillation, are the same in all sectors. For example, pumps increase the pressure of liquids, decanters separate immiscible liquids (e.g., water from oils), or reactors cause a chemical transformation (e.g., biomass saccharification). Every process unit has one or more inputs and outputs. Those inputs/outputs are known as process streams. They can represent materials or energy flows, including losses. The process flowsheet is performed to mimic the real plant, either as a batch or continuous process. In continuous operations, the flow streams

never stop between unit operations (Lekan Olanrewaju, 2023), while in batch processes several tasks can be performed in the same unit, following the so-called product recipe, where the amount, order and conditions of each task are fixed in discreet time intervals. Batch processes are characterized by time dependency, as all operations occur in time sequences. Each batch goes through a series of steps (e.g., mixing, heating, reacting, cooling). It is flexible to handle different products and variations in production cycles. In continuous processes, the production never stops and there is constant material flow through equipment. It is advised for large-scale, high-volume productions, as it is a steady and stable process (Vidhya H, 2017).

Chemical engineers use CPS to develop or retrofit process facilities. With the aid of CPS, chemical engineers can determine the overall potential effects of process modifications in a specific area; predict capital and operational expenditures; audit or estimate emissions and evaluate optimization and integration alternatives. Additionally, CPS are used to give answers to what-if scenarios. The background technology of CPS has advanced the recent years to a point that detailed models can (partly) replace expensive pilot-scale projects (Casavant and Côté, 2004).

There are several CPS applications, commonly used nowadays, both freeware and under a license. By far, the most widely used commercial software under payment are Aspen Plus and Hysys (AspenTech Inc., 2024). These two software have become *the facto* the standard application in many continuous processes. There are other process simulators in the market, like CADSIM Plus (Aurel Inc, 2019), CHEMCAD (Chemstations, 2024), Gensim (Khosrovian et al., 2008), and the one used in this thesis, which is SuperPro Designer by Intelligen Inc (Nirupam Pal et al., 2008), whose main advantage is their focus on batch processes, the flexibility to use non-databank components, and the inclusion of the unit operations most used in the batch sector. On the contrary spectrum lies the open-source software, that are free and accessible to anyone. Software such as DWSIM (Tangsiwong et al., 2020), COCO simulator (Jasper Van Baten et al., 2010), OpenModelica (Fritzson et al., 2019) are some of the CPS that do not require paid licensed subscriptions.

It is only the nature of the materials being physically or chemically transformed that are unique, an aspect that is the core of any process simulator: the prediction of the physical properties of pure components and mixtures in a wide range of conditions. Materials in large-scale industries are often measured in thousands of tons, energy used is measured in megawatts (MWh), and costs and profits are measured in millions of euros.

2.2.2 Sequential modular or simultaneous

The sequential modular strategy solves the process flowsheet module by module in a sequence. Each unit operation is treated as a separate module, and the calculations proceed from one module to the next, using the output from the previous module as the input to the next. In the sequential modular strategy, all units are solved in a predefined order of calculation. One of the advantages

of this method of flowsheet operation, is that each unit can be tested and debugged independently. It is quite simple to understand and manage, especially when it involves linear processes and typically requires less computational effort for simpler flowsheets. Some of the disadvantages of this method, is that it can struggle while converging, especially in complex flowsheets with multiple recycling streams. It can also, require many iterations to converge when dealing with large, highly interconnected systems. This strategy finds applications in simple processes, with few recycles or preliminary designs and initial screening studies (Umeda and Nishio, 1972).

On the contrary, in the simultaneous modular strategy, all unit operations are represented by equations and these equations are solved together as a system, as a global solution. It finds applications on complex flowsheets, as it needs to formulate and solve large sets of equations. It exhibits robust convergence with ease, in highly interconnected systems with many recycles. One of its big advantages is its optimization capability for large complex simultaneous process design problems with many constraints and multiple objectives are considered (Kisala et al., 1987). On its disadvantages spectrum, lie the complexity of advanced mathematical techniques and solvers, as well as it can be very computationally intensive, especially for large systems.

Both strategies can be applied to both continuous and batch processes, as simultaneous and sequential modules are computational approaches describing the flowsheet operations. Although, the sequential modular strategy is more relevant to batch processes, cause of the stepwise nature of batch operations. A simultaneous modular strategy can effectively optimize the entire batch cycle. On the other hand, in continuous processes, sequential strategy fits for simple, linear and straightforward processes, while, simultaneous strategy excels in solving complex, interconnected systems and provides robust optimization (Umeda and Nishio, 1972).

2.2.3 Sizing and rating unit operations

Chemical process simulators (CPS) have the ability to calculate and perform auto sizing (design) in their unit operations characteristics such as equipment dimensions, heat transfer exchange value, pressure drop, etc., based on mechanisms they possess (sizing algorithms) that estimate the relevant parameters on available simulation data and if data are missing, interpolation mechanisms estimate them. The default material of construction for all equipment is usually carbon steel. Users can review the sizing and materials of construction and override estimated sizes (in case they do not agree with the auto-estimated data from the system), revise materials of construction, and enter values for unsized equipment.

For example, based on some of the user's simulation data, e.g. temperature, CPS models will automatically calculate the equipment material of the adequate thermal conductivity, heat capacity, and other relevant parameters that the material will be able to withstand according to the input variable of temperature that has been given by the user. Accordingly, if pressure or flow rate has been given by the user, then CPS will auto-estimate the size of the pipelines or the equipment unit,

their diameter, and pressure drop according to a model such as Bernoulli's equation. CPS use standardized models to estimate the above parameters. Standards like Tubular Exchanger Manufacturers Association (TEMA), Log Mean Temperature Difference (LMTD) or Effectiveness-NTU (Number of Transfer Units) are common models for heat exchanger sizing relevant to industry norms (Magazoni et al., 2019), while the Souders-Brown equation is for distillation column sizing (Austrheim et al., 2007).

Complementary to sizing algorithms, come the rating algorithms which evaluate the performance of existing equipment to determine if it meets the required standards under certain operating conditions. For example, performance evaluation for a heat exchanger would be to determine if the specific unit can meet the required heat duty with the given configuration and operating conditions. Moreover, it can also evaluate the impact of fouling on heat transfer efficiency and pressure drop (Ahilan et al., 2015). For the distillation columns, a rating algorithm will evaluate if an existing column can achieve the desired separation with the current tray or packing configuration and operating conditions. Similarly, hydraulic analysis assesses the hydraulic performance, including pressure drop and flooding conditions.

Overall, sizing and rating share some underlying principles and calculations such as thermodynamic property calculations, heat and mass balance conservation, and phase equilibrium calculations, especially critical for distillation columns ensuring accurate separation predictions (Korotkova and Kasyanov, 2022). Rigorous Distillation Models (RADFRAC) and McCabe-Thiele method are models that are used in sizing and rating of distillation columns (Seedat et al., 2021).

2.2.4 Simulation results

At the end of the flowsheet process, the complete mass and energy balance inventory is obtained. Product yields, or water and waste effluents and GHG emissions are part of the mass balances, while energy transformations involving heating, cooling, and electricity account for the energy balances. Energy balances determine how much heat/cold in MJ, or electricity in kWh, is needed to generate a certain amount of steam, and a pump to move a liquid amount from a tank to another process unit; adding all these needs, the overall balance determines how much energy is required to produce the final product. Each unit process requires a different amount of heat or cooling duty and a different set of configurations. Heat exchangers are commonly used when heat duty is required to increase and cooling agents such as chilled or tap water is used when heating demands to decrease. Heating is conducted by steam generation from the cogeneration unit. High-pressure steam usually is converted into electricity and low-pressure steam is used for heating (Romero-García et al., 2016).

To obtain data for the study's environmental and economic analysis (Fanourakis et al., 2024), the biorefinery plant, simulation software such as SuperPro Designer v9.0 was used (Nirupam Pal et al., 2008). The OPTB biorefinery was modeled using the SuperPro Designer simulator. This model

was validated with laboratory experimental data from the literature (Romero-García et al., 2016; Sánchez et al., 2013).

The models are used to generate the mass and energy balances of the biorefinery plants that are used to compute the life cycle inventory (LCI) (see section A4, 7.0) development and subsequently for the environmental impact analysis (LCIA) (see section A5, 7.0). Additional data, such as the sizing of the units, generated from the simulators is used to perform the techno-economic analysis, considering the annual cost of the process in operational and capital expenditures.

2.2 Economic analysis

A project's total budget investment can be categorized in part as capital expenditure (CAPEX) and operational expenditure (OPEX), which is further defined as fixed or variable. CAPEX costs include fixed costs, essential to start a project (e.g., equipment purchase, property or land purchase, installations, and fixed materials such as technology). CAPEX items are permanent assets for the investor and usually do not involve annual depreciation. OPEX on the contrary, involves raw materials, labor costs, utilities, rent, and generally costs that depreciate over time. OPEX fixed costs refer to fixed operational costs that are essential for the project to operate even without production, such as certain raw materials related to machinery, maintenance costs, various contingencies, and taxes. For the estimation of CAPEX and OPEX (fixed, variable) different methods exist and are adapted per the goal and scope of each study separately. CAPEX and OPEX formulas can be adapted in a simple form (Ioannou et al., 2018), for scientific analysis or in a more complex form, including various contingencies (Sinnott and Towler, 2009). The more complex version of these formulas is implemented, the likely more accurate in their economic predictions will be. The studies, utilize economic formulas from Sinnott and Towler (Sinnott and Towler, 2009). For a more detailed presentation of the formulas used please refer to section 7.2 Appendix.

One of the pivot players in determining the profitability of the investment is the net present value (NPV) indicator. The positive and negative cash flows (income-expenses) in the projected lifetime of the plant, provide the information if a project is profitable ($NPV > 0$), or unprofitable ($NPV < 0$). One of the key aspects to consider is the project lifetime, which normally can range from 15 to 20 years.; in our case, 25 years of plant operation is considered, a value that is in accordance with the literature (Servian-Rivas et al., 2022).

According to the profits, which stem from revenues minus annual expenses, the payoff time of the project is estimated in years. Internal rate of return (IRR) is the percentage, responsible for making NPV equal to zero, which means the project will offset its investment but without additional profits or losses. The total annualized cost (TAC) is a metric that estimates the total annual cost of the project both in terms of CAPEX and OPEX, multiplied by the annualized factor (AF) that varies according to the interest rate. Finally, the return on investment (ROI) is a performance metric indicator, that is used to evaluate the efficiency of an investment and compare this metric with

other investment metrics. A high ROI would signify a successful investment, as that would mean with low-cost investment a high-profit income is born.

Depreciation refers to the annual reduction of value in assets that occurs due to usage, wear and tear, or obsolescence. Depreciation methods normally appear in four different types.

1. Straight-line method
2. Double declining balance
3. Units of production
4. Sum of years digits

In the studies, the (1) straight-line depreciation method is adopted, meaning that it is kept stable throughout the years of operation and because it is the simplest method of all, while the others entail a bit more complexity. In essence, straight-line method depreciation is a linear method, keeping a fixed average value of depreciation every year, for the whole plant's lifetime. In essence, the total capital cost is divided over the total plant's lifetime in years, to get the average annual value in depreciation. On the other hand, (2) double declining balance, is a method that expenses a larger amount in the first years of operation as opposed to the later years. This comes in handy, in assets like cars, for example, which tend to be more productive in their early years or tend to lose more of their value back then (Kieso et al., 2022). Its estimation is similar to (1). The only difference lies, that the division of the capital cost is done stepwise, with the useful in life years, recurrently every year until the end of its lifetime and multiplied by double the depreciation factor.

While, (3) units of production method, implies that the depreciation will be dependent on the total hours of plant's operation or the amount of products produced over its lifetime, demonstrating variations in its annual value, in cases plants are not fully operating all days per year. Or in some cases, not the complete hours. Finally, (4) sum of years digits depreciation is very similar to (2), with the only difference that this kind of method is an accelerated depreciation method that divides the sum of the years of a plant's lifetime over the remaining years, and not the capital cost, multiplied by the depreciation base, which is not double, to estimate the final value (Kieso et al., 2022).

Finally, to estimate the production cost, a levelized cost formula was used, which takes CAPEX and OPEX divided by the total annual production (TAP) of our products, to estimate the production cost of the functional unit or for a single produced item. For a more detailed synopsis of the technoeconomic analysis please consult the appendix of article 1, section 7.0.

A techno-economic analysis without a comparison with another investment would not tell much. Therefore, we compare the economic indicators with similar projects to understand the strengths and weaknesses of the investment and suggest possible methods to revise where possible. All the economic data and values are prone to change due to inflation and were accessed by literature and the global online marketplace during the years 2023-24.

2.3 Life cycle assessment

With growing environmental concerns becoming key discussion points and influencing policymakers, public administrators, businesses, and individuals, the integration of environmental considerations into complex societal decisions has gained significant value in recent years. To facilitate this, numerous environmental assessment tools have been developed to assess and benchmark environmental impacts. These tools include Life Cycle Assessment (LCA), Environmental Impact Assessment (EIA), Environmental Risk Assessment (ERA), Cost-Benefit Analysis (CBA), and Material Flow Analysis (MFA). Among these, LCA and the life cycle perspective have garnered increasing interest, as evidenced by their incorporation into EU legislation, such as the Integrated Product Policy, Eco-design Directive, or Environmental Product Declarations.

LCA serves as a valuable support tool for decision-makers by evaluating the environmental burdens associated with products or technologies. The LCA methodology is evolving and several organizations such as SETAC, the United Nations Environment Program (UNEP), and universities are actively involved in the continuous development of LCA. Unlike other environmental tools, LCA provides a comprehensive assessment that includes all types of impacts under three main areas of protection: Human Health, Environment, and Natural Resources. The distinctive feature of LCA is its "system thinking" approach, which focuses on products and technologies from a life cycle perspective. This broad scope helps to avoid problem-shifting, such as transferring impacts from one phase of the life cycle to another, from one region to another, or from one environmental issue to another.

LCA can be defined as a comprehensive and systematic approach to evaluating the environmental impacts of products, processes, or services throughout their entire life cycle. This methodology is essential for understanding and mitigating the environmental implications of biorefinery operations considering the whole value chain. LCA provides a robust framework for identifying, quantifying, and analyzing the environmental burdens associated with all stages of a product's life, from raw material extraction through production, use, and disposal.

LCA is established by the International Organization for Standardization (ISO) standards 14040 and 14044 (ISO, 2006a, 2006b). It consists of four main phases.

1. Phase 1: Goal and scope definition.
2. Phase 2: Life cycle inventory analysis.
3. Phase 3: Life cycle impact assessment.
4. Phase 4: Life cycle interpretation.

An LCA study is inherently iterative, meaning that earlier phases may need revisiting based on the findings of later phases. The four phases of LCA are detailed in the following sections.

2.3.1 Goal and scope definition

In the first step, the goal and scope of the project are defined. In this phase, the intended use of the LCA is established, whether for internal decision-making, public disclosure, or regulatory compliance. This phase also includes the underlying reasons for conducting the study, such as identifying environmental hotspots, comparing alternative products, or exploring pathways of improvement (Pajula et al., 2017). Additionally, the target audience of the LCA is also defined in the goal step, whether the analysis is intended for stakeholders, consumers, investors, or regulatory bodies.

In the scoping stage, the system boundaries are defined. These boundaries involve all the processes necessary to perform the function, from the raw materials up to the end-use phase, including consumption, incineration, or recycling. If the scenario is for the product's entire lifetime, then is called "cradle-to-grave", meaning that the product or service is evaluated for its inputs and outputs to the environment, from the raw materials up till the end-of-life of the product (e.g., incineration, sequestration). Alternatively, a shorter path scenario would be "cradle-to-gate", which means the evaluation starts with raw material up to the point of delivery, excluding the end-life use. Fig.4 illustrates these two scenarios of life cycle assessment. More information on all possible alternatives can be found elsewhere (Schelte et al., 2021), as in some cases, they depend on the type of products (e.g., from "cradle to wheel" for liquid fuels).

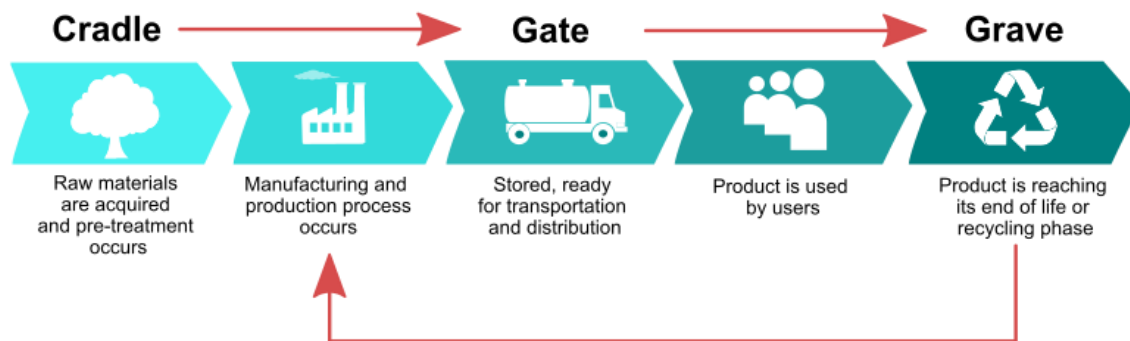


Figure 4: Simplified life cycle assessment scenarios.

After defining the boundaries, the next step in the scoping phase is determining the respective functional unit (FU). The FU quantifies the product or service delivered by the system and serves as a reference for comparing alternative products or processes. Typically, it takes the form of a mass or energy output (e.g., 1 kg, 1 MWh, 1 MJ, etc) related to the final produced outcome of the activity/inventory process.

In some cases, the process may entail a more complex functional unit that is a mixture of two or more products (i.e., multi-functional systems). This complexity usually arises due to the production of additional coproducts, produced simultaneously during the process of manufacturing the main product. The inventories are then scaled to their respective functional unit considered, ensuring that all inputs and outputs are appropriately accounted for in relation to the defined FU.

In defining the system boundaries, it is crucial to address the occurrence of co-products, system expansion, and allocation methods. The system boundary must align with the study's goal, ensuring consistency and relevance. Assumptions and limitations play a vital role in phase 1, as they can significantly influence the results, data quality, and the overall reproducibility and reliability of the study. Regarding allocation methods, all activities are classified primarily as either cut-off processes or allocation at the point of substitution (APOS) processes (Wernet G. et al., 2016). This classification system assumes a linkage between the supply and distribution of impacts among producers and consumers of products or services, encompassing both allocation and substitution.

Different classification methods include "allocation, cut-off by classification," "allocation, cut-off, EN15804," "allocation at the point of substitution (APOS)," and "substitution, consequential, long-term." The main difference between "allocation, cut-off by classification" and "allocation at the point of substitution (APOS)" lies in their treatment of waste and recyclable materials. Users can choose the most appropriate model for their LCA analysis, understanding the potential effects on their study's goals and scope. In these studies, the APOS method is utilized, as it allocates part of the waste impact to the production while enabling recycling, resulting in a reduced overall burden (see section A4, 7.2) (Wernet G. et al., 2016). This approach ensures a more accurate representation of the environmental impacts associated with the life cycle of products and processes, thereby supporting the decision-making process.

2.3.2 Life cycle inventory analysis

The Life Cycle Inventory (LCI) phase involves data collection and calculation procedures to quantify relevant inputs and outputs of a product system (ISO, 2006a, 2006b). At the core of inventory analysis is the gathering of data concerning the foreground system (Fig. 5), which is used as input for the modeling phase. The final inventory should correspond to the reference flow that meets the previously defined functional unit (FU).

The LCI phase demands substantial time and effort due to the challenges of collecting high-quality data for all processes involved. The first step is to identify all processes involved in the system under investigation. This starts by identifying the unit process that outputs the reference flow, which satisfies the function quantified by the FU. From there, all upstream and downstream processes of the foreground system are determined. Then, the data collection should cover each unit process within the defined system boundaries and include i) energy inputs, raw materials,

ancillary inputs, other physical inputs, ii) products, co-products, and waste, iii) emissions to air, discharges to water and soil, and iv) other environmental aspects.

The LCI is usually completed by relying on different sources. High-quality primary data, obtained from direct measurements at specific sites or derived from such measurements, should be prioritized despite the time and resource demands involved. When primary data is not available, the material and energy flows can be estimated using secondary data from similar processes, or by utilizing information from technical reports, scientific literature, and LCI databases such as Ecoinvent (Wernet G. et al., 2016). Moreover, process simulations can be utilized to complete the LCI of the foreground system while for the background system databases are usually employed (Fig.5). The simulations enable the estimation of material and energy flows by modeling the processes under study, providing detailed data that might be otherwise difficult to obtain directly. By simulating different scenarios and operational conditions, process simulations enhance the accuracy and completeness of the LCI, ensuring a more robust and comprehensive environmental assessment. Notably, it is sometimes possible to apply cut-offs, which imply not accounting for one or more inputs or outputs if these do not carry more than a certain percentage of the total environmental impact.

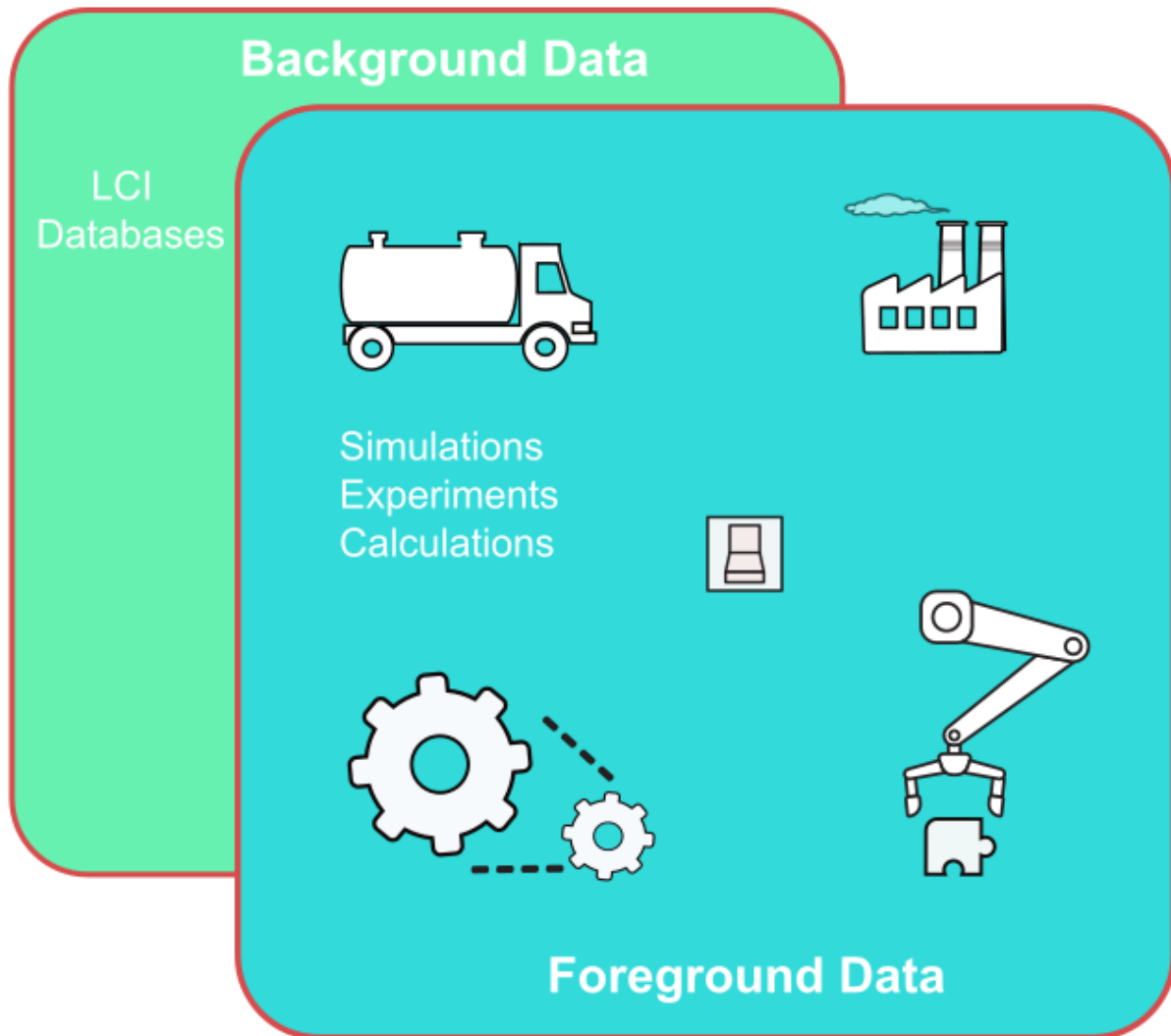


Figure 5: Integration of background and foreground systems in life cycle inventory analysis.

The final step in the LCI analysis involves creating detailed models and calculating LCI results. This stage is critical as it synthesizes all collected data into a comprehensive representation of the system under study. These LCI results serve as the foundational data set for the subsequent Life Cycle Impact Assessment (LCIA) phase, where the inventory data is translated into meaningful indicators of environmental performance.

2.3.3 Life cycle impact assessment

The third phase of an LCA study, the Life Cycle Impact Assessment (LCIA), converts the elementary flows from the LCI into environmental impact scores. This phase evaluates the extent

to which each flow (e.g., direct emissions or resource use) contributes to environmental impacts. LCIA aims to make results more environmentally relevant, understandable, and easier to communicate by using environmental impact categories.

The ISO 14040/14044 standards distinguish mandatory and optional steps for the LCIA phase. The mandatory steps include the selection of impact categories, classification and characterization. In the initial step, the specific environmental impact categories to be assessed are identified. During the classification, each LCI flow is assigned to one or more impact categories based on its potential effects. Finally, the characterization involves quantifying the contributions of LCI flows to each impact category, and determining the magnitude of their impact.

In LCIA phase, the mathematical process of converting inventory data into environmental impacts involves multiplying the inventory flows by the characterization factors. This relationship is illustrated in Equation 1:

$$EI_c = \sum_i^n CF_{i,c} \cdot LCI_i \quad \text{Eq. 1}$$

In this equation, each inventory flow LCI_i is multiplied by its corresponding characterization factor $CF_{i,c}$, which reflects the potential environmental impact per unit of the flow. The results are then summed to yield the total impact score EI_c for the specified category.

The characterization step in LCA can occur at either midpoint or endpoint levels. Midpoint characterization aggregates the elementary flows from the life cycle inventory based on their potential to contribute to the same environmental impact category. To translate midpoint indicators to endpoint indicators, additional modeling is necessary, often referred to as damage or severity modeling. Endpoint indicators relate the outputs of midpoint indicators to broader Areas of Protection (AoP), such as human health, ecosystems, and natural resources. Endpoint indicators represent the outcomes of the environmental cause-effect chain initiated by the elementary flows assessed in the LCI, whereas midpoint indicators lie in between these stages and correspond to actual environmental impacts.

Finally, normalization, weighting, and grouping are optional steps in LCIA that might help to interpret the results for a broad audience. The normalization involves scaling the results of different impact categories to a common reference scale which allows for comparisons between impacts that have different units or magnitudes. After normalization, weighting assigns relative importance or priority to different impact categories based on societal or stakeholder values. This step involves incorporating qualitative or quantitative criteria to reflect the preferences or priorities of stakeholders regarding environmental impacts. Mathematically, the weighted impact score SS (single score indicator) for each impact category can be expressed as:

$$SS = \sum_c^n EI_c \cdot W_c \quad \text{Eq. 2}$$

Where EI_c is the characterized impact score for the impact category obtained from the characterization phase of LCIA, W_c is the weighting factor or coefficient assigned to impact category c . Note that weighting factors are derived based on various criteria, including scientific evidence, policy objectives, stakeholder preferences, or ethical considerations. They are often normalized to ensure they sum up to 1 or 100%, indicating the relative contribution of each impact category to the overall environmental impact assessment (Soares et al., 2006). Finally, grouping might be applied that involves consolidating similar impact categories into broader categories to simplify the interpretation of results. It aims to reduce complexity and make the information more comprehensible and actionable for decision-makers.

2.3.4 Life cycle interpretation

In the fourth phase of the LCA study, once LCIA results are obtained, practitioners must interpret them while considering the study's objectives, underlying assumptions, potential errors, and sources of uncertainty, including data quality and modeling principles. Typically, LCIA results are analyzed to identify hotspots across different life cycle stages, delving into specific processes within those stages. This hotspot analysis highlights the primary contributors to environmental impacts in terms of life cycle phases, processes, and flows. Moreover, the phenomenon of burden shifting is often addressed to assess how environmental impacts are redistributed across different stages or components of a product's life cycle. Burden shifting refers to the potential for environmental impacts to be transferred from one stage of the life cycle or impact category to another. This analysis is crucial because it helps ensure that improvements in one part of the life cycle do not inadvertently lead to increased impacts elsewhere.

The interpretation phase also includes the identification of significant issues based on the results of previous steps, such as completeness, sensitivity, and consistency it is recommended to conduct a completeness check to ensure all necessary information and data are available and accurate for a reliable interpretation. If any information is missing or incomplete, it must be determined whether it is crucial for meeting the LCA's goals and scope. Following completeness verification, the ISO advises conducting a sensitivity analysis to understand how uncertainties in inputs affect the LCA outcomes.

In conclusion, the interpretation phase synthesizes environmental impacts across all life cycle stages to draw insights into product or process sustainability. It highlights key environmental hotspots, addresses study reliability by discussing uncertainties, and offers actionable recommendations for improvement. These conclusions guide stakeholders in making informed decisions to enhance sustainability across industries.

2.3.5 Environmental databases, methods, and software tools

Environmental LCI databases, LCIA methods, and software tools are critical components in conducting LCA studies, providing essential data, methods, and tools for assessing environmental impacts across product life cycles. In Table 1, relevant LCI databases, methods, and software tools are included.

Environmental LCI databases serve as repositories of data on the inputs (resources) and outputs (emissions and waste) associated with various processes and products throughout their life cycles. These databases compile information from industry, academic research, and governmental sources, ensuring comprehensive coverage across different sectors and geographical regions. Common examples include databases such as Ecoinvent (Wernet G. et al., 2016) or Agri-footprint (Corrado et al., 2018), most of them require a commercial license to access the datasets.

Software tools integrate LCI databases and LCIA methods into user-friendly platforms, facilitating LCA modeling and analysis. Among the tools available, SimaPro is a versatile and widely used software tool that integrates multiple LCI databases and LCIA methods, enabling customizable LCA studies. GaBi software is also employed and provides access to comprehensive LCI data and supports detailed LCA calculations and scenario evaluations. There are also open-source software offering flexibility in LCA modeling and scenario analysis such as Open-LCA and Brightway, the latter a Python-based software framework recently developed.

In typical LCA practices, various sets of category indicators, formulated through specific characterization models, are consolidated into frameworks known as LCIA methods. These methods, such as ReCiPe, CML, TRACI, EDIP, LIME, and IMPACT 2002+, are commonly integrated into LCA software tools (Table 1). With an expanding array of LCIA methods and indicators available, selecting the most suitable one for a practitioner's study necessitates a thorough understanding of each method's primary attributes. It is also crucial to consider the ongoing evolution and integration of these methods, as they undergo continuous updates and refinements over time.

In these studies, the ReCiPe 2016 LCIA methodology (Huijbregts et al., 2017) is employed, as the which was first co-developed in 2008 through cooperation between RIVM, Radboud University Nijmegen, Leiden University, and PRé Sustainability (PRé, 2016). ReCiPe 2016, is an improvement of its earlier 2008 version. The ReCiPe model is frequently updated to include new data and research achievements. Some of the ReCiPe model advantages over its predecessors such as CML 2000 and Eco-indicator 99, are:

- a. The broadest set of midpoint categories.
- b. Where possible, it utilizes impact mechanisms that have a global scope.
- c. Unlike other approaches, it does not include potential impacts from future extractions in the impact assessment but assumes those impacts are included in the inventory analysis.

Table 1: List of LCA-related methods, tools, and databases (A.P. Acero et al., 2015)

LCIA methods	Software LCA	LCI databases
<u>ReCiPe 2008-2016</u> (Huijbregts et al., 2017)	SimaPro v7.0-9.0 (Grzesik and Guca, 2011)	Ecoinvent v2.0-3.8 (Wernet G. et al., 2016)
<u>TRACI v2.1</u> (Bare, 2011)	OpenLCA v1.7 (Pamu et al., 2022)	Gabi (Pe International AG, 2012)
<u>Impact 2002+</u> (Jolliet et al., 2003)	REET.net (Cai et al., 2022)	AUSLCI (Giurco et al., 2008)
<u>ILCD 2011</u> (EC-JRC, 2012)	GaBi v5.0 (Pe International AG, 2012)	ELCD (Yang et al., 2020)
<u>IPCC 2007/2013</u> (Calvin et al., 2023)	Umberto LCA v10.0 (Iswara et al., 2020)	USLCI (Alberta Carpenter, 2012)
<u>USEtox</u> (Rosenbaum et al., 2008)		US EPA (Curran and Young, 1996)
<u>Product Environmental Footprint (PEF)</u> (European Commission, 2021)		Agri-Footprint (Corrado et al., 2018)
<u>AWARE</u> (Boulay et al., 2018)		IDEA v2.0 Japan (JEMAI and AIST, 2024)
Accumulated Exceedance (European Union, 2021)		SPINE@CPM (Tivander, 2013)
Eco-indicator 95-99 (Godkoop et al., 1998)		LCA-Food (Nielsen P H et al., 2003)
<u>Environmental Footprint (EF) method 3.0</u> (European Commission, 2021)		Korea LCI database (Jang et al., 2024)
<u>CML 2001</u> (Dreyer et al., 2003)		
<u>CED v1.09</u> (Puig et al., 2013)		
USES–LCA (Van Zelm et al., 2009)		
TEAM and DAYCENT (Del Grosso et al., 2005)		
CML 2000 (Mehmeti and Canaj, 2022)		
CML-IA (Castanheira and Freire, 2017)		
LIME-2 (Itsubo and Inaba, 2003)		
EDIP (Sharaai et al., 2011)		
CML 2 baseline 2000 (Dreyer et al., 2003)		
Ecological Scarcity 2013 v1.0 (Randall and Heijungs, 2023)		

ReCiPe 2016 distinguishes a broader scope compared to other methods, featuring 18 midpoint categories (see Table 2), surpassing CML-IA and TRACI 2.1 which have 10 midpoint categories, and the Product Environmental Footprint (PEF) with 14 (Feng et al., 2023). This extensive coverage allows ReCiPe 2016 to assess environmental impacts comprehensively across various dimensions in space and time, encompassing numerous potential damage pathways. Moreover, unlike EF 3.0 and similar methods limited to a European scope (Loganathan et al., 2023). It also utilizes mechanisms that have a global scope, along with the ones of local scope, in contrast to other methods such as the EF 3.0 method, which only focuses on European level (Loganathan et al., 2023). ReCiPe 2016 includes both global and local impact mechanisms. Another distinctive feature of ReCiPe 2016 is its consideration of potential future impacts within the inventory analysis, contrasting with methods that incorporate them separately (Catalán and Sánchez, 2020).

Stavropoulos et al., (2016) compared ReCiPe with Eco-indicator 99 and IMPACT 2002+ for the environmental impact assessment of manufacturing cylinder heads for both a diesel and a petrol automotive powertrain. In this comparison analysis, ReCiPe demonstrates higher score values, than the other two, followed by Eco-indicator 99. ReCiPe also demonstrates positive values in categories such as ecosystem quality, whereas Eco-indicator 99, shows negative values and IMPACT 2002+ values are much lower than the other two. Therefore, ReCiPe as an evaluator surpasses the other two in terms of precision. Similarly, in the study of Castanheira et al. (2017), where they performed LCA on biodiesel produced from palm oil in Colombia, they implemented a comparison analysis of two different LCIA methods. ReCiPe and CML-IA methods were significantly different and came with contradictory results for photochemical oxidation and eutrophication categories. For the photochemical oxidation analysis, CML performs 50% lower for biogas captured and flared than for biogas released, while for ReCiPe, there is no significant difference between the two biogas management options. Additionally, eutrophication impacts with CML vary among various fertilization schemes, while for ReCiPe method is constant. In the same study, terrestrial acidification showed a significant difference of 10-40% higher impact in ReCiPe than in CML due to a higher ReCiPe characterization factor for NH_3 (more than 50%).

Table 2 summarizes the 18 midpoint impact categories of the ReCiPe 2016 model. Midpoint indicators focus on single environmental problems (e.g., acidification, global warming, eutrophication, etc), while endpoint indicators show an aggregated environmental impact sustained in three pillars: 1) effect on human health; 2) biodiversity; and 3) resource scarcity. The categories span a wide range of assessments starting from Global Warming Potential (GWP), up to Land Use (LU) or Water Consumption (WC). Note that many gases can provoke GWP and to consider their relative impact we take advantage of the CO_2 -equivalent metric, but first, a conversion is necessary to be made. For example, 1 kg nitrous oxide (NO_x) has an equivalent of 298 kg CO_2 eq, therefore multiplication of the element's mass with the kg CO_2 eq metric is required to estimate the overall GWP. Equivalently, other GHGs such as methane (CH_4) have a respective 25 kg CO_2 eq. per 1 kg. Chlorofluorocarbons (CFCs), are a group of gases with very high GWP values, starting with Trichlorofluoromethane (CFC-11), which has the smallest GWP value at 6,226 kg CO_2 eq (Sari

Siitonen, 2024). It is profound, that although CO₂ as a greenhouse gas prevails in the atmosphere in terms of quantity, its GWP value is only 1 kg CO₂ eq, therefore all the other gases are more potent in “trapping” heat and rising to the planet’s overheating. CFC production and consumption, especially, is regulated by the Montreal Protocol (Auffhammer et al., 2005).

Table 2: ReCiPe 2016 impact categories and their units.

Impact category	Units
Global warming potential (GWP)	kg CO ₂ eq*
Stratospheric ozone depletion (SOD)	kg CFC11 eq
Ionizing radiation (IR)	kBq Co-60 eq
Ozone formation, Human health (OF, HH)	kg NO _x eq
Fine particulate matter formation (FPMF)	kg PM _{2.5} eq
Ozone formation, Terrestrial ecosystems (OF, TE)	kg NO _x eq
Terrestrial acidification (TA)	kg SO ₂ eq
Freshwater eutrophication (FER)	kg P eq
Marine eutrophication (MER)	kg N eq
Terrestrial ecotoxicity (TE)	kg 1,4-DCB**
Freshwater ecotoxicity (FE)	kg 1,4-DCB
Marine ecotoxicity (ME)	kg 1,4-DCB
Human carcinogenic toxicity (HCT)	kg 1,4-DCB
Human non-carcinogenic toxicity (HNCT)	kg 1,4-DCB
Land use (LU)	m ² a crop eq
Mineral resource scarcity (MRS)	kg Cu eq
Fossil resource scarcity (FRS)	kg oil eq
Water consumption (WC)	m ³
*eq	Equivalent (eq)
Chlorofluorocarbon	CFC
PM _{2.5}	Particle Matter of 2.5 μm
**DCB	Dichlorobenzene (DCB)

To calculate the impact predicted for a given time horizon there are three different approaches:

- Individualistic (I) perspective, which is based on short-term (20 years) interest and impact types that are undisputed and technologically optimistic regarding human adaptation (Huijbregts et al., 2017).
 - Hierarchist (H) perspective is based on a scientific consensus regarding the time frame and validity of impact mechanisms, which is fixed as a 100-year prediction.
- Finally for a 1,000+ year prediction due to an Egalitarian perspective, which is based on the most precautionary measures, considering the longest time frame and all impact pathways for which data are available (Huijbregts et al., 2017)

ReCiPe 2016 model calculates the three endpoint aggregation pillars through its nine damage pathways (Fig. 6). Each line of the diagram involves the use of different characterization factors.

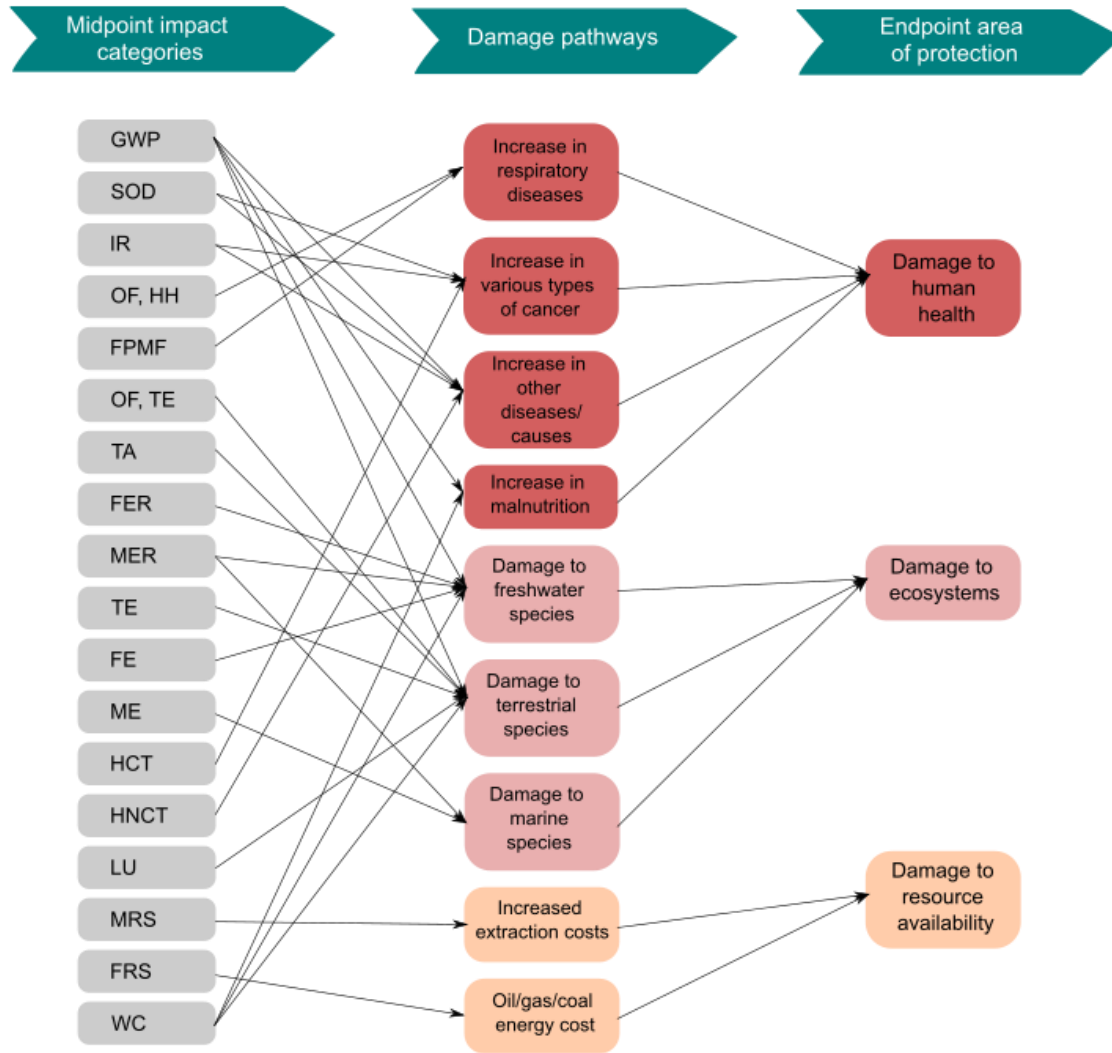


Figure 6: ReCiPe 2016 model to visually indicate the transformation from mid-point to endpoint indicators.

The endpoint levels are labeled as:

- 1) Damage to human health (DALYs),
- 2) Damage to biodiversity/ecosystems (species. yr),
- 3) Damage to resource availability (USD2013),

They signify the point where potential damage in these areas is no longer recoverable, whereas midpoint indicators are approximated damage that still can be reversed. There is a way to convert midpoints to endpoints as it simplifies the interpretation of the LCIA results; however, uncertainty increases. In Fig. 6, the interconnected relationship among impact categories (midpoints), damage pathways, and endpoints is visually explained.

3. Case study: Olive-tree pruning biorefinery

3.1 Summary

This study explores the integration of bioenergy with carbon capture and storage (BECCS) into a biorefinery system that converts olive tree prunings into bioethanol and antioxidants. With a capacity to process 1,500 tons of prunings daily, the biorefinery yields an annual production of around 12,000 tons of antioxidants (purity > 60%) and 78,000 tons of bioethanol. Utilizing a holistic approach involving process simulations and life cycle assessment, our analysis covers technical, economic, and environmental dimensions across two scenarios differing in design and heating source: natural gas or a BECCS system using olive prunings. Findings reveal the potential for BECCS to drastically reduce the carbon footprint, potentially achieving net-negative emissions (-84.37 kg CO₂eq per 1.00 kg of bioethanol and 0.15 kg antioxidants produced). However, these environmental gains are counterbalanced by economic and environmental challenges, with investment and operating costs nearly doubling and leading to complex environmental trade-offs related to eutrophication (+75%), increased water consumption (+45%), and expanded land use (+80%). Nevertheless, the premium nature of carbon-negative products, coupled with growing awareness and supportive policy frameworks, may overcome these economic barriers. This study highlights the importance of holistic evaluation when integrating CCS into biorefineries facilitating informed decision-making to address unintended adverse effects and promoting sustainability.

3.2 Introduction

The European (EU) Green Deal, with its commitment to achieving climate neutrality by 2050, is built upon three fundamental pillars: fostering energy efficiency, promoting renewable energy, and incorporating clean mobility systems (Calvin et al. 2023). A pivotal player in achieving the long-term climate goals will be the deployment of carbon dioxide removal (CDR) strategies. CDR encompasses practices and technologies aimed at removing carbon dioxide (CO₂) from the atmosphere, thereby compensating for emissions from industries and sectors that are difficult to decarbonize. CDR should be understood as an indispensable complement to the primary focus on rapid decarbonization because the extent of the CDR required hinges on delayed reductions in

emissions (Calvin et al., 2023; Galán-Martín et al., 2021b). Estimates range from hundreds of billions to several trillion metric tons of CO₂ removal depending on factors such as residual emissions, emission reduction rates, natural carbon sinks, and technological advances (Galán-Martín et al., 2021b). Given the scale of this unprecedented challenge, governments and businesses must start promoting and scaling up CDR strategies sustainably (Calvin et al., 2023).

The CDR portfolio encompasses various technological solutions and practices, including afforestation, reforestation, soil carbon sequestration, biochar production, direct air capture and sequestration (DACCS), enhanced weathering, ocean fertilization, and bioenergy with carbon capture and storage (BECCS), among others (Matušík et al., 2020; Minx et al., 2018). BECCS stands out for its ability to produce energy and marketable bio-based products while removing CO₂, provided the removed CO₂ exceeds emissions across the value chains (Bello et al., 2020; Negri et al., 2021; Tanzer and Ramírez, 2019). Notably, these bio-based products generated such as bioethanol, hydrogen, or electricity can replace fossil-based equivalents, providing further environmental benefits. BECCS involves absorbing CO₂ through biomass growth which is subsequently released during the biomass conversion processes and captured and securely stored in underground geological sites, ensuring its long-term sequestration out of the atmosphere. Despite the interest and its expected future role, there is only one large-scale BECCS industrial facility in operation today, situated in Illinois and producing bioethanol, with the capability to capture one million tons of CO₂ per year (Global CCS Institute Ltd, 2019). Meanwhile, there are several initiatives currently operating on a small scale and others in various stages of deployment (Global CCS Institute Ltd, 2019). Nevertheless, numerous challenges still need to be addressed to unlock the potential of BECCS, including the high costs, environmental considerations, and governance issues.

The BECCS concept lies at the heart of biorefineries, industrial facilities designed to produce multiple products from different biomass feedstock. These facilities can integrate carbon capture and storage (CCS) technologies to capture the biogenic CO₂ emissions generated during the conversion processes (e.g., fermentation, gasification, or direct combustion) that would be otherwise released back into the atmosphere. Then, the captured CO₂ is stored ensuring its long-term sequestration, while delivering bio-based energy, biofuels, and other chemicals with multiple applications (Galán-Martín et al., 2022b). There are also opportunities and markets for utilizing the captured CO₂ (Xu et al., 2010). However, carbon capture and utilization (CCU) applications differ from CDR because the CO₂ will eventually return to the atmosphere.

Traditionally, biorefineries suffer from economic competitiveness, and integrating or retrofitting them with CCS technologies will add an extra cost. Nevertheless, the current record prices of carbon permits and the emergence of incentives for CCS are opening new avenues for BECCS projects (Laude et al., 2011). Consequently, a comprehensive understanding of the technical, economic, and environmental implications surrounding the large-scale deployment of biorefineries coupled with CCS is crucial to ensure their sustainable implementation and contribution to the climate goals (Almada Pérez Deborah et al., 2023).

This study focuses on the valorization of olive pruning tree biomass (OPTB), which presents significant opportunities for utilization in biorefinery schemes. OPTB is an abundant biomass resource in the EU Mediterranean region (Galán-Martín et al., 2022b), arising from the pruning of olive trees in the late winter or early spring in the form of leaves and branches. This pruning serves to enhance olive tree structure, stimulate new growth, and increase fruit production. Spain alone accounts for more than 2.70 million hectares of olive groves, yielding up to 4.0 tonnes of OPTB per hectare annually (Galán-Martín et al., 2022b). Notably, this lignocellulosic biomass has traditionally been underutilized and regarded as waste, often burned in the field or incorporated crushed, and chipped into soils. Hence, there is a great opportunity to valorize this residual biomass and transform it into a potential feedstock for biorefineries that can be integrated with CCS technologies and contribute to national and global CDR commitments (Galán-Martín et al., 2022b).

Numerous studies have explored the value of utilizing OPTB in various contexts, including experimental investigations and research delving into technical feasibility, economic aspects, and environmental performance. Romero-García et al. (2016) analyzed the economic and efficiency aspects of a biorefinery producing bioethanol and antioxidants from OPTB, finding that small-capacity biorefineries focusing on natural antioxidants displayed strong economic attractiveness. Similarly, Susmozas et al. (Susmozas et al., 2019) conducted a techno-economic assessment of an OPTB-based biorefinery, showing its viability in producing ethanol, xylitol, antioxidants, and electricity, achieving energy self-sufficiency. More recently, Servian-Rivas et al. (Servian-Rivas et al., 2022) expanded on this by performing a life cycle assessment of two distinct OPTB-based biorefinery schemes. One configuration produced ethanol, xylitol, and antioxidants, while the other solely focused on the production of antioxidants. Their findings underscored the economic importance of antioxidants and the reduced environmental impacts of bio-based products compared with their business-as-usual production methods. The study also emphasized the importance of optimizing heating, water, and energy requirements, particularly through the combustion of residual biomass for steam and power cogeneration. Another line of research delved into the environmental trade-offs associated with biorefinery systems, such as the ecological negative side-effects arising from carbon reduction benefits in biomass-based power plants (Pang et al., 2017) while other studies proposed strategies to mitigate collateral environmental damages through recycling and integration (Martinez-Hernandez and Hernandez, 2018; Ramirez-Contreras et al., 2020).

Building upon this previous research on OPTB-based biorefineries, this study takes a comprehensive approach by conducting an integrated environmental and techno-economic assessment (ETEA) of a multiproduct OPTB-based biorefinery coupled with a CCS system to produce bioethanol and antioxidants. To this end, we rely on a combination of process simulation (validated with experimental data) and life cycle assessment (LCA). Within this framework, the OPTB undergoes a cascading transformation, yielding high-value-added products, such as antioxidants and bioethanol. To meet the energy demands of the entire biorefinery (including

heating and cooling), a BECCS cogeneration plant is integrated, utilizing OPTB as its primary fuel source. The novelty of this work is twofold. Firstly, it stands as the pioneering study that integrates an OPTB-based biorefinery with a BECCS system, presenting the potential to deliver carbon-negative bio-based products contributing to the CDR efforts. Secondly, from an environmental perspective, we conduct a comprehensive assessment across several environmental categories, extending beyond the scope of climate change impacts. This holistic approach allows exploring the potential occurrence of burden-shifting—a phenomenon where resolving one environmental challenge inadvertently gives rise to another.

3.2.2 Olive pruning tree biomass-based biorefinery. Scenario definition.

This study centers on a biorefinery that converts OPTB into two valuable bio-products: antioxidants and bioethanol. Antioxidants are high-value compounds with potential applications in the food, cosmetic and pharmaceutical sectors. Bioethanol serves as an eco-friendly substitute for fossil gasoline in vehicles or chemical plants, contributing to reducing fossil fuel dependency and advancing energy independence.

The ETEA study considers the entire supply chain of the biorefinery system, encompassing all the stages that ensure the timely and efficient delivery of feedstocks and products. The initial phase involves the preparation and acquisition of OPTB, which consists of branches and leaves resulting from olive tree pruning. These prunings are collected and stacked in piles and chipped before their transportation to the biorefinery facility. The transportation of the feedstock typically relies on trucks, assuming an average distance of 100 km to the biorefinery. Ideally, the biorefinery should be strategically located in proximity to the feedstock source, ensuring sufficient and steady supply. Upon arrival at the biorefinery facility, the OPTB feedstock undergoes various processing and conditioning stages, involving equipment like shredders, grinders, and extractors, which vary according to the biorefining pathway. The pretreated OPTB is subsequently processed in parallel in the antioxidant and bioethanol production subsystems, each equipped with specialized machinery (see section 3.2.3.1 for a detailed description of the process flowsheet). Ultimately, the antioxidants and bioethanol are produced, which are prepared for distribution from biorefinery plants. The distribution of the bioproducts to customers and their usage phase are not considered in this study as we follow a cradle-to-gate approach.

In this study, we examine two alternative scenarios of the OPTB-biorefinery system outlined below (Fig.7). These scenarios differ in the design and the energy source employed to power the processes of the biorefinery plant. The first scenario, denoted as “BIOR NG”, represents the conventional or business-as-usual approach utilizing natural gas to fulfill the heating and cooling requirements necessary for the various biorefinery processes. In contrast, the alternative scenario, labeled as “BIOR CCS”, integrates a BECCS technology to capture the biogenic CO₂ released from the fermentation unit (bioethanol subsystem) and the cogeneration unit, which burns OPTB and residual biomass to meet the energy requirements of the plant. The BIOR CCS scenario thus includes CO₂ capture, compression, transportation via pipeline, and the CO₂ geological injection

ensuring secure long-term storage. These two scenarios are assessed and compared regarding technical, economic, and environmental performances.

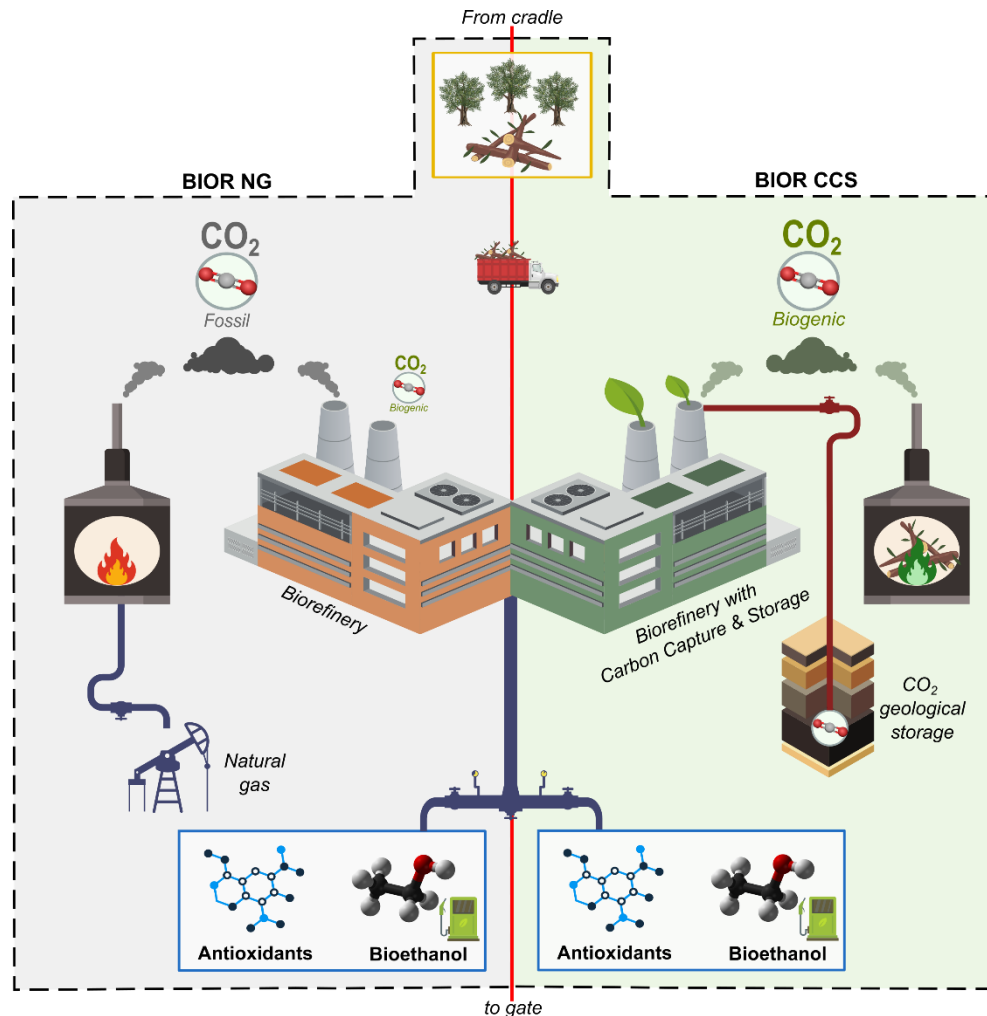


Figure 7: Graphical overview of the two scenarios for the olive pruning tree biomass-based biorefinery. On the left, the fossil BIOR NG scenario, which relies on natural gas to power the biorefinery. On the right, the alternative scenario BIOR CCS shows the integration of bioenergy with carbon capture and storage subsystem.

3.2.3 Methods description

The comprehensive ETEA assessment of the OPTB-based biorefinery entails the integration of process simulation and LCA. The ensuing subsections offer an in-depth explanation of these methodologies.

3.2.3.1 Modeling of the biorefinery with CCS

The biorefinery system comprises five interconnected subsystems, as illustrated in Fig.8: the feedstock (SS1), the antioxidant (SS2), the bioethanol (SS3), the wastewater treatment (SS4), and the cogeneration unit (SS5).

The primary biomass feedstock utilized is OPTB, serving dual purposes in the production of bioethanol and antioxidants, as well as in direct combustion for heat generation.

The OPTB-based biorefinery plant was simulated in SuperPro Designer v9.0. The model was validated with experimental data (Romero-García et al., 2016). The system contains 55 unit operations, 7 reactors, and 22 heat exchangers (details of the simulation, refer to Appendix A1 and A2). The BIOR CCS scenario would include the BECCS additional subsystem to capture, compress, and transport the biogenic CO₂ captured, which was modeled as in (Galán-Martín et al., 2021a). The potential site for the biorefinery is the Andalusia region in southern Spain, known for having the highest number of olive groves globally, resulting in a substantial amount of OPTB available (Galán-Martín et al., 2022b). However, it is important to note that determining the optimal location, design, and operational considerations of the biorefinery are beyond the scope of the current study. The process begins with the collection of the OPTB at the olive grove, followed by chipping before transportation to the biorefinery plant. Upon arrival, a series of pretreatment steps are executed, including the conditioning phase (removing impurities like soil, small stones, leaves, etc.), as well as grinding and sieving to homogenize the particle size from 4 to 10 mm. For the antioxidant subsystem (SS2 in Fig.8), the daily feed comprises 1,500 t of OPTB in dry weight (dw). The choice of this production capacity was based on several factors, including the availability of biomass in the proposed region to locate the biorefinery (Jaén, Spain), industry standards, and the scale at which the biorefinery model was found to operate optimally according to previous work (Romero-García, 2016). The biomass enters the aqueous extraction system, resulting in the separation of liquid and solid streams. Approximately 20% (w/w) of the material is solubilized (Martínez-Patiño et al., 2015) with a 20% (w/v) solid/liquid ratio (Conde et al., 2009). The liquid phase is then processed in a non-ionized adsorption chromatography column to purify the natural antioxidants. This purification process involves the addition of a substantial amount of non-ionic hydrophobic resin and ethyl acetate at 3:1 (v/v) liquid-solvent ratio. The ethyl acetate operates in a closed circuit, which subsequently undergoes ultrafiltration to separate sugars (oligomers and mannitol). The remaining solution is pervaporated and distilled, resulting in a product with a purity of 99% (w/w). This filtered liquid contains phenolic compounds, with a concentration of 3.1 g gallic acid equivalent per 100 g of OPTB, representing a high-value-added product that includes the initial presence of mannitol (Martínez-Patiño et al., 2015).

Under these conditions, the recovery rate of phenolic compounds reached 55%, with an extract purity of 36.95 % (g gallic acid equivalent /g ethyl acetate extract). In the ethyl acetate extracts, most of the natural antioxidants including hydroxytyrosol, oleuropein, tyrosol, and 3,4-dihydroxybenzaldehyde can be found. These antioxidants have widespread applications in the pharmaceutical, food, medicine, and cosmetic sectors (Romero-García et al., 2016). The outcome

of this process is a mixture of antioxidants (12,082 t/yr) with a purity greater than 60% (w/w) achieving an antioxidant recovery rate higher than 80%. The chromatography column was loaded with a stream of 125 g ethyl acetate extract/L, using a ratio of 45.5% (v/v) load stream/resin. The eluent for this process consisted of slightly acidic water (0.01% H₂SO₄) at a ratio of 8 (v/v) (Romero-García et al., 2016).

The extracted solids undergo a filtration process and enter the bioethanol production subsystem (SS3 in Fig.8) (Romero-García et al., 2016). The OPTB solids were subjected to a 30% (w/v) successive solid loading pretreatment, using a mixture of water and phosphoric acid (0.5% (w/v)). The hydrolysis pretreatment is conducted at 170 °C for a duration of 10 minutes. The addition of an overliming agent, calcium hydroxide, helps to maintain the pH level at 10. This pretreatment effectively breaks down the hemicellulose and cellulose structures.

Following the pretreatment, the dissolved sugars are further processed through co-saccharification and enzymatic fermentation, resulting in the recovery of nearly 70% of the sugars in both the hydrolysate and the saccharification. In the subsequent co-fermentation stage, a modified microorganism (*Escherichia coli* MS04) was used to ferment all the glucose and over 93% of the xylose (Romero-García et al., 2016). Nutrients were added to feed the microorganisms, and KOH was added to maintain the pH level at 7. The ethanol produced achieves a yield of 90.20 % of the theoretical maximum (Martínez-Patiño et al., 2015). The final separation stage involves the extraction of ethanol through a double-column sequential rectifying-stripping distillation system. This process achieves an ethanol concentration of 91.00 % and a purity of 99.70 % after molecular sieves (azeotropic distillation). In total, the annual production of bioethanol amounts to 78,074 t/yr.

The wastewater generated from SS2 and SS3 enters SS4 for treatment within a sequential continuous anaerobic-aerobic reactor system. In the initial anaerobic reactor, biogas is produced consisting of 41.00 % methane and 59.00 % carbon dioxide by volume. Subsequently, a clarifier separates the solids from liquids. The separated solids are directed toward a vacuum filter and to the cogeneration unit for combustion, while the treated liquids are recycled for use as process water. Within the cogeneration unit (SS5 in Fig.8), natural gas or residual biomass along with OPTB are combusted at high temperatures, resulting in the production of high and low-pressure steam (depending on the scenario assessed). This steam will generate the heat and cooling energy demands to cover the needs of the plant. In the BIOR NG scenario, process biomass residues and natural gas are combusted to cover the energy requirements of the biorefinery. On the other hand, in the BIOR CCS, the cogeneration unit is powered by the utilization of process residues and OPTB as feedstock. In both scenarios, 69.50% of heating demands are covered by process residual biomass, while 30.50% is covered either by natural gas or OPTB.

A detailed report on the simulation results for the biorefinery is provided in the appendix, sections A1 and A2.

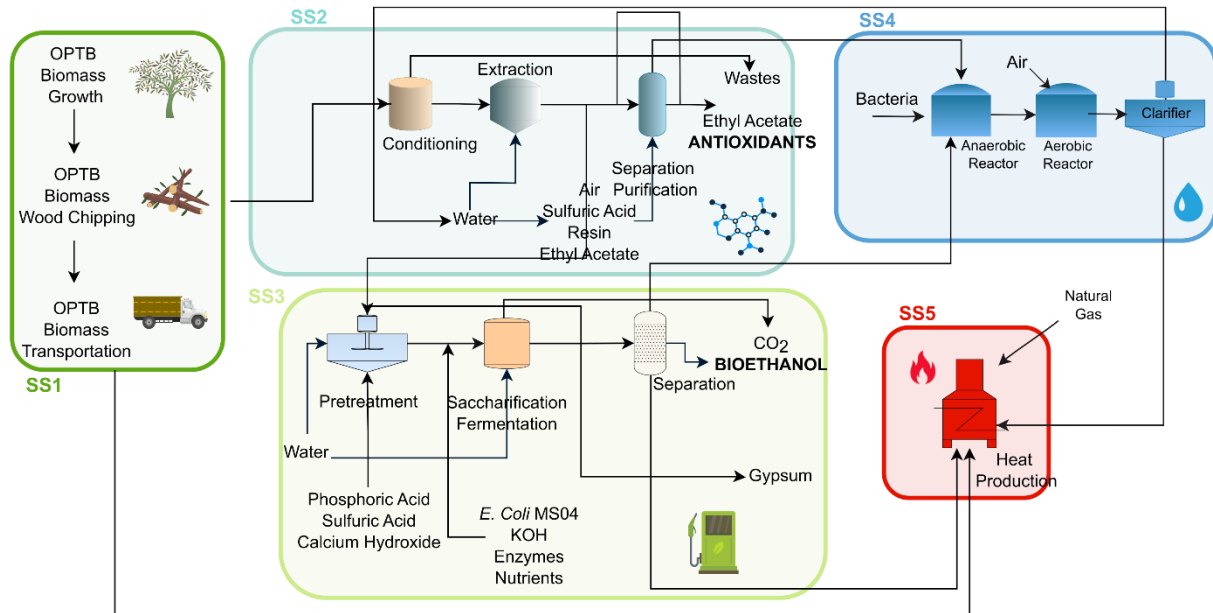


Figure 8: Schematic flowsheet of the olive pruning tree biomass biorefinery system comprising five subsystems: SS1: Feedstock subsystem, SS2: Antioxidant subsystem, SS3: Bioethanol subsystem, SS4: Wastewater treatment subsystem, SS5: Cogeneration subsystem.

3.2.3.2 Economic assessment

In the economic evaluation, the goal is to compare the scenarios based on a common functional unit (FU), i.e., to compare the total annual cost (TAC) to produce 1 kg of bioethanol and 0.15 kg of antioxidants. To perform these calculations, it is assumed a plant's lifetime of 25 years, taking into account the simulation results for a processing capacity of 1,500 t OPTB dw/day. The TAC includes both the capital expenditures (CAPEX) and operational expenditures (OPEX) associated with biorefinery production as detailed in reference (Ganat Tarek Al Arbi Omar, 2020) and described in Eq.1

$$TAC = AF * CAPEX + OPEX(\text{fix}, \text{vr}) \quad (1)$$

CAPEX includes one-time long-term investments (Pritha Banerjee, 2022) which are annualized using the capital annualization factor (AF) and an interest rate of 6.00 %. The AF is calculated as in Eq. 2.

$$AF = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (2)$$

The OPEX encompasses both fixed and variable costs (*fix*, *vr*) associated with ongoing operations,

including expenses related to raw materials, utilities, labor, and maintenance costs. As for the *CAPEX*, the equipment costs were determined using correlations from Sinnott and Towler (Sinnott and Towler, 2009). See details on the calculations in Appendix section A.3.

Finally, Equation 3 was employed to estimate the levelized cost of the biorefinery (*LCOB*) per functional unit (Lehtveer and Emanuelsson, 2021) by considering the *CAPEX*, the variable and fixed operating expenditures ($OPEX_{fix}$ and $OPEX_{var}$, respectively) and the total annual production of the biorefinery (*TAP*, in kg).

$$LCOB = \frac{CAPEX * AF + OPEX_{fix} + OPEX_{var}}{TAP} \quad (3)$$

Furthermore, the economic evaluation also includes economic metrics to assess the financial viability of the biorefinery, including the net present value (*NPV*), the payback time (*PBT*), and the return on investment (*ROI*). A detailed description of the economic calculations and the *CAPEX* and *OPEX* parameters can be found in the Appendix (section A3).

3.2.3.3 Sensitivity analysis and breakeven point

A sensitivity analysis of the economic assessment was performed by defining optimistic and pessimistic scenarios considering maximum and minimum costs for the parameters involved (costs of raw materials and utilities). The parameters defined on the cost parameters are detailed in Table A.5. The results of the sensitivity analysis are presented with error bars in Fig.9 depicting the pessimistic and optimistic uncertainty cost ranges.

Moreover, a breakeven point analysis was conducted to determine the minimum selling price of bio-based products for the BIOR CCS scenarios that make the *NPV* equal to one for the BIOR NG scenario. The breakeven point serves as a pivotal metric, indicating the price threshold at which the revenues generated from selling the bio-based products of the alternative BIOR CCS (premium pricing considerations) become competitive compared to the fossil counterparts (BIOR NG scenario). To conduct the breakeven point analysis, the selling price of the bioethanol and antioxidants in the BIOR CCS are increased (without altering those of the BIOR NG scenario) until equilibrium was achieved in *NPV* between both scenarios. Moreover, a complementary analysis was performed to determine the tax credit that should be provided per CO_2 sequestered to incentivize the BIOR CCS scenario.

3.2.3.4 Life Cycle Assessment

To comprehensively evaluate the environmental impacts of the OPTB-based biorefinery, we employed LCA, a standardized methodology to evaluate the potential environmental impacts of a system considering its entire life cycle. LCA adheres to the steps and guidelines outlined in ISO 14040 (ISO, 2006b) and 14044 (ISO, 2006a).

The first phase involves defining the goal and scope. In this study, the objective is to assess and compare the environmental impacts associated with the production of bioethanol and antioxidants,

considering the OPTB-based biorefinery scenarios described in section 3.2.2. Our approach adopts a cradle-to-gate scope, with the system boundaries from the acquisition of raw materials, growth of biomass, pretreatment of olive tree prunings, its transportation to the plant, and all subsequent processes at the biorefinery facility, up to the delivery of the bio-based products at the biorefinery gate (excluding the end-use phase). For illustration, we consider a cradle-to-grave scenario assuming that the bioethanol is incinerated resulting in emissions equivalent to 1.90 kg CO₂ per kg of bioethanol combusted. These direct emissions are estimated assuming the complete combustion of the ethanol. Furthermore, an attributional approach that assigns all impacts to the bio-based products considering that the life cycle of the product system remains fixed was followed. The multifunctional unit entails the simultaneous and coupled production of 1 kg of bioethanol and 0.15 kg of antioxidants, derived from the division of the total feedstock daily input by the total daily production of bioethanol and antioxidants (results from the simulation). This functional unit ensures a fair comparison of the BIOR NG and BIOR CCS scenarios which is the main objective of this study. Note that dividing the biorefinery into mono-functional systems and refraining from utilizing allocation procedures were avoided, as these can introduce significant uncertainty and greatly influence the results.

The second phase of the LCA involves the Life Cycle Inventory (LCI), which entails identifying and quantifying all inputs and outputs of the system over its entire life cycle (e.g., raw materials, energy, emissions to air). Data for the foreground system (the biorefinery production site) were obtained from the mass and energy balances of the plant simulation implemented in SuperPro Designer v9.0 (Table A.1 and Table A.7 in Appendix). Data for the background system were retrieved using datasets from Ecoinvent v3.8 (Wernet G. et al., 2016) and completed with literature to fill the gaps. Note that we account for the impacts associated with the pruning raw material employed in the biorefinery, including all relevant processes of growing olive trees, including fertilizers, pesticides, nutrients, land occupation techniques, and irrigation among others. For this, the ‘Olive fruit production – ES’ dataset from Ecoinvent v3.8 was used and allocated all inputs and outputs between the olive fruit and the prunings based on an economic factor as detailed in Appendix section A.4. Also considered chipping and mulching pretreatment activities as well as transportation using a lorry for a 100 km distance from the olive groves. The complete inventory of the OTPB is provided in Table A.6 in the Appendix. Moreover, for the cogeneration unit (SS5) in the BIOR CCS, we primarily rely on previous work modeling a BECCS system (Galán-Martín et al., 2021a) by adapting it to our specific context by considering the olive pruning as input. In essence, the BECCS system comprises a heat and power cogeneration plant integrated with post-combustion CO₂ capture technology using monoethanolamine solvent (with a 90% capture efficiency). In total, 1.69 kg of biogenic CO₂ is captured per kWh delivered with the BECCS system, calculated based on an OTPB carbon content of 49.40%, a chip-to-kWh ratio of 0.841 kg, and accounting for the own energy requirements of the CCS system. Once captured, the CO₂ is compressed to 110 bar and transported via a pipeline 200 km for secure storage in a deep saline aquifer. Note that this study incorporates illustrative assumptions regarding the supply chain (e.g., biomass and CO₂ transportation distances), which may not apply to all regional contexts.

Therefore, each project needs to consider its unique characteristics and regional aspects when implementing our model. All the detailed LCIs tables for the entire biorefinery system can be found in section A4 of the appendix (Tables A6-7). Concerning the third phase, the life cycle impact assessment (LCIA), the inventory was implemented in SimaPro v9.0. To transform the inventory entries into environmental impacts, the ReCiPe 2016 (Hierarchist perspective) (Huijbregts et al., 2017) was employed. In particular, midpoint category indicators that allow assessing the climate change impact through the Global Warming (GWP) indicator (carbon footprint measured in kg CO₂ eq) were used. Notably, as we deal with a BECCS system, the biogenic CO₂ embodied in the OPTB is modeled as a negative entry from fossil CO₂ emissions in the system. Hence, a negative input of -1.52 kg CO₂ per kg of pruning was estimated estimating a water content of 27.60% and a carbon content, on a dry basis, of 49.40%, as per the Phyllis2 database (TNO Biobased and Circular Technologies, 2024). Additionally, we considered seventeen other indicators referring to particular environmental problems including stratospheric ozone depletion (SOD), ionizing radiation (IR), ozone formation, human health (OF, HH), fine particulate matter formation (FPMF), ozone formation, terrestrial ecosystems (OF, TE), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), terrestrial ecotoxicity (TE), freshwater ecotoxicity (FE), marine ecotoxicity (ME), human carcinogenic toxicity (HCT), human non-carcinogenic toxicity (HNCT), land use (LU), mineral resource scarcity (MRS), fossil resource scarcity (FRS) and water consumption (WC).

This holistic approach considering the midpoint categories offers a comprehensive assessment of the broad environmental implications of the biorefinery, providing an understanding of its overall environmental sustainability.

3.3 Results and Discussion

3.3.1 Economic performance

The results of the economic analysis are presented in Fig.9. Note that the key distinction between the two scenarios lies in the costs of the heating needs. In the case of the BIOR NG scenario, which relies on natural gas, the heating cost is 89.70 €/MWh, whereas for the BIOR CCS scenario, the costs escalate to 160.00 €/MWh. Considering the central values for the cost parameters, due to the increased investment and operational costs associated with CCS technology, the BIOR CCS scenario emerges as a more expensive alternative compared to the business-as-usual BIOR NG scenario, with costs of 4.70 vs. 3.48 € per functional unit, respectively. These cost values are aligned with those reported in the literature for bioethanol production from biomass, ranging from 0.86 up to 1.50 €/kg (Romero-García et al., 2016; Sánchez et al., 2013). Notably, the costs are higher due to antioxidant production, which mounts up to 7.33 €/0.15 kg (Romero-García et al., 2016).

Even under the most optimistic cost data, the cost of the BIOR CCS scenario (3.93 € per functional unit) would be higher than the pessimistic estimates for the BIOR NG scenario (3.74 € per functional unit). This is attributed to the substantial upfront investments necessary for establishing the CCS infrastructure, which pose a financial barrier for stakeholders contemplating BECCS deployment. These investments entail not only the development of CCS technology within the biorefinery but also the construction of CO₂ transportation and storage infrastructure. Furthermore, BIOR CCS necessitates additional energy and biomass feedstocks to sustain the BECCS process, further increasing the economic burden.

Regardless of the scenario, the OPEX outweighs CAPEX, comprising 64.13% and 73.46% of the BIOR NG and BIOR CCS scenarios, respectively. It is worth noting that the primary contributor to total costs in both scenarios is heating and cooling, accounting for over 44.83% and 59.18% in each respective scenario. Following this, the costs associated with the OPTB biomass raw material and enzymes contribute 30.00% and 23.00% in both scenarios, while other factors such as ethyl acetate, other chemicals, and bacteria collectively contribute 14.00% of the total OPEX. In both scenarios, the heating-related expenses were excluded (Fig.9, pie chart).

The CAPEX represents a substantial portion of the overall cost, amounting to 35.87% and 26.54% in the BIOR NG and BIOR CSS scenarios, respectively. The primary cost driver within the CAPEX is the total equipment cost, accounting for over 50.00 % of the total, followed by the costs associated with the inside battery limits that contribute nearly half of the total CAPEX (49.00%).

The remaining 1% of CAPEX can be attributed to various factors including outside battery limits and other contingencies (see parameters in the Appendix, section A3).

The NPV in the BIOR NG scenario stands at 1.00 billion €, whereas for the BIOR CCS worsens up to -74.12 million € (detailed economic parameters are provided in Table A4 of the Appendix). Similarly, the BIOR CCS underperforms compared to the BIOR NG in other financial metrics. For example, the PBT for the BIOR CCS is more than double (14.00 vs 6.17 years), while the ROI is less than half (7.16% vs 16.20%). The worse economic performance in the BIOR CCS scenario may be attributed to the higher upfront costs or excessive operating expenses, with the heating requirements from BECCS as the main driver of the overall costs (Fig.9). The poorer economic performance in the BIOR CCS scenario may be attributed to higher upfront costs or excessive operating expenses, with heating requirements from BECCS being the main driver of overall costs (see Fig.9). However, it is important to acknowledge the uncertainties inherent in these calculations, particularly concerning the dependency on volatile natural gas prices, which can be influenced by geopolitical tensions, supply disruptions, and shifts in energy policies. Additionally, other factors such as technological advancements, new regulatory frameworks, and market dynamics could also impact the economic viability of the BIOR CCS scenario. Therefore, while the current analysis provides valuable insights, ongoing monitoring and adaptation to evolving circumstances are essential for robust decision-making in transitioning toward more sustainable energy systems.

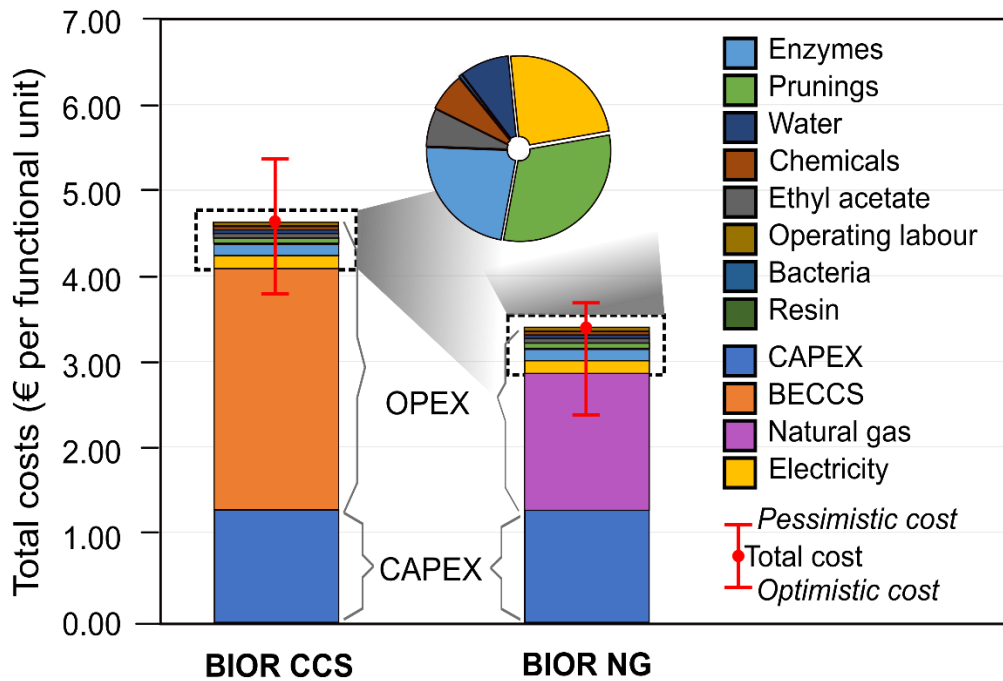


Figure 9: Costs breakdown of the two scenarios. The column on the left BIOR CCS integrates bioenergy with carbon capture and storage (BECCS) within the biorefinery. The column on the right corresponds to the BIOR NG scenario, which relies on natural gas to power the biorefinery. Error bars depict the pessimistic and optimistic cost estimates according to the sensitivity analysis conducted.

The results of the break-even point analysis show that increasing slightly the price of the antioxidants to 11 €/kg (Alibaba Group, 2023; Servian-Rivas et al., 2022) and the price of bioethanol to 3.85 €/kg (METRO, 2023) would bring the BIOR CCS scenario close to the break-even point where the NPV equals zero. This price for bioethanol is aligned with current market prices, which typically range from 3.85 to 4.60 € per liter (Laboratorio SYS, 2023; METRO, 2023). Moreover, increasing the selling price of the bio-based products by 25.50% would make the BIOR CCS competitive compared to the BIOR NG scenario (NPV of BIOR CCS equal to that of the BIOR NG). Hence, a prior investigation showed that carbon-negative products attract consumers, potentially increasing sales by an average of 60% (Hong et al. 2023). Both willingness to pay a premium for carbon-negative products and for carbon credits reflect growing environmental awareness and changes in consumer preferences. This shift in consumer behavior could be pivotal in promoting carbon-negative business models and overcoming economic barriers. Moreover, the introduction of carbon-negative bio-products presents an opportunity for market differentiation and competitive advantage, which may position the industry at the forefront of sustainability-driven innovation.

In addition to the premium nature of the products, the regulatory environment will play a pivotal role in shaping market dynamics for carbon-negative products. Various policies and incentives

have already been implemented to create a conducive market environment for carbon-negative products. Hence, recently the EU approved the EU carbon removal certification framework which aims to develop a voluntary certification to incentivize scale-up carbon removal activities sustainably (European Commission, 2022). This regulatory framework will encourage the implementation of carbon removal business models by stimulating both public and private financing options as well as voluntary carbon markets and eco-labeling initiatives which will contribute to scaling up production effectively. Furthermore, the CDR efforts are being incentivized and rewarded through various means such as direct subsidies, and taxes, which can help offset the additional expenses. Hence, it was found that a subsidy or tax credit of 9.75 € per tonne of CO₂ sequestered would render the NPV of the BIOR CCS scenario positive while increasing it up to 132.35 € per tonne of CO₂ sequestered would make it economically attractive compared to the BIOR NG, reaching the break-even point. Notably, the tax credit value to make the BIOR CCS profitable is lower than the Q45 tax credit provided by the United States for carbon sequestration, highlighting the potential to promote and support biorefineries with CCS.

3.3.2 Environmental performance

Starting by assessing the carbon footprint using the Global Warming (GW) indicator from ReCiPe 2016 (Huijbregts et al., 2017) Fig.10 provides a detailed breakdown of the carbon footprint of both scenarios. In the BIOR CCS scenario, the carbon footprint reaches net negative emissions, totaling -84.37 kg CO₂eq for the production of 1 kg of bioethanol and 0.15 kg of antioxidants. Conversely, the business-as-usual scenario (BIOR NG) shows a positive carbon footprint of +28.22 kg of CO₂eq per FU. The negative outcome of BIOR CCS is due to the heating requirements of the biorefinery (280 MJ per FU) being met by burning residual biomass and OPTB in the cogeneration plant with CCS. During the combustion process, the biogenic CO₂ released is captured and stored deep underground. This energy will be provided with a carbon intensity of -0.30 CO₂eq/MJ. Furthermore, the almost pure biogenic CO₂ released during the fermentation is also directed to the CCS systems and captured. Note, that all these biogenic CO₂ are modeled as a negative flow in the LCA calculations which compensates for all the positive GHG of the biorefinery system. Additionally, results in Fig.10 account for end-use phase emissions, assuming that the bioethanol is combusted and contributes to positive emissions in the "bioethanol combustion" category. To put context, considering that the biorefinery at scale would produce 213,900 kg of bioethanol and 33,100 kgs of antioxidants per day, this equates to around 7.60 million tonnes of CO₂ eq that would be captured annually. This amount of CDR solely provided by the biorefinery plant would represent approximately 2.80% of the annual GHG emissions in Spain (Macrotrends LLC, 2022).

Analyzing the carbon footprint breakdown, the antioxidant subsystem (SS2 in Fig.8) is the main contributor to the carbon footprint representing 55.80% and 48.70% of the positive GHG in BIOR NG and BIOR CCS scenarios, respectively. This can be attributed to the utilization of ethyl acetate, its recycling loop after a double stripping distillation column, as well as the energy demands required for the purification of polyphenols. After the antioxidant subsystem, in the BIOR NG, subsystems SS3 and SS5 represent 16.54% and 19.43% of the total carbon footprint, respectively.

In contrast, in the BIOR CCS scenario, the positive GHG emissions from the CCS system contribute substantially to the carbon footprint (29.73% of the positive emissions). Additionally, in the BIOR CCS, we observe carbon-negative contributions from subsystems SS2, SS3, and SS5, contingent on their energy requirements being supplied by the carbon-negative heating from BECCS.

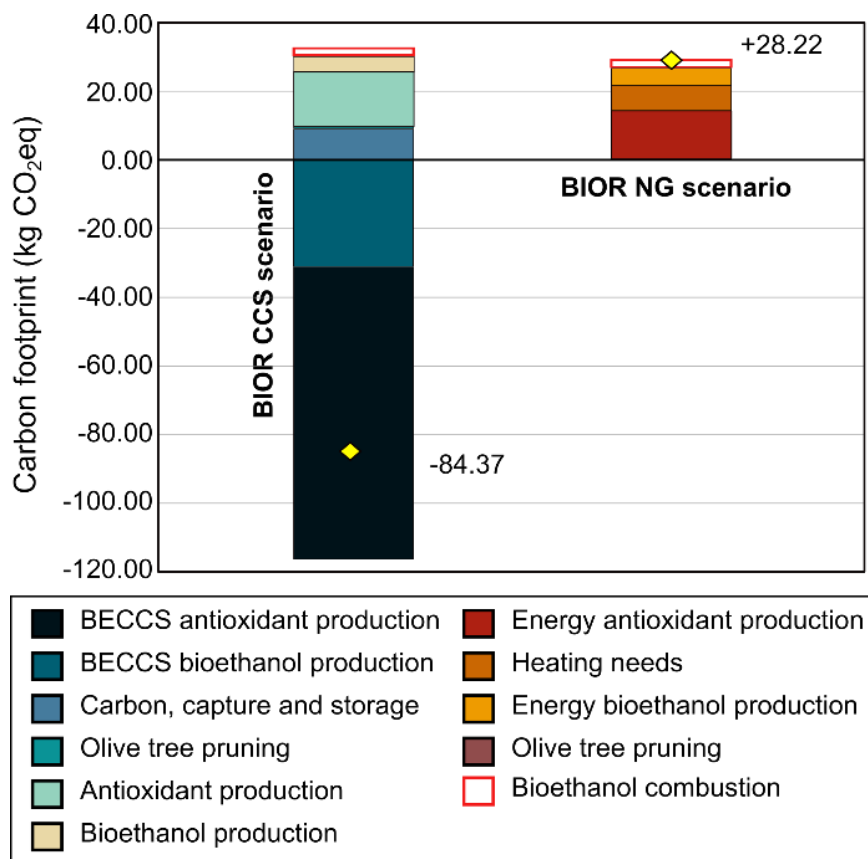


Figure 10: Breakdown of the carbon footprint for the BIOR NG and BIOR CCS scenarios for the production of 1 kg of bioethanol and 0.15 kg of antioxidants.

We next report the results of the 17 remaining midpoint impact categories of the ReCiPe 2016 methodology to compare the environmental performance of the BIOR NG and BIOR CCS scenarios. Fig.11 shows the relative environmental impact of the scenarios across the 17 categories while the absolute values in the specific units are provided in Table A.8 in the Appendix. Although the BIOR CCS scenario outperformed BIOR NG in the Global Warming category (as shown in Fig.10), a different picture emerges when analyzing the remaining categories. Notably, the BIOR CCS exhibits higher environmental footprints than BIOR NG across all the impact categories. This indicates that the advantages gained in terms of climate change mitigation might come at the expense of exacerbating other environmental issues (collateral damages), some of which display notable discrepancies between the scenarios. The increase in the impact is largely attributed to the

higher need for OPTB raw materials required to cover the heating requirements of the biorefinery and energy required for the CCS system. Note that despite the OPTB being mainly considered today as residue, we allocate environmental burden to this biomass waste generated at the agricultural phase of olive production (see appendix, section A4).

The environmental impact is of particular concern in the BIOR CCS scenario when compared to the BIOR NG in terrestrial ecotoxicity (TE), marine eutrophication (MER), land use (LU), and fossil resource scarcity (FRS). In the case of eutrophication (MER), BIOR CCS presents an impact particularly high, 75% higher than the BIOR NG scenario. This increase is mainly attributed to the nitrogen and phosphorus fertilizers associated with olive cultivation (OPTB) and the production of monoethanolamine. Moreover, land use (LU) is nearly 80% more extensive in the BIOR CCS scenario due to the land transformation and occupation attributed to olive tree cultivation, which is linked to the OPTB feedstock. Similarly, water consumption (WC) is 45% higher in the BIOR CCS scenario, again attributed to the increased irrigation demands. In our assumptions, it is considered that only 25% of the agricultural area is irrigated (1,500 m³/ha year). Additionally, the impact in the toxicity-related categories (TA, TE, HNCT, and FE) is also higher, likely due to the various chemicals involved in the process.

Analyzing the breakdown of impacts presented in Fig.11, the antioxidant subsystem (SS2) combined with BECCS are the main drivers in most impact categories, representing between 21.53% and 69.98% of the total impact depending on the specific category. The high-energy demand with the antioxidant subsystem, which accounts for 73.65% of the total energy requirements of the biorefinery, leads to the attribution of all impacts associated with the energy source to this particular subsystem. For some impact categories, such as stratospheric ozone depletion, terrestrial ecotoxicity, and human non-carcinogenic toxicity, the antioxidant separation is the main contributor.

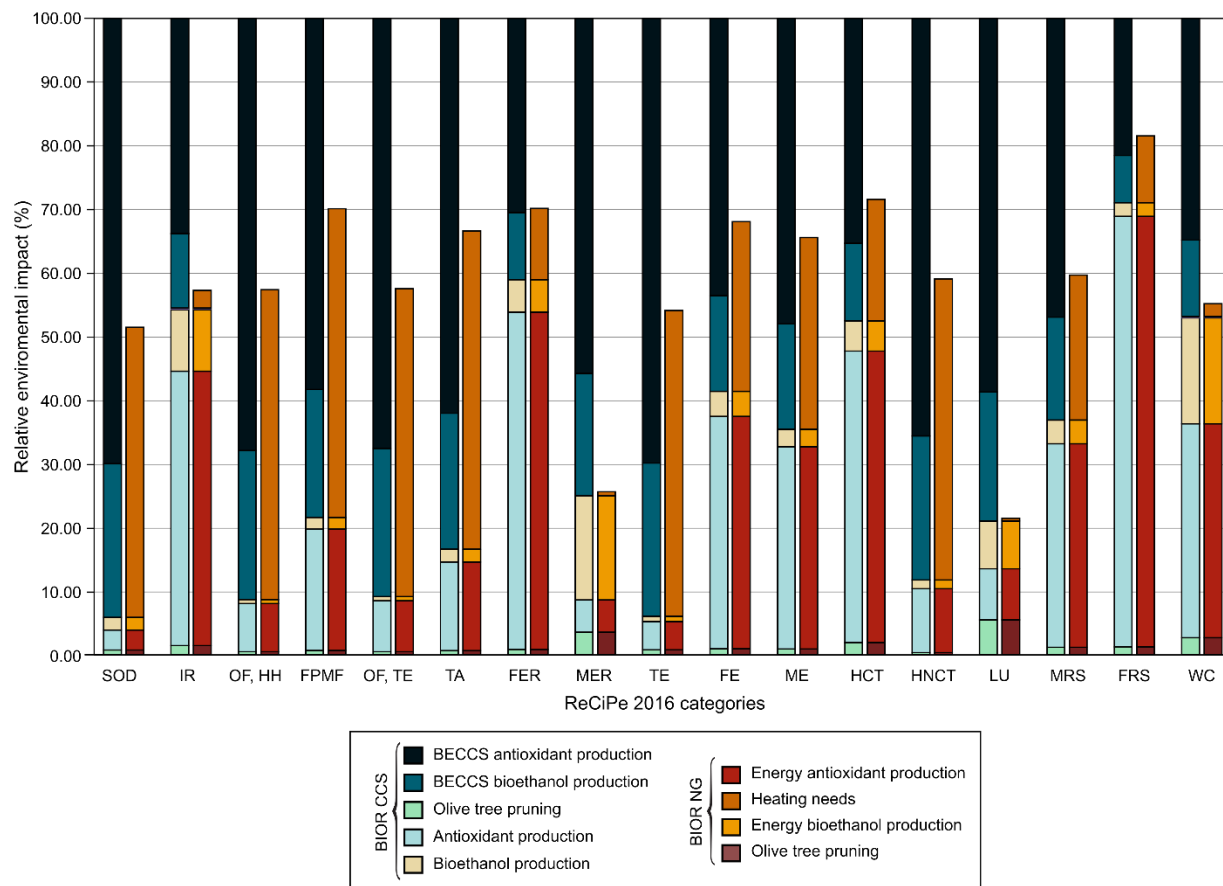


Figure 11: Comparative environmental implications of the two biorefinery scenarios. The column on the left BIOR CCS scenario integrates bioenergy with carbon capture and storage within the biorefinery. The column on the right corresponds to the BIOR NG scenario, which relies on natural gas to power the biorefinery. SOD: stratospheric ozone depletion, IR: Ionizing radiation, OF, HH: ozone formation, human health, FPMF: Fine particulate matter formation, OF, TE: ozone formation, terrestrial ecosystems, TA: terrestrial acidification, FER: freshwater eutrophication, MER: marine eutrophication, TE: terrestrial ecotoxicity, FE: freshwater ecotoxicity, ME: marine ecotoxicity, HCT: human carcinogenic toxicity, HNCT: human non-carcinogenic toxicity, LU: land use, MRS: mineral resource scarcity, FRS: fossil resource scarcity and WC: water consumption.

The presence of environmental trade-offs associated with the BIOR CCS underscores the importance of preventing or minimizing them. Most of the collateral damages are attributed to the increased consumption of olive pruning in the BIOR CCS scenario to satisfy the heating demands. However, these unintended consequences attributed to the biorefinery strategy due to we allocate burdens to the pruning residues should not overlook the value derived from residue valorization as otherwise these prunings would be burned or chopped and used as mulch in the olive orchard entailing both economic and environmental burdens. Nevertheless, to mitigate eutrophication, which is primarily driven by nutrient runoff (attributed to olive pruning from olive production), targeted measures such as buffer zones and precision agriculture techniques may help reduce nutrient loading in adjacent water bodies. Similarly, for water consumption and land use,

implementing improved and sustainable agricultural practices during the agricultural phase will aid in mitigating these footprints. Some strategies may include the implementation of drip irrigation systems to minimize water loss through evaporation and runoff or the application of organic mulch around olive trees to conserve soil moisture. Concerning land use, increasing density or transitioning to agroforestry systems may help maximize land use efficiency and biodiversity. All of these considerations play a pivotal role in determining the optimal site for our biorefinery. By evaluating potential sites against criteria related to environmental impact mitigation, including proximity to water bodies, existing land use patterns, and biodiversity hotspots, the biorefinery could be strategically positioned to minimize its environmental footprint while maximizing its socio-economic benefits.

3.4 Conclusion case study

In this work, we rely on process simulation and LCA methodologies to delve into the interplay of the technical, economic, and environmental implications surrounding the integration of BECCS into a biorefinery that converts OTPB into bioethanol and antioxidants.

On the economic front, the adoption of BECCS comes with substantial financial implications. It entails higher upfront investments and operational costs due to the intricate CCS infrastructure. In our analysis, we observed that the BIOR CCS scenario ultimately incurs a 30% higher cost compared to the business-as-usual scenario (BIOR NG). Nonetheless, it is important to note that the costs associated with BECCS projects are expected to decrease over time as technology advances and economies of scale come into play. To overcome these economic barriers and logistical challenges, the EU has introduced various funding mechanisms, legislative frameworks, and strategic initiatives such as the Innovation Fund, the Connecting Europe Facility, the Just Transition Fund, and the EU certification system for carbon removals which collectively represent an opportunity to facilitate the adoption of large-scale BECCS projects. Hence, the results demonstrated that integrating insights from consumer behavior, policy interventions, and regulatory frameworks is crucial. The higher production costs associated with the carbon-negative bioproducts delivered may find a receptive market among environmentally conscious consumers who are increasingly willing to pay premium prices to support carbon offset projects. Furthermore, strategic policy interventions, such as carbon taxes can play a pivotal role in offsetting the initial capital costs, rendering BECCS economically appealing in the long run and expediting CCS infrastructure development.

On the environmental dimension, integrating CCS into the biorefinery allows for reducing substantially the carbon footprint even reaching a negative emissions balance due to the energy-intensive processes being met with carbon-negative energy. This achievement could be a game-changer in the ongoing efforts to combat climate change and promote CDR initiatives in the biorefinery context. However, these environmental gains are not without their own set of challenges. Hence, this study sheds light on a complex trade-off. Notably, we have identified areas

of concern related to eutrophication, water consumption, and land use, most of them related to the higher utilization of OTPB. These environmental trade-offs are crucial in selecting the best location for the biorefinery aimed at mitigating environmental footprint and enhancing socio-economic advantages.

Additionally, scaling up a biorefinery coupled with CCS will involve technical and logistical complexities throughout the entire value chain. It will require significant infrastructure development, including the biomass processing and conversion processes itself, storage facilities for securing a reliable biomass supply, CO₂ capture system, and transportation network and storage sites for CO₂. Identifying and addressing technical, economic, and environmental challenges across the value chain before full-scale deployment is key. It requires optimal siting strategies, considering the proximity to biomass sources and availability of suitable geological formations for CO₂ storage, adherence to regulatory requirements, effective logistical planning including partnerships with biomass suppliers to ensure uninterrupted operations, and community engagement to ensure project viability and social acceptance.

In conclusion, this research underscores the importance of taking a holistic view in shaping decision-making and policy formulation for the integration of CCS into biorefinery systems. While this integration holds immense promise in terms of reducing carbon emissions, it also poses technical, economic, and environmental challenges. It is imperative for decision-makers, policymakers, and stakeholders to recognize the multi-dimensional nature of these challenges and to prioritize sustainable practices. By integrating insights from consumer behavior research, designing effective regulatory frameworks, and competitive positioning, scalability challenges might be overcome towards unlocking the CDR potential and fostering long-term business resilience by delivering carbon-negative bio-products.

4. General conclusions

Here, we highlight the importance of the findings regarding both economic and environmental factors of the case study. From the economic perspective, it is estimated that BECCS is around 30% more costly than its counterpart conventional (BAU) fossil fuel plant. We expect that the high costs associated with BECCS projects could decrease over time as technology advances and economies of scale come into play. To overcome these economic barriers and logistical challenges, the EU has introduced various funding mechanisms, legislative frameworks, and strategic initiatives such as the Innovation Fund, the Connecting Europe Facility, the Just Transition Fund, and the EU certification system for carbon removals which collectively represent an opportunity to facilitate the adoption of large-scale BECCS projects. Hence, the results demonstrated that integrating insights from consumer behavior, policy interventions, and regulatory frameworks is crucial. The higher production costs associated with the carbon-negative bioproducts delivered may find a receptive market among environmentally conscious consumers who are increasingly

willing to pay premium prices to support carbon offset projects. Furthermore, strategic policy interventions, such as carbon taxes can play a pivotal role in offsetting the initial capital costs, rendering BECCS economically appealing in the long run and expediting CCS infrastructure development. In a nutshell, the ideal economic scenario would be to turn BECCS biorefinery into the same profit margin as the conventional (BAU) fossil-based one, and the study sheds light on this direction.

On the environmental scope, of the study, results indicate that this initiative has carbon-negative emissions, with BECCS, capturing not only the CO₂ produced but additionally carbon dioxide from the atmosphere. This milestone does come with a set of adverse and unwanted effects as the betterment in one category brings a set of worsening in other categories such as eutrophication, acidification, land use, and water consumption. Most of them, are related to the increased biomass demand. These environmental trade-offs are crucial in selecting the best location for the biorefinery aimed at mitigating environmental footprint and enhancing socio-economic advantages. As technologies advance and through proper training, a better understanding of these principles will help local communities making them environmentally aware and through social engagement will contribute to emerge new economic opportunities and employment in the field by fostering novel precision agriculture practices for the natural ecosystem preservation and economic growth as more job opportunities will emerge. The massive land exploitation could give opportunities to several other agricultural areas to develop and flourish. For BECCS to operate in olive groves, the necessity of merging smaller clusters of land will be considered, by resolving a land segregation legal obstacle as Jaén is dominated by the ownership of small farmers owning small pieces of land, making the management of those areas very challenging. The massive farming loads such as fertilizers, nutrients, irrigation, and pesticides can be better managed in big areas owned by few owners. Big corporations can implement novel techniques to protect the environment and humper water eutrophication and soil degradation with expensive land infrastructure adjustments. Moreover, with precision management, many of the effluents can be recycled or traded to other adjacent activities. Additional economic benefits of the marketing of natural antioxidants and biofuels that biorefineries produce will bring to local communities. Opportunities for recycling wastes and promoting sustainability would be to exploit residues of biomass combustion, also known as biochar to enhance soil fertility and carbon capture as biochar reacts with CO₂ forming stable mineralized compounds. These sorts of byproducts can also be traded to other industries for exchange of heat waste.

5. Future work

Future work involves delving into a more detailed analysis of factors that contribute to burden shift incidence and taking preventive measures to minimize its impact. The employment of lean

solvents, like deep eutectic solvents (DES) (Zhang et al., 2022) might help reduce the toxicity and fossil-based dependency of the biorefinery processes, as they can be produced by biobased materials (Usmani et al., 2023). Lean solvents require low heating. They perform faster during fermentation and entail a significantly higher yield production than conventional catalysts (Shishov et al., 2022). A disadvantage of lean solvents remains the high cost. Additional, measures would be to exploit waste heat from other industries, therefore, reducing even further the dependency on new biomass cultivation for BECCS. For Spain, specifically, waste heat valorization could be transferred from the north part of Spain (Basauri industrial area) to Andalusia, if the cost could be afforded (Cordis EU, 2023). Finally, a more eco-friendly carbon capture method such as membrane gas separation or cryogenic carbon capture (CCC) technologies (Gkotsis et al., 2023), instead of amines, might help to reduce the impact of producing them, as amines entail high toxicity during production and significant cost (Knaak et al., 1997). Alternatively, incorporating a thermal stripping process, that reverses the chemical reaction and regenerates any sort of solvent used for carbon capture, in order to recycle it back to the stream, would be an interesting idea for saving cost and impact (Lin and Rochelle, 2016).

Employing any of the above methods to reduce environmental impact in future CDR projects, coupled with biomass biorefineries, will additionally entail their respective techno-economic analysis to align environmental goals with the economy of scale, stakeholder involvement, public engagement, and shaping of regulatory frameworks.

As technology advances, more and more biorefineries and other fossil-based industries will shift towards a green low-carbon economy. It is our unique duty, as humanity to save future generations from experiencing the negative side effects of climate change and reducing our carbon footprint is one of our challenges.

6 References

- Ahilan, C., Edwin Raja Dhas, J., Somasundaram, K., Sivakumaran, N., 2015. Performance assessment of heat exchanger using intelligent decision making tools. *Appl Soft Comput* 26, 474–482. <https://doi.org/10.1016/J.ASOC.2014.10.018>
- Aitor P. Acero, Cristina Rodríguez, Andreas Ciroth, 2015. LCIA methods. Impact assessment methods in Life Cycle Assessment and their impact categories. Berlin, Germany.
- Alberta Carpenter, 2012. U.S. Life Cycle Inventory Database. [WWW Document]. National Renewable Energy Laboratory (NREL). URL <https://www.nrel.gov/analysis/lci.html> (accessed 4.24.24).

- Alberts, B., Johnson, A., Lewis, J., Raff, M., Roberts, K., Walter, P., 2002. Chloroplasts and Photosynthesis. New York: Garland Science.
- Alibaba Group, 2023. Beton Supply Oleuropein, Hydroxytyrosol, Olive Leaf Extract - Buy Olive Leaf Extract Powder,Olive Leaf Extract, Oleuropein,Olive Leaf Extract Oleuropein Hydroxytyrosol Product on Alibaba.com [WWW Document]. URL <https://tinyurl.com/mrxy4ea7> (accessed 10.23.23).
- Almada Pérez Deborah, Ángel Galán-Martín, Mar Contreras, M. del, Eulogio Castro, 2023. Integrated techno-economic and environmental assessment of biorefineries: review and future research directions. *Sustain Energy Fuels* 7, 4031–4050. <https://doi.org/10.1039/D3SE00405H>
- Almena, A., Thornley, P., Chong, K., Röder, M., 2022. Carbon dioxide removal potential from decentralised bioenergy with carbon capture and storage (BECCS) and the relevance of operational choices. *Biomass Bioenergy* 159, 106406. <https://doi.org/10.1016/J.BIOMBIOE.2022.106406>
- Analyst, C., 2023. Global Chemical and Petrochemicals, Specialty Chemicals, Elastomer and Rubber, Fertilizer and Feedstock - Latest Chemical Prices, News and Market Analysis | ChemAnalyst [WWW Document]. URL <https://www.chemanalyst.com/> (accessed 10.23.23).
- AspenTech Inc., 2024. Aspen Plus | Leading Process Simulation Software | AspenTech [WWW Document]. AspenTech Inc. URL <https://www.aspentech.com/en/products/engineering/aspen-plus> (accessed 5.29.24).
- Ataeian, M., Liu, Y., Canon-Rubio, K.A., Nightingale, M., Strous, M., Vadlamani, A., 2019. Direct capture and conversion of CO₂ from air by growing a cyanobacterial consortium at pH up to 11.2. *Biotechnol Bioeng* 116, 1604. <https://doi.org/10.1002/BIT.26974>
- Auffhammer, M., Morzuch, B.J., Stranlund, J.K., 2005. Production of chlorofluorocarbons in anticipation of the Montreal Protocol. *Environ Resour Econ (Dordr)* 30, 377–391. <https://doi.org/10.1007/S10640-004-4222-0/METRICS>
- Aurel Inc, 2019. CADSIM Plus – Aurel [WWW Document]. Aurel Systems Inc. URL <https://www.aurelsystems.com/cadsim-plus/> (accessed 5.29.24).
- Austrheim, T., Gjertsen, L.H., Hoffmann, A.C., 2007. Is the Souders–Brown equation sufficient for scrubber design? An experimental investigation at elevated pressure with hydrocarbon fluids. *Chem Eng Sci* 62, 5715–5727. <https://doi.org/10.1016/J.CES.2007.06.014>
- Babin, A., Vaneckhaute, C., Iliuta, M.C., 2021. Potential and challenges of bioenergy with carbon capture and storage as a carbon-negative energy source: A review. *Biomass Bioenergy* 146, 105968. <https://doi.org/10.1016/J.BIOMBIOE.2021.105968>

- Bare, J., 2011. TRACI 2.0: The tool for the reduction and assessment of chemical and other environmental impacts 2.0. *Clean Technol Environ Policy* 13, 687–696. <https://doi.org/10.1007/S10098-010-0338-9>
- Bellapart R&D, 2023. World Energy Efficiency Day — Bellapart [WWW Document]. Paula Arbós. URL <https://www.bellapart.com/world-energy-efficiency-day/> (accessed 4.10.24).
- Bello, S., Galán-Martín, Á., Feijoo, G., Moreira, M.T., Guillén-Gosálbez, G., 2020a. BECCS based on bioethanol from wood residues: Potential towards a carbon-negative transport and side-effects. *Appl Energy* 279, 115884. <https://doi.org/10.1016/J.APENERGY.2020.115884>
- Berger, N.J., Lindorfer, J., Fazeni, K., Pfeifer, C., 2022. The techno-economic feasibility and carbon footprint of recycling and electrolysing CO₂ emissions into ethanol and syngas in an isobutene biorefinery. *Sustain Prod Consum* 32, 619–637. <https://doi.org/10.1016/J.SPC.2022.05.014>
- Blackett Matthew, 2023. Climate change could trigger more earthquakes and volcanoes | World Economic Forum [WWW Document]. World Economic Forum. URL <https://www.weforum.org/agenda/2023/08/climate-change-trigger-earthquakes-volcanoes/> (accessed 4.18.24).
- Boulay, A.M., Bare, J., Benini, L., Berger, M., Lathuillière, M.J., Manzardo, A., Margni, M., Motoshita, M., Núñez, M., Pastor, A.V., Ridoutt, B., Oki, T., Worbe, S., Pfister, S., 2018. The WULCA consensus characterization model for water scarcity footprints: assessing impacts of water consumption based on available water remaining (AWARE). *IJOLCA* 23, 368–378. <https://doi.org/10.1007/S11367-017-1333-8/FIGURES/2>
- Burgueño Salas, E., 2023. Spain: greenhouse gas emissions share by sector | Statista [WWW Document]. MITECO. URL <https://www.statista.com/statistics/1322798/distribution-of-ghg-emissions-by-sector-spain/> (accessed 4.10.24).
- Cabral, R.P., Bui, M., Mac Dowell, N., 2019. A synergistic approach for the simultaneous decarbonisation of power and industry via bioenergy with carbon capture and storage (BECCS). *IJGGC* 87, 221–237. <https://doi.org/10.1016/J.IJGGC.2019.05.020>
- Cai, H., Wang, X., Kim, J.H., Gowda, A., Wang, M., Mlade, J., Farbman, S., Leung, L., 2022. Whole-building life-cycle analysis with a new GREET® tool: Embodied greenhouse gas emissions and payback period of a LEED-Certified library. *Build Environ* 209, 108664. <https://doi.org/10.1016/J.BUILDENV.2021.108664>
- Calvin, K., Dasgupta, D., Krinner, G., Mukherji, A., Thorne, P.W., Trisos, C., Romero, J., Aldunce, P., Barrett, K., Blanco, G., Cheung, W.W.L., Connors, S., Denton, F., Diongue-Niang, A., Dodman, D., Garschagen, M., Geden, O., Hayward, B., Jones, C., Jotzo, F., Krug, T., Lasco, R., Lee, Y.-Y., Masson-Delmotte, V., Meinshausen, M., Mintenbeck, K., Mokssit, A., Otto, F.E.L., Pathak, M., Pirani, A., Poloczanska, E., Pörtner, H.-O., Revi, A.,

- Roberts, D.C., Roy, J., Ruane, A.C., Skea, J., Shukla, P.R., Slade, R., Slangen, A., Sokona, Y., Sörensson, A.A., Tignor, M., van Vuuren, D., Wei, Y.-M., Winkler, H., Zhai, P., Zommers, Z., Hourcade, J.-C., Johnson, F.X., Pachauri, S., Simpson, N.P., Singh, C., Thomas, A., Totin, E., Alegría, A., Armour, K., Bednar-Friedl, B., Blok, K., Cissé, G., Dentener, F., Eriksen, S., Fischer, E., Garner, G., Guivarch, C., Haasnoot, M., Hansen, G., Hauser, M., Hawkins, E., Hermans, T., Kopp, R., Leprince-Ringuet, N., Lewis, J., Ley, D., Ludden, C., Niamir, L., Nicholls, Z., Some, S., Szopa, S., Trewin, B., van der Wijst, K.-I., Winter, G., Witting, M., Birt, A., Ha, M., 2023. IPCC, 2023: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, H. Lee and J. Romero (eds.)]. IPCC, Geneva, Switzerland. <https://doi.org/10.59327/IPCC/AR6-9789291691647>
- Casavant, T.E., Côté, R.P., 2004. Using chemical process simulation to design industrial ecosystems. *J Clean Prod* 12, 901–908. <https://doi.org/10.1016/J.JCLEPRO.2004.02.034>
- Castanheira, É.G., Freire, F., 2017. Environmental life cycle assessment of biodiesel produced with palm oil from Colombia. *IJOLCA* 22, 587–600. <https://doi.org/10.1007/S11367-016-1097-6>
- Catalán, E., Sánchez, A., 2020. Solid-State Fermentation (SSF) versus Submerged Fermentation (SmF) for the Recovery of Cellulases from Coffee Husks: A Life Cycle Assessment (LCA) Based Comparison. *Energies* 2020 13, 2685. <https://doi.org/10.3390/EN13112685>
- Chemstations, 2024. CHEMCAD | Chemical Engineering Simulation Software by Chemstations [WWW Document]. Chemstations. URL <https://www.chemstations.com/CHEMCAD/#search> (accessed 5.29.24).
- Conde, E., Cara, C., Moure, A., Ruiz, E., Castro, E., Domínguez, H., 2009. Antioxidant activity of the phenolic compounds released by hydrothermal treatments of olive tree pruning. *Food Chem* 114, 806–812. <https://doi.org/10.1016/J.FOODCHEM.2008.10.017>
- Cordis EU, 2023. Exploring waste heat valorisation in Spain [WWW Document]. Coralis project EU. URL <https://cordis.europa.eu/article/id/445753-exploring-waste-heat-valorisation-in-spain> (accessed 6.11.24).
- Corrado, S., Castellani, V., Zampori, L., Sala, S., 2018. Systematic analysis of secondary life cycle inventories when modelling agricultural production: A case study for arable crops. *J Clean Prod* 172, 3990. <https://doi.org/10.1016/J.JCLEPRO.2017.03.179>
- Curran, M.A., Young, S., 1996. Report from the EPA conference on streamlining LCA. *IJOLCA* 1, 57–60. <https://doi.org/10.1007/BF02978640>

- Dees, J.P., Sagues, W.J., Woods, E., Goldstein, H.M., Simon, A.J., Sanchez, D.L., 2023. Leveraging the bioeconomy for carbon drawdown. *GC 25*, 2930–2957. <https://doi.org/10.1039/D2GC02483G>
- Del Grosso, S.J., Mosier, A.R., Parton, W.J., Ojima, D.S., 2005. DAYCENT model analysis of past and contemporary soil N₂O and net greenhouse gas flux for major crops in the USA. *Soil Tillage Res 83*, 9–24. <https://doi.org/10.1016/J.STILL.2005.02.007>
- Dimian, A.C., Bildea, C.S., Kiss, A.A., 2014. *Integrated Design and Simulation of Chemical Processes*. Elsevier 2nd, 887.
- Directorate-General for Climate Action, 2023. How climate change is disrupting rainfall patterns and putting our health at risk - European Commission [WWW Document]. European Commission. URL <https://tinyurl.com/24344xss> (accessed 4.18.24).
- Directorate-General for Energy, European Commission, Internal energy market, 2018. Study on the quality of electricity market data of transmission system operators, electricity supply disruptions, and their impact on the European electricity markets. Copenhagen.
- Dreyer, L.C., Niemann, A.L., Hauschild, M.Z., 2003. Comparison of three different LCIA methods: EDIP97, CML2001 and eco-indicator 99: Does it matter which one you choose? *IJOLCA 8*, 191–200. <https://doi.org/10.1007/BF02978471/METRICS>
- Dubey, A., Arora, A., 2022. Advancements in carbon capture technologies: A review. *J Clean Prod 373*, 133932. <https://doi.org/10.1016/J.JCLEPRO.2022.133932>
- EC-JRC, 2012. Basque Ecodesign Center - ILCD 2011 + (versión 1.0.9, mayo 2016) [WWW Document]. Joint Research Centre of the European Commission. URL <https://tinyurl.com/3h2nfdca> (accessed 4.23.24).
- Endesa S.A., 2023. Electricity Tariffs: Find your electricity offer | Endesa [WWW Document]. URL <https://www.endesa.com/en/catalog/light> (accessed 10.23.23).
- Environmental Protection Agency, 2024. Understanding Global Warming Potentials | US EPA [WWW Document]. US EPA. URL <https://www.epa.gov/ghgemissions/understanding-global-warming-potentials> (accessed 6.19.24).
- European Commission, 2024. Consequences of climate change - European Commission [WWW Document]. Directorate-General for Climate Action. URL https://climate.ec.europa.eu/climate-change/consequences-climate-change_en (accessed 6.18.24).
- European Commission, 2021. Commission recommendation (EU) 2021/2279 On the use of the Environmental Footprint methods to measure and communicate the life cycle environmental performance of products and organizations [WWW Document]. Official Journal of the

- European Union. URL <https://eplca.jrc.ec.europa.eu/EnvironmentalFootprint.html> (accessed 4.24.24).
- European Commission, 2020. In focus: Energy efficiency in buildings - European Commission [WWW Document]. European Commission. URL https://commission.europa.eu/news/focus-energy-efficiency-buildings-2020-02-17_en (accessed 5.14.24).
- European Union, 2021. Average Accumulated Exceedance (AAE) of critical loads of acidity and nutrient nitrogen by acid and nitrogen deposition for the UK, 2015-2017 - Data Europa EU [WWW Document]. Environmental Information Data Centre. URL <https://rb.gy/9lyach> (accessed 4.24.24).
- Eurostat, 2023. Natural gas price statistics - Statistics Explained [WWW Document]. URL <https://tinyurl.com/348famb3> (accessed 10.23.23).
- Fanourakis, S., Romero-García, J.M., Castro, E., Jiménez-Esteller, L., Galán-Martín, Á., 2024. Economic and environmental implications of carbon capture in an olive pruning tree biomass biorefinery. *J Clean Prod* 456, 142361. <https://doi.org/10.1016/J.JCLEPRO.2024.142361>
- Feng, H., Zhao, J., Hollberg, A., Habert, G., 2023. Where to focus? Developing a LCA impact category selection tool for manufacturers of building materials. *J Clean Prod* 405, 136936. <https://doi.org/10.1016/J.JCLEPRO.2023.136936>
- Fernández-Lobato, L., López-Sánchez, Y., Blejman, G., Jurado, F., Moyano-Fuentes, J., Vera, D., 2021. Life cycle assessment of the Spanish virgin olive oil production: A case study for Andalusian region. *J Clean Prod* 290, 125677. <https://doi.org/10.1016/J.JCLEPRO.2020.125677>
- Fritzson, P., Pop, A., Asghar, A., Bachmann, B., Braun, W., Braun, R., Buffoni, L., Casella, F., Castro, R., Danós, A., Franke, R., Gebremedhin, M., Lie, B., Mengist, A., Moudgalya, K., Ochel, L., Palanisamy, A., Schamai, W., Söhlund, M., Thiele, B., Waurich, V., Östlund, P., 2019. The OpenModelica Integrated Modeling, Simulation, and Optimization Environment. Proceedings of The American Modelica Conference 2018, October 9-10, Somberg Conference Center, Cambridge MA, USA 154, 206–219. <https://doi.org/10.3384/ECP18154206>
- Galán-Martín, Á., Contreras, M. del M., Romero, I., Ruiz, E., Bueno-Rodríguez, S., Eliche-Quesada, D., Castro-Galiano, E., 2022a. The potential role of olive groves to deliver carbon dioxide removal in a carbon-neutral Europe: Opportunities and challenges. *Renewable and Sustainable Energy Reviews* 165, 112609. <https://doi.org/10.1016/J.RSER.2022.112609>
- Galán-Martín, Á., Contreras, M. del M., Romero, I., Ruiz, E., Bueno-Rodríguez, S., Eliche-Quesada, D., Castro-Galiano, E., 2022b. The potential role of olive groves to deliver carbon

- dioxide removal in a carbon-neutral Europe: Opportunities and challenges. *Renewable and Sustainable Energy Reviews* 165, 112609. <https://doi.org/10.1016/J.RSER.2022.112609>
- Galán-Martín, Á., Tulus, V., Díaz, I., Pozo, C., Pérez-Ramírez, J., Guillén-Gosálbez, G., 2021a. Sustainability footprints of a renewable carbon transition for the petrochemical sector within planetary boundaries. *One Earth* 4, 565–583. <https://doi.org/10.1016/J.ONEEAR.2021.04.001>
- Galán-Martín, Á., Vázquez, D., Cobo, S., Mac Dowell, N., Caballero, J.A., Guillén-Gosálbez, G., 2021b. Delaying carbon dioxide removal in the European Union puts climate targets at risk. *NC* 2021 12, 1–12. <https://doi.org/10.1038/s41467-021-26680-3>
- Gambhir, A., Tavoni, M., 2019. Direct Air Carbon Capture and Sequestration: How It Works and How It Could Contribute to Climate-Change Mitigation. *One Earth* 1, 405–409. <https://doi.org/10.1016/J.ONEEAR.2019.11.006>
- Ganat Tarek Al Arbi Omar, 2020. CAPEX and OPEX Expenditures. In: *Technical Guidance for Petroleum Exploration and Production Plans*. Springer Briefs in Applied Sciences and Technology Springer, Cham, 53–56. https://doi.org/10.1007/978-3-030-45250-6_8
- Gattuso, J.P., Williamson, P., Duarte, C.M., Magnan, A.K., 2021. The Potential for Ocean-Based Climate Action: Negative Emissions Technologies and Beyond. *FIC* 2, 575716. <https://doi.org/10.3389/FCLIM.2020.575716/BIBTEX>
- Giurco, D., Schmidt, P., McClellan, B., 2008. Australian Life Cycle Initiative (AusLCI) & CSRP database: Australian data. Open publications of UTS scholars.
- Gkotsis, P., Peleka, E., Zouboulis, A., 2023. Membrane-Based Technologies for Post-Combustion CO₂ Capture from Flue Gases: Recent Progress in Commonly Employed Membrane Materials. *Membranes* 13, 898. <https://doi.org/10.3390/MEMBRANES13120898>
- Global CCS Institute Ltd, 2019. Global Status of CCS Report: 2019 - Global CCS Institute [WWW Document]. URL <https://tinyurl.com/y8a8wb94> (accessed 10.10.23).
- Goedkoop, M., Hofstetter, P., Müller-Wenk, R., Spriemsma, R., 1998. The Eco-Indicator 98 explained. *IJOLCA* 3, 352–360. <https://doi.org/10.1007/BF02979347/METRICS>
- Government of Spain, 2020. Strategic energy and climate framework.
- Grzesik, K., Guca, K., 2011. Screening study of life cycle assessment (LCA) of the electric kettle with SimaPro Software. *Geomatics and Environmental Engineering* 5, 57–68.
- Günther, P., Ekardt, F., 2022. Human Rights and Large-Scale Carbon Dioxide Removal: Potential Limits to BECCS and DACCS Deployment. *Land (Basel)* 11, 2153. <https://doi.org/10.3390/LAND11122153>

- Guo, S., Li, Y., Wang, Y., Wang, L., Sun, Y., Liu, L., 2022. Recent advances in biochar-based adsorbents for CO₂ capture. *CCS&T* 4, 100059. <https://doi.org/10.1016/J.CCST.2022.100059>
- Hilmi, N., Chami, R., Sutherland, M.D., Hall-Spencer, J.M., Lebleu, L., Benitez, M.B., Levin, L.A., 2021. The Role of Blue Carbon in Climate Change Mitigation and Carbon Stock Conservation. *FIC* 3, 710546. <https://doi.org/10.3389/FCLIM.2021.710546/BIBTEX>
- Huijbregts, M.A.J., Steinmann, Z.J.N., Elshout, P.M.F., Stam, G., Verones, F., Vieira, M., Zijp, M., Hollander, A., van Zelm, R., 2017. ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level. *IJOLCA* 22, 138–147. <https://doi.org/10.1007/S11367-016-1246-Y/TABLES/2>
- IndexBox, 2023. EU Potassium Hydroxide Market Report: Suppliers, Buyers, [WWW Document]. URL <https://tinyurl.com/5n93m9d3> (accessed 10.23.23).
- IndexBox Inc., 2024. Ethyl Acetate Price in Spain - 2023 - Charts and Tables - IndexBox.
- InterMesh., 2023. IndiaMART - Indian Manufacturers Suppliers Exporters Directory, India Exporter Manufacturer [WWW Document]. Ltd, InterMesh. . URL <https://www.indiamart.com/> (accessed 10.23.23).
- Ioannou, A., Angus, A., Brennan, F., 2018. Parametric CAPEX, OPEX, and LCOE expressions for offshore wind farms based on global deployment parameters. *Energy Sources, Part B: Economics, Planning and Policy* 13, 281–290. <https://doi.org/10.1080/15567249.2018.1461150>
- IPCC, 2022. Emissions Trends and Drivers. In IPCC, 2022: Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. *Climate Change 2022 - Mitigation of Climate Change* 215–294. <https://doi.org/10.1017/9781009157926.004>
- ISO, 2006a. ISO - ISO 14044:2006 - Environmental management — Life cycle assessment — Requirements and guidelines [WWW Document]. URL <https://www.iso.org/standard/38498.html> (accessed 10.23.23).
- ISO, 2006b. ISO - ISO 14040:2006 - Environmental management — Life cycle assessment — Principles and framework [WWW Document]. URL <https://www.iso.org/standard/37456.html> (accessed 10.23.23).
- Iswara, A.P., Farahdiba, A.U., Nadhifatin, E.N., Pirade, F., Andhikaputra, G., Muflihah, I., Boedisantoso, R., 2020. IOP Conference Series: Earth and Environmental Science A Comparative Study of Life Cycle Impact Assessment using Different Software Programs. *IOP Conf Ser Earth Environ Sci.* <https://doi.org/10.1088/1755-1315/506/1/012002>

- Itsubo, N., Inaba, A., 2003. A new LCIA method: LIME has been completed. *IJOLCA* 8, 305. <https://doi.org/10.1007/BF02978923>
- James M. Omernik, Glenn E. Griffith, Jeffrey T. Irish, Colleen B. Johnson, 2018. Alkalinity and Water | U.S. Geological Survey [WWW Document]. Water Science School. URL <https://www.usgs.gov/special-topics/water-science-school/science/alkalinity-and-water> (accessed 5.20.24).
- Jang, H.-J.; Wang, S.-J.; Tae, S.-H.; Zheng, P.-F, Jang, H.-J., Wang, S.-J., Tae, S.-H., Zheng, Peng-Fei, 2024. Establishment of an Environmental Impact Factor Database for Building Materials to Support Building Life Cycle Assessments in China. *Buildings* 2024, Vol. 14, Page 228 14, 228. <https://doi.org/10.3390/BUILDINGS14010228>
- Jasper Van Baten, R. Taylor, H. Kooijman, 2010. Using Chemsep, COCO and other modeling tools for versatility in custom process modeling [WWW Document]. Conference: 2010 AIChE Annual Meeting. URL <https://tinyurl.com/33veae56> (accessed 5.29.24).
- JEMAI, AIST, 2024. IDEA – Inventory Database for Environmental Analysis [WWW Document]. TCO2 Co. Ltd. URL <https://idea-lca.com/en/> (accessed 4.28.24).
- Jolliet, O., Margni, M., Charles, R., Humbert, S., Payet, J., Rebitzer, G., Rosenbaum, R., 2003. IMPACT 2002+: A New Life Cycle Impact Assessment Methodology. *IJOLCA* 8, 324–330. <https://doi.org/10.1007/BF02978505>
- Khosrovian, K., Pfahl, D., Garousi, V., 2008. GENSIM 2.0: A customizable process simulation model for software process evaluation. *LNICS 5007 LNCS*, 294–306. https://doi.org/10.1007/978-3-540-79588-9_26
- Kieso, D.E., Weygandt, J.J., Warfield, T.D., 2022. *Intermediate Accounting (18th ed.)*, 18th ed. Wiley.
- Kilpatrick Kerry, 2014. 5 Greatest Waste of Energy in Older Buildings [WWW Document]. The energy alliance group of North America. URL <https://energyalliancegroup.org/5-greatest-waste-of-energy-older-buildings/> (accessed 5.14.24).
- Kisala, T.P., Trevino-Lozano, R.A., Boston, J.F., Britt, H.I., Evans, L.B., 1987. Sequential modular and simultaneous modular strategies for process flowsheet optimization. *Comput Chem Eng* 11, 567–579. [https://doi.org/10.1016/0098-1354\(87\)87003-5](https://doi.org/10.1016/0098-1354(87)87003-5)
- Knaak, J.B., Leung, H.W., Stott, W.T., Busch, J., Bilsky, J., 1997. Toxicology of mono-, di-, and triethanolamine. *Rev Environ Contam Toxicol* 149, 1–86. https://doi.org/10.1007/978-1-4612-2272-9_1
- Koch, P., 2023. Where limits to growth are tangible: the olive sector in Jaén and its bioeconomic future. *Sustain Sci* 18, 661–674. <https://doi.org/10.1007/S11625-022-01236-6/TABLES/2>

- Korotkova, T.G., Kasyanov, G.I., 2022. Analysis of the rectifying separation of H₂O–D₂O mixture into light and heavy water by means of mathematical modeling. *FCT* 17, 189–200. <https://doi.org/10.32362/2410-6593-2022-17-3-189-200>
- Laboratorio SYS, C.N. y A., 2023. Bioethanol 99.5% Vegetable Origin 5 Liters Myhome - SYS Laboratory [WWW Document]. URL <https://tinyurl.com/2p9sutcm> (accessed 10.16.23).
- Lamb, W.F., Gasser, T., Roman-Cuesta, R.M., Grassi, G., Gidden, M.J., Powis, C.M., Geden, O., Nemet, G., Pratama, Y., Riahi, K., Smith, S.M., Steinhauser, J., Vaughan, N.E., Smith, H.B., Minx, J.C., 2024. The carbon dioxide removal gap. *Nature Climate Change* 2024 14:6 14, 644–651. <https://doi.org/10.1038/s41558-024-01984-6>
- Lampitt, R.S., Achterberg, E.P., Anderson, T.R., Hughes, J.A., Iglesias-Rodriguez, M.D., Kelly-Gerreyn, B.A., Lucas, M., Popova, E.E., Sanders, R., Shepherd, J.G., Smythe-Wright, D., Yool, A., 2008. Ocean fertilization: a potential means of geoengineering? *PTOTRS: M,P,ES* 366, 3919–3945. <https://doi.org/10.1098/RSTA.2008.0139>
- Laude, A., Ricci, O., Bureau, G., Royer-Adnot, J., Fabbri, A., 2011. CO₂ capture and storage from a bioethanol plant: Carbon and energy footprint and economic assessment. *International Journal of Greenhouse Gas Control* 5, 1220–1231. <https://doi.org/10.1016/J.IJGGC.2011.06.004>
- Lehtveer, M., Emanuelsson, A., 2021. BECCS and DACCS as Negative Emission Providers in an Intermittent Electricity System: Why Levelized Cost of Carbon May Be a Misleading Measure for Policy Decisions. *FIC* 3, 647276. <https://doi.org/10.3389/fclim.2021.647276>
- Lekan Olanrewaju, 2023. Batch Processing vs. Continuous Processing [WWW Document]. MaintainX. URL <https://www.getmaintainx.com/learning-center/batch-processing-vs-continuous-processing> (accessed 5.26.24).
- Lin, Y.J., Rochelle, G.T., 2016. Approaching a reversible stripping process for CO₂ capture. *CEJ* 283, 1033–1043. <https://doi.org/10.1016/J.CEJ.2015.08.086>
- Ling, H., Liu, S., Wang, T., Gao, H., Liang, Z., 2019. Characterization and Correlations of CO₂ Absorption Performance into Aqueous Amine Blended Solution of Monoethanolamine (MEA) and N, N-Dimethylethanolamine (DMEA) in a Packed Column. *EAF* 33, 7614–7625. https://doi.org/10.1021/ACS.ENERGYFUELS.9B01764/SUPPL_FILE/EF9B01764_SI_001.PDF
- Ling, J.L.J., Yang, W., Park, H.S., Lee, H.E., Lee, S.H., 2023. A comparative review on advanced biomass oxygen fuel combustion technologies for carbon capture and storage. *Energy* 284, 128566. <https://doi.org/10.1016/J.ENERGY.2023.128566>

- Loganathan, G., Allais, F., Cespi, D., 2023. Bio-Based Chemicals from Dedicated or Waste Biomasses: Life Cycle Assessment for Evaluating the Impacts on Land. *SC 4*, 184–196. <https://doi.org/10.3390/SUSCHEM4020014>
- Loumou, A., Giourga, C., 2003. Olive groves: “The life and identity of the Mediterranean.” *AAHV 20*, 87–95. <https://doi.org/10.1023/A:1022444005336>
- Macrotrends LLC, W.B.G., 2022. Spain Greenhouse Gas (GHG) Emissions 1990-2023 | MacroTrends [WWW Document]. World Bank editorial style guide (English). Washington, D.C. : World Bank Group. URL <https://tinyurl.com/4n9y7n4d> (accessed 9.13.23).
- Magazoni, F.C., Cabezas-Gómez, L., Alvariño, P.F., Saiz-Jabardo, J.M., 2019. Thermal performance of one-pass shell-and-tube heat exchangers in counter-flow. *BJCE 36*, 869–883. <https://doi.org/10.1590/0104-6632.20190362S20180424>
- Maggiotto, G., Colangelo, G., Milanese, M., de Risi, A., 2023. Thermochemical Technologies for the Optimization of Olive Wood Biomass Energy Exploitation: A Review. *Energies 2023*, Vol. 16, Page 6772 16, 6772. <https://doi.org/10.3390/EN16196772>
- Martínez-Patiño, J.C., Romero-García, J.M., Ruiz, E., Oliva, J.M., Álvarez, C., Romero, I., Negro, M.J., Castro, E., 2015. High Solids Loading Pretreatment of Olive Tree Pruning with Dilute Phosphoric Acid for Bioethanol Production by *Escherichia coli*. *Energy and Fuels 29*, 1735–1742. <https://doi.org/10.1021/EF502541R>
- Mathilde Fajardy, Carl Greenfield, 2024. Bioenergy with Carbon Capture and Storage - Energy System - IEA [WWW Document]. International Energy Agency (IEA). URL <https://rb.gy/697o1v> (accessed 6.13.24).
- Matušík, J., Hnátková, T., Kočí, V., 2020. Life cycle assessment of biochar-to-soil systems: A review. *J Clean Prod 259*, 120998. <https://doi.org/10.1016/J.JCLEPRO.2020.120998>
- Mehmeti, A., Canaj, K., 2022. Environmental Assessment of Wastewater Treatment and Reuse for Irrigation: A Mini-Review of LCA Studies. *Resources 2022*, Vol. 11, Page 94 11, 94. <https://doi.org/10.3390/RESOURCES11100094>
- METRO, C., 2023. Bioetanol CALIDOR 15 L (3x5 L) | MAKRO Marketplace [WWW Document]. Makro España. URL <https://tinyurl.com/mpfm3atv> (accessed 8.15.23).
- Minx, J.C., Lamb, W.F., Callaghan, M.W., Fuss, S., Hilaire, J., Creutzig, F., Amann, T., Beringer, T., De Oliveira Garcia, W., Hartmann, J., Khanna, T., Lenzi, D., Luderer, G., Nemet, G.F., Rogelj, J., Smith, P., Vicente Vicente, J.L., Wilcox, J., Del Mar Zamora Dominguez, M., 2018. Negative emissions—Part 1: Research landscape and synthesis. *Environmental Research Letters 13*, 063001. <https://doi.org/10.1088/1748-9326/aabf9b>
- Mohammad Abu Zahra, Erik Gjernes, 2010. Environmental impacts of amine emissions during post combustion capture. Stoke Orchard.

- Mohammed B Alqaragully, Hazim Algubury, Aseel Aljeboree, Ayad F. Alkaim, 2015. Monoethanolamine: Production Plant [WWW Document]. Res J Pharm Biol Chem Sci. URL <https://tinyurl.com/4mhsbpnd> (accessed 6.14.24).
- Negri, V., Galán-Martín, Á., Pozo, C., Fajardy, M., Reiner, D.M., Mac Dowell, N., Guillén-Gosálbez, G., 2021. Life cycle optimization of BECCS supply chains in the European Union. Appl Energy 298, 117252. <https://doi.org/10.1016/J.APENERGY.2021.117252>
- Nielsen P H, Nielsen A M, Weidema B P, Dalgaard R, Halberg N, 2003. LCA-Food: A Database for Basic Foods - 2.-0 LCA consultants [WWW Document]. Danish Institute of Agricultural Sciences. URL <https://lca-net.com/projects/show/lifecycle-assessment-basic-food/> (accessed 4.28.24).
- Nirupam Pal, Charles Siletti, Demetri Petrides, 2008. Superpro Designer: An Interactive Software Tool for Designing and Evaluating Integrated Chemical, Biochemical, and Environmental Processes [WWW Document]. AIChE Annual Meeting. URL <https://tinyurl.com/3u8pazaj> (accessed 5.21.24).
- Olsson, O., Becidan, M., Bang, C., Abdalla, N., Bürck, S., Fehrenbach, H., Harris, Z.M., Thrän, D., Cavalett, O., Cherubini, F., Hennig, C., 2022. Deployment of BECCUS value chains From concept to commercialization Synthesis Report.
- Pajula, T., Behm, K., Vatanen, S., Saarivuori, E., 2017. Managing the life cycle to reduce environmental impacts. Dynamics of Long-Life Assets: From Technology Adaptation to Upgrading the Business Model 93–113. https://doi.org/10.1007/978-3-319-45438-2_6
- Pamu, Y., Kumar, V.S.S., Shakir, M.A., Ubbana, H., 2022. Life Cycle Assessment of a building using Open-LCA software. Mater Today Proc 52, 1968–1978. <https://doi.org/10.1016/J.MATPR.2021.11.621>
- Pan, S.Y., He, K.H., Lin, K.T., Fan, C., Chang, C.T., 2022. Addressing nitrogenous gases from croplands toward low-emission agriculture. npj Climate and Atmospheric Science 2022 5:1 5, 1–18. <https://doi.org/10.1038/s41612-022-00265-3>
- Pe International AG, 2012. GaBi: Software and database contents for Life Cycle Engineering. [WWW Document]. PIAG,. URL <https://sphera.com/product-sustainability-gabi-data-search/> (accessed 4.12.24).
- Peter Baldwin, 2009. Capturing CO2: Gas Compression vs. Liquefaction [WWW Document]. POWER. URL <https://www.powermag.com/capturing-co2-gas-compression-vs-liquefaction/> (accessed 6.11.24).
- PRé, 2016. ReCiPe - PRé Sustainability [WWW Document]. PRé Sustainability. URL <https://pre-sustainability.com/articles/recipe/> (accessed 5.1.24).

- Pritha Banerjee, D.V., 2022. Capex vs Opex | Top 8 Best Differences (with Infographics) [WWW Document]. URL <https://www.wallstreetmojo.com/capex-vs-opex/> (accessed 9.22.23).
- Puig, R., Fullana-i-Palmer, P., Baquero, G., Riba, J.R., Bala, A., 2013. A Cumulative Energy Demand indicator (CED), life cycle based, for industrial waste management decision making. *WM* 33, 2789–2797. <https://doi.org/10.1016/J.WASMAN.2013.08.004>
- Randall, A., Heijungs, R., 2023. Deconstructing and Reconstructing the Theoretical Basis of the Ecological Scarcity Method. *Sustainability* 2023, Vol. 15, Page 16515 15, 16515. <https://doi.org/10.3390/SU152316515>
- Restrepo-Valencia, S., Walter, A., 2023. BECCS opportunities in Brazil: Comparison of pre and post-combustion capture in a typical sugarcane mill. *IJGGC* 124, 103859. <https://doi.org/10.1016/J.IJGGC.2023.103859>
- Riedl, D., Byrum, Z., Li, S., Pilorgé, H., Psarras, P., Lebling, K., 2023. 5 Things to Know About Carbon Mineralization. *Journal of CO2 Utilization* 40. <https://doi.org/10.1016/j.jcou.2020.101196>
- Rodriguez-Stanley, S., Ahmed, T., Zubaidi, S., Riley, S., Akbarali, H.I., Mellow, M.H., Miner, P.B., 2004. Calcium carbonate antacids alter esophageal motility in heartburn sufferers. *Dig Dis Sci* 49, 1862–1867. <https://doi.org/10.1007/S10620-004-9584-1>
- Romero-García, J.M., Sanchez, A., Rendón-Acosta, G., Martínez-Patiño, J.C., Ruiz, E., Magaña, G., Castro, E., 2016. An Olive Tree Pruning Biorefinery for Co-Producing High Value-Added Bioproducts and Biofuels: Economic and Energy Efficiency Analysis. *Bioenergy Res* 9, 1070–1086. <https://doi.org/10.1007/s12155-016-9786-3>
- Rosenbaum, R.K., Bachmann, T.M., Gold, L.S., Huijbregts, M.A.J., Jolliet, O., Juraske, R., Koehler, A., Larsen, H.F., MacLeod, M., Margni, M.D., McKone, T.E., Payet, J., Schuhmacher, M., van de Meent, D., Hauschild, M.Z., 2008. USEtox - The UNEP-SETAC toxicity model: Recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment [WWW Document]. *IJOLCA*. URL <https://www.usetox.org/> (accessed 4.24.24).
- Saharudin, D.M., Jeswani, H.K., Azapagic, A., 2023. Bioenergy with carbon capture and storage (BECCS): Life cycle environmental and economic assessment of electricity generated from palm oil wastes. *Appl Energy* 349, 121506. <https://doi.org/10.1016/J.APENERGY.2023.121506>
- Salary team, 2023. Power Plant Operator Average Salary in Spain 2023 - The Complete Guide [WWW Document]. Salary explorer team . URL <https://tinyurl.com/4pcdh4uj> (accessed 10.23.23).

- Sánchez, A., Sevilla-Güitrón, V., Magaña, G., Gutierrez, L., 2013. Parametric analysis of total costs and energy efficiency of 2G enzymatic ethanol production. *Fuel* 113, 165–179.
<https://doi.org/10.1016/J.FUEL.2013.05.034>
- Sari Siitonen, 2024. Trichlorofluoromethane, CFC-11 / R-11 (CCl3F) - OpenCO2.net [WWW Document]. OpenCO2Net. URL <https://rb.gy/69ve70> (accessed 5.28.24).
- Schelte, N., Severengiz, S., Schünemann, J., Finke, S., Bauer, O., Metzen, M., 2021. Life cycle assessment on electric moped scooter sharing. *Sustainability (Switzerland)* 13.
<https://doi.org/10.3390/SU13158297>
- Seedat, N., Kauchali, S., Patel, B., 2021. A graphical method for the preliminary design of ternary simple distillation columns at finite reflux. *S Afr J Chem Eng* 37, 99–109.
<https://doi.org/10.1016/J.SAJCE.2021.04.005>
- Servian-Rivas, L.D., Pachón, E.R., Rodríguez, M., González-Miquel, M., González, E.J., Díaz, I., 2022. Techno-economic and environmental impact assessment of an olive tree pruning waste multiproduct biorefinery. *FABP* 134, 95–108.
<https://doi.org/10.1016/J.FBP.2022.05.003>
- Sharaai, A.H., Mahmood, N.Z., Sulaiman, A.H., 2011. Life cycle impact assessment (LCIA) using EDIP 97 method: An Analysis of potential impact from potable water production. *SRAE* 6, 5658–5670. <https://doi.org/10.5897/SRE11.287>
- Shishov, A., Markova, U., Nizov, E., Melesova, M., Meshcheva, D., Krekhova, F., Bulatov, A., 2022. Fast and energy-effective deep eutectic solvent-based microextraction approach for the ICP-OES determination of catalysts in biodiesel. *CTATA* 7, 100071.
<https://doi.org/10.1016/J.CTTA.2022.100071>
- Siegert Martin, Haywood Alan, Lunt Dan, Flierdt Van Tina, 2020. What ancient climates tell us about high carbon dioxide concentrations in Earth's atmosphere | Grantham Institute – Climate Change and the Environment | Imperial College London [WWW Document]. Imperial College London. URL <https://tinyurl.com/2ksjp8e6> (accessed 5.14.24).
- Sinnott, R.K., Towler, Gavin., 2009. *Chemical engineering design*. Butterworth-Heinemann 5th, 1255.
- Smith, D.C., 2002. The National Renewable Energy Laboratory: NREL: The first 25 years and the future. *Refocus* 3, 54–56. [https://doi.org/10.1016/S1471-0846\(02\)80089-0](https://doi.org/10.1016/S1471-0846(02)80089-0)
- Soares, S.R., Toffoletto, L., Deschênes, L., 2006. Development of weighting factors in the context of LCIA. *J Clean Prod* 14, 649–660.
<https://doi.org/10.1016/J.JCLEPRO.2005.07.018>

- Stavropoulos, P., Giannoulis, C., Papacharalampopoulos, A., Foteinopoulos, P., Chryssolouris, G., 2016. Life Cycle Analysis: Comparison between Different Methods and Optimization Challenges. *Procedia CIRP* 41, 626–631. <https://doi.org/10.1016/J.PROCIR.2015.12.048>
- Steyn, M., Oglesby, J., Turan, G., Zapantis, A., Gebremedhin, R., Al Amer, N., Havercroft, I., Ivory-Moore, R., Yang, X., Abu Zahra, M., Pinto, E., Rassool, D., Williams, E., Consoli, C., Minervini, J., 2022. Global status of CCS 2022.
- Susmozas, A., Moreno, A.D., Romero-García, J.M., Manzanares, P., Ballesteros, M., 2019. Designing an olive tree pruning biorefinery for the production of bioethanol, xylitol and antioxidants: A techno-economic assessment. *Holzforschung* 73, 15–23. <https://doi.org/10.1515/HF-2018-0099/MACHINEREADABLECITATION/RIS>
- SustainOlive, 2024. Importance of the Olive grove in the Mediterranean Basin [WWW Document]. Muffin group. URL <https://sustainolive.eu/importance-olive-grove-mediterranean-basin/?lang=en> (accessed 6.11.24).
- Tamme, E., Beck, L.L., 2021. European Carbon Dioxide Removal Policy: Current Status and Future Opportunities. *Frontiers in Climate* 3, 682882. <https://doi.org/10.3389/FCLIM.2021.682882/BIBTEX>
- Tangsriwong, K., Lapchit, P., Kittijungjit, T., Klamrassamee, T., Sukjai, Y., Laonual, Y., 2020. Modeling of chemical processes using commercial and open-source software: A comparison between Aspen Plus and DWSIM. *IOP Conf Ser Earth Environ Sci* 463, 012057. <https://doi.org/10.1088/1755-1315/463/1/012057>
- Tanzer, S.E., Ramírez, A., 2019. When are negative emissions negative emissions? *Energy Environ Sci* 12, 1210–1218. <https://doi.org/10.1039/C8EE03338B>
- Team, Editorial., 2023. Water prices compared in 36 EU-cities • Water News Europe [WWW Document]. URL <https://tinyurl.com/mu929a8r> (accessed 10.23.23).
- Tivander, J., 2013. Mapping of CPM LCA database SPINE format to ILCD data format. Göteborg.
- Trenda, E., 2023. Olives: average price Spain 2021 | Statista [WWW Document]. URL <https://tinyurl.com/ysnb55pk> (accessed 10.23.23).
- Umeda, T., Nishio, M., 1972. Comparison Between Sequential and Simultaneous Approaches in Process Simulation. *IAECPDAD* 11, 153–160. https://doi.org/10.1021/I260042A001/ASSET/I260042A001.FP.PNG_V03
- United Nations Environment, 2022. How do greenhouse gases actually warm the planet? [WWW Document]. UNEP website. URL <https://www.unep.org/news-and-stories/story/how-do-greenhouse-gases-actually-warm-planet> (accessed 5.6.24).

- Usmani, Z., Sharma, M., Tripathi, M., Lukk, T., Karpichev, Y., Gathergood, N., Singh, B.N., Thakur, V.K., Tabatabaei, M., Gupta, V.K., 2023. Biobased natural deep eutectic system as versatile solvents: Structure, interaction and advanced applications. *Science of The Total Environment* 881, 163002. <https://doi.org/10.1016/J.SCITOTENV.2023.163002>
- Van Zelm, R., Huijbregts, M.A.J., Van De Meent, D., 2009. USES-LCA 2.0-a global nested multi-media fate, exposure, and effects model. *International Journal of Life Cycle Assessment* 14, 282–284. <https://doi.org/10.1007/S11367-009-0066-8/METRICS>
- Vidhya H, 2017. Difference between Continuous and Batch Process | Continuous vs Batch Process | MindsMapped [WWW Document]. Mindsmapped. URL <https://www.mindsmapped.com/difference-between-continuous-and-batch-process/> (accessed 6.10.24).
- Wernet G., B.C., Steubing B, R., J. Moreno-Ruiz E., Weidema B., 2016. The ecoinvent database Version 3 (Part I): overview and methodology [WWW Document]. *IJOLCA*. <https://doi.org/10.1007/s11367-016-1087-8>
- Xu, Y., Isom, L., Hanna, M.A., 2010. Adding value to carbon dioxide from ethanol fermentations. *Bioresour Technol* 101, 3311–3319. <https://doi.org/10.1016/J.BIORTECH.2010.01.006>
- Yang, J., Zeng, Y., Ekwaro-Osire, S., Nispel, A., Ge, H., 2020. Environment-Based Life Cycle Decomposition (eLCD): Adaptation of EBD to Sustainable Design. *JOIDAPS* 24, 5–28. <https://doi.org/10.3233/JID200018>
- Zhang, L., Zhao, X., Chen, L., Zhang, X., 2022. Pretreatment with fermentable and recyclable deep eutectic solvent (DES) for improving resource utilization of biomass. *Ind Crops Prod* 190, 115868. <https://doi.org/10.1016/J.INDCROP.2022.115868>

7. Appendix

Additional material to the content presented in the thesis is included in this document. In section A1, the simulation model is presented together followed by the mass and energy balance results (section A2). In section A3, we present the economic assessment calculations together with the cost parameters employed. Section A4, includes the life cycle inventories (LCIs) for the biorefinery. Finally, section A5 shows the environmental impact results in absolute terms and section A.6 the nomenclature.

A1. Process model in SuperPro Designer

The simulation model was developed in SuperPro Designer v9.0. It consists of 55 unit operations, 7 reactors, and 22 heat exchangers. The model is built upon laboratory experimental data on olive tree pruning treatment, hydrolysis, and fermentation (Romero-García et al., 2016). Additional data on the equipment was taken from the literature (Sánchez et al., 2013).

Figures 12-15A show the simplified process flowsheets for the subsystems of the multiproduct olive pruning tree biomass (OPTB) biorefinery. Note that due to the size of the flowsheet, some figures do not correspond to a unique subsection of the multiproduct plant.

Overall, the olive pruning tree biomass enters the biorefinery through the conditioning section where the biomass is homogenized and cleaned of wastes and particles (Fig.12A). Then it is processed with continuous extraction to solubilize before filtration. The liquid portion is sent to the chromatography column to separate and purify polyphenols and natural antioxidants. Then the extracted OPTB from SS2 enters the SS3 subsystem where it is pretreated with weak acid and water to dissolve the lignocellulosic structure and isolate lignin (Fig.13A). The forwarded hydrolysates are processed through saccharification and fermentation with enzymes and bacteria to consume the glucose and produce bioethanol (Fig.13A). Lignin is converted to ash and ends up in the cogeneration unit (SS5). Wastewater from SS2 and SS3 is treated with a sequential anaerobic-aerobic process to produce biogas, sludge, and liquid (Fig.14A). After a clarifier, the liquid is recycled to the biorefinery as process water, while biogas and sludge are sent to SS5 for incineration (Fig.15A). In SS5 residual biomass and biogas produce heating. Please note that it also combusts OPBT for the BIOR_CCS scenario and natural gas for the BIOR_NG scenario.

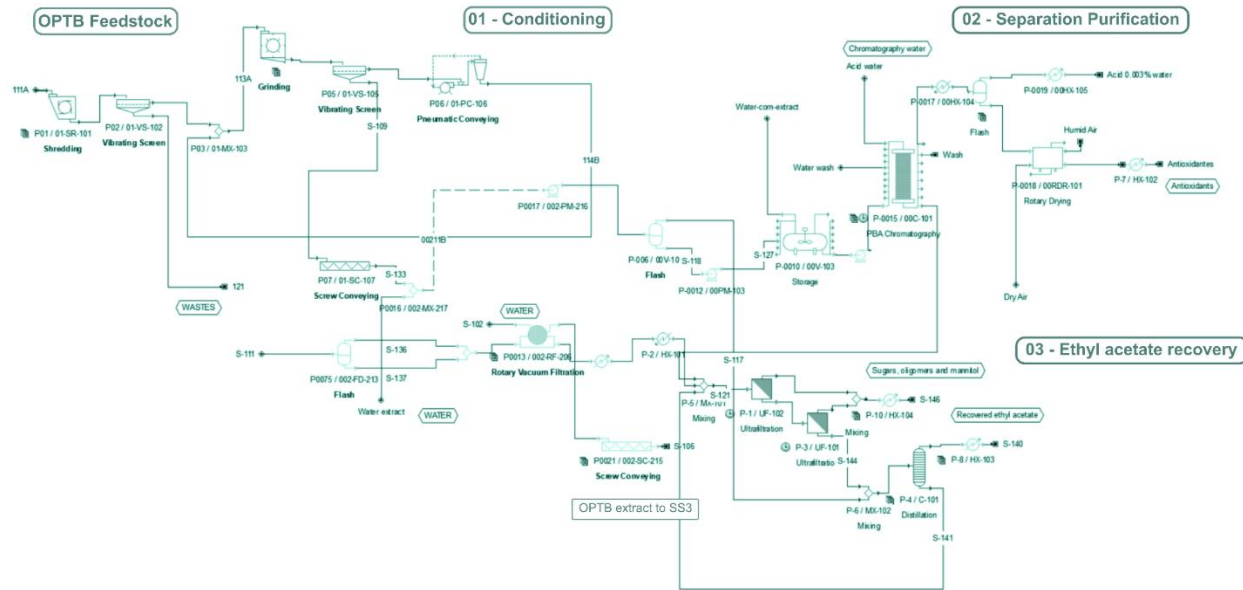
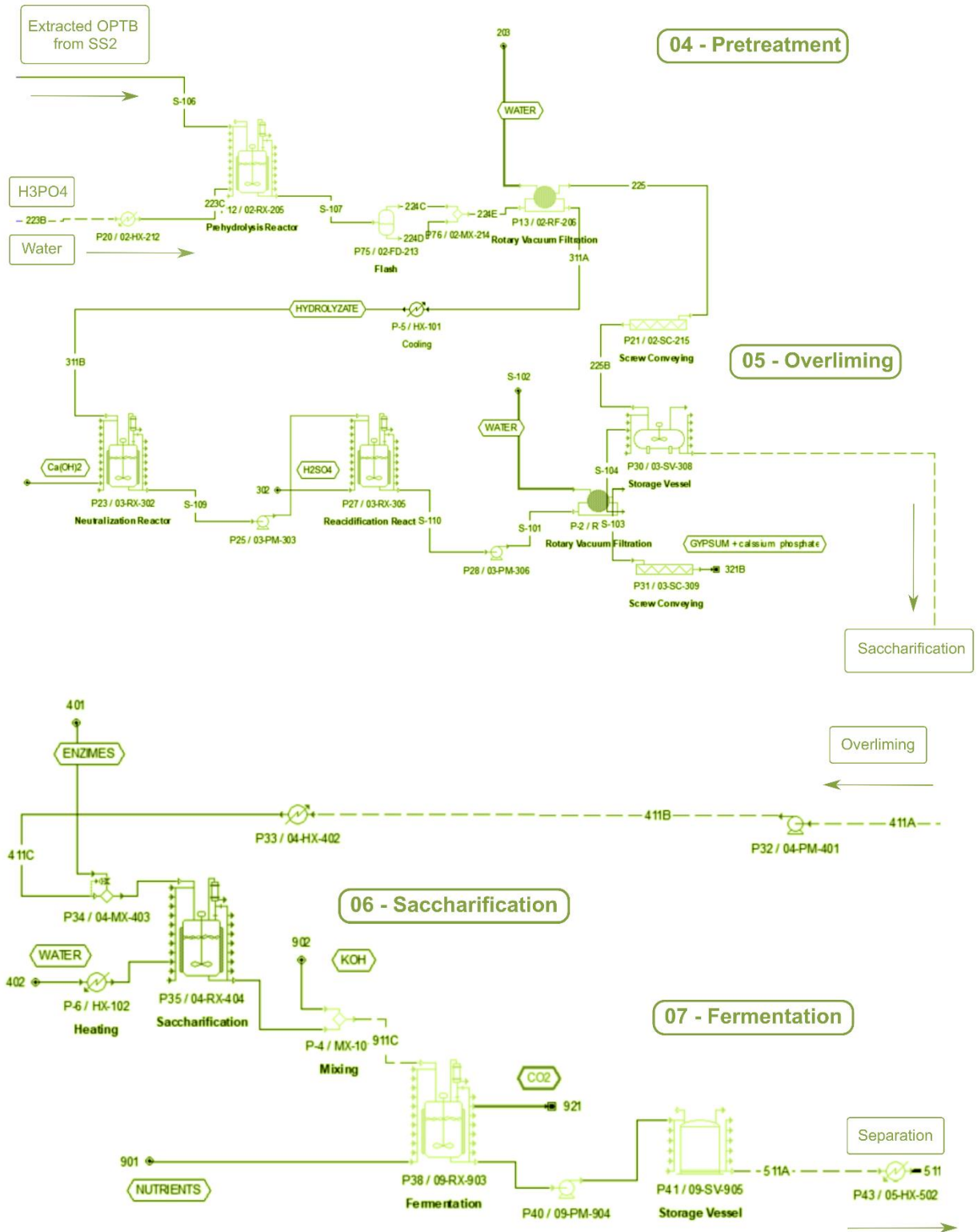


Figure 12A Flowsheet of the antioxidant plant [SS2 in Fig.8 section 3.2.3.1].



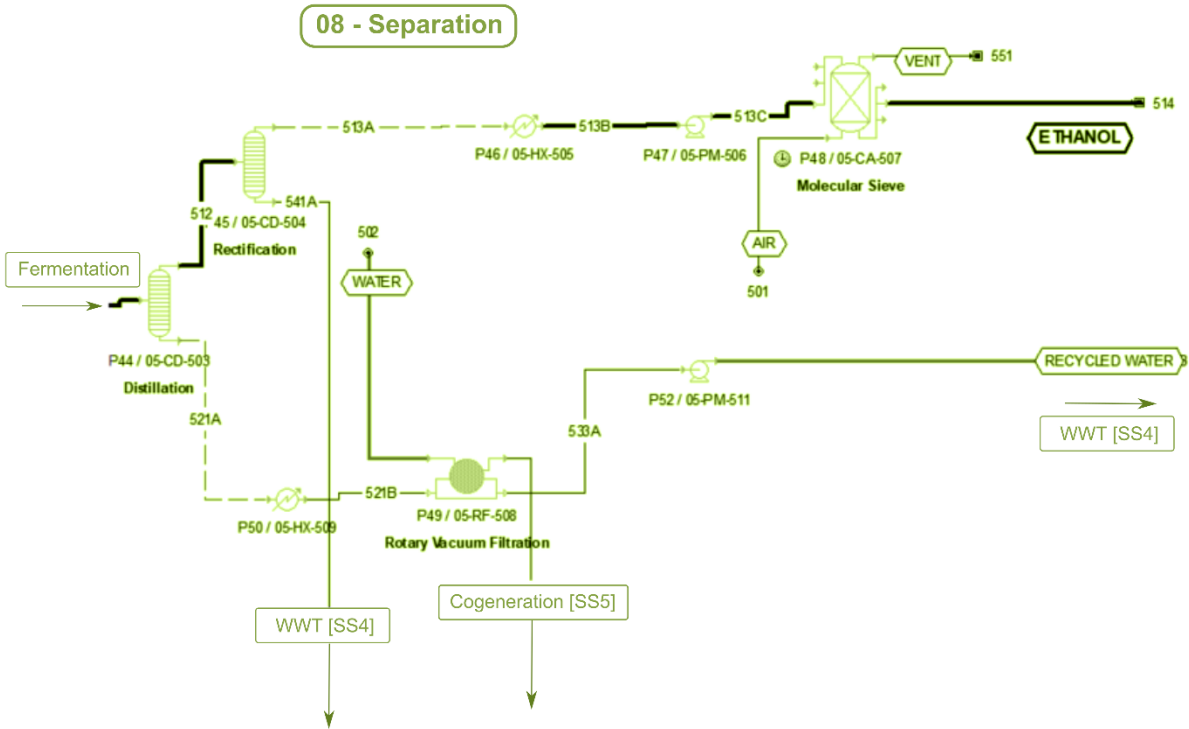


Figure 13A. Flowsheets for the bioethanol plant [SS3 in Fig.8, section 3.2.3.1].

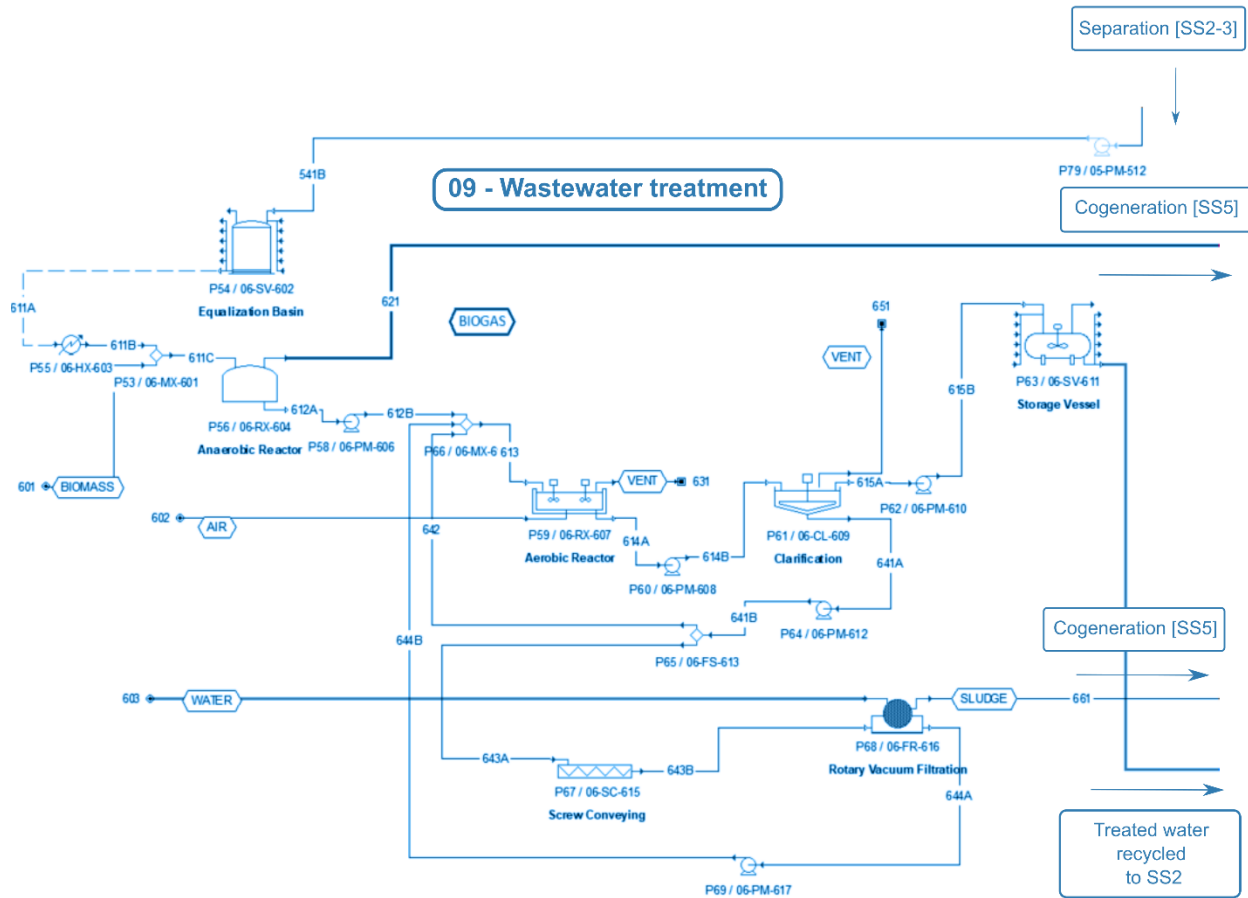


Figure 14A Flowsheet for the wastewater treatment plant [SS4 in Fig.8, section 3.2.3.1].

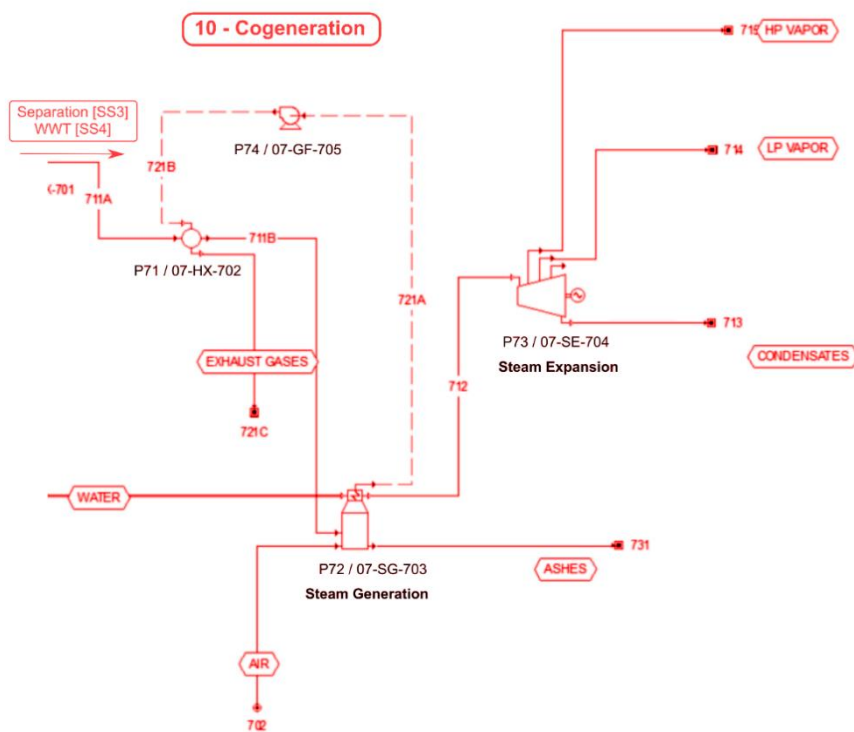


Figure 15A Simplified flowsheet for the cogeneration plant [SS5 in Fig.8, section 3.2.3.1].

A2. Heating and cooling demands

Table A.1 shows the energy requirements (heating/cooling) retrieved from the simulation.

Table A.1. Heating/cooling demands for the biorefinery.

Extraction and purification of the antioxidants	Heating (MJ)	Cooling (MJ)
P008 Heater	6,495.00	-
Aqueous extractor	-	3.82
P002 Heater	-	2,074.00
Flash Drum	3,984.00	-
P0026 Heater	-	3,045.00
Extractor	78.98	-
P2 Heater	2,455.00	-
P004 Heater	306.18	-
Flash drum 2	1,368.00	-
P0017 Heater	3,818.00	-
Flash drum 3	32,922.00	-
P0019 Heater	-	33,179.00

P7 Heater	-	8.03
Ethyl acetate recovery	Heating MJ	Cooling MJ
Ultrafiltration 1	-	1,651.00
P10 Heater	-	1,057.00
Distillation column	3,292.00	2,466.00
P8 Heater	-	1,566.00
Pretreatment	Heating MJ	Cooling MJ
P08 Heater	1,654.00	-
Pre-Soaking	-	0.50
P11 Heater	2,060.00	-
P20 Heater	1,175.00	-
Prehydrolysis reactor	-	0.32
Flash drum	-	1,177.00
P5 Cooling	-	1,072.00
Overliming	Heating MJ	Cooling MJ
Neutralization reactor	-	1.29
Reacidification reactor	-	4.78
Saccharification	Heating MJ	Cooling MJ
P33 Heater	-	963.75
P6 Heater	548.49	-
Saccharification tank	-	221.22
Fermentation	Heating MJ	Cooling MJ
P37 Heater	-	727.77
Fermentation tank	-	509.25
P43 Heater	3,744	-
Distillation column	5,423.00	5,360
Separation	Heating MJ	Cooling MJ
Rectification column	754.92	712.08
P46 Heater	-	636.08
P50 Heater	-	3,588
WWT	Heating MJ	Cooling MJ
P55 Heater	-	318.31
Cogeneration	Heating MJ	Cooling MJ
P71 Heat exchanger	18,127.00	-
P74 Centrifugal fanning	-	265.71
Steam expansion	-	1,302.00
Total	129,685.00	61,911.00
Total per functional unit [1 kg bioethanol + 0.15 kg antioxidants]*	189.75	90.58
Total energy demands per FU	280 MJ perFU	

*To estimate the total heating/cooling demands per FU, the accumulation of MJ was divided by the total mass of bio-products produced. The plant produces 213.9 tones of bioethanol and 33.1 tones of antioxidants per day (Romero-García et al., 2016).

A3. Economic assessment

The economic calculations are primarily based on Sinnott et al. (Sinnott and Towler, 2009). The economic assessment considers a plant life period of 25 years, assuming a fixed annual profit and depreciation. The interest rate was fixed at 6.00 %. The tax rate was set to 25 %.

The Capital Expenditures (CAPEX) are estimated following equation (A.1) which provides the total capital costs of the plant ($Eibl$) as the summation of all equipment.

$$Eibl = \sum_{e \in \text{Equipment}} [C_i ((1+Fp)Fmi + (Finc + Fei + Fcve + Fab + Fpnc + Fepe))] \quad (\text{A.1})$$

Where C_i is the parameter for the equipment estimation (C_i), data were retrieved from the literature (Sánchez et al., 2013). Fp is 0.80, $Finc$, $Fcve$, and $Fepe$ are 0.30, Fei and Fab are 0.20, and $Fpnc$ is 0.10. For the material factor of equipment (Fmi) consult Table A.3. For a detailed explanation of the acronyms consult Table A.2.

Note that Eq (A.1) includes parametric contingencies such as the ones listed in Inside Battery Limits (IBL) (Sinnott and Towler, 2009) concerning additional costs such as instrumentation, piping, electrical, control, civil engineering, additional spaces-buildings, painting and coating, equipment edification.

For the operational cost expenditure (OPEX), both fixed and variable costs were considered. Outside Battery Limits (OBL) (Sinnott and Towler, 2009) include mainly design and engineering contingencies (equation (A.2)):

$$FCC = Eibl(1+Fobl)(1+Fde+Fcn) \quad (\text{A.2})$$

where FCC is for fixed capital cost. $Eibl$ stands for the summation of all the equipment calculated as in equation A.1. $Fobl$ is 0.40, Fde is 0.30 and Fcn stands for 0.10 (see Table A.2).

To estimate OPEX, the operational fixed cost (OF_c) is calculated (equation (A.3)).

$$OF_c = OL(1+Fmso) + Eibl(Fmnc + Fplc) \quad (\text{A.3})$$

where OL is for operating labor, $Fmso$ is 2.13, $Fmnc$ is 0.05 and $Fplc$ is 0.03 (Table A.2). The additional OPEX is considered variable and refers to the summation of all raw materials, utilities, and consumables, whose prices may fluctuate due to inflation (Table A.4). Table A.2 summarizes the values of the aforementioned contingencies and corrections.

Table A.2.: Contingencies and correction factors employed in the economic calculations.

Acronym	Description	Value
<i>Fp</i>	Piping	0.80
<i>Fmi</i>	Material factor of equipment	see Table A.3.
<i>Finc</i>	Instrumentation and control	0.30
<i>Fei</i>	Electrical infrastructure	0.20
<i>Fcve</i>	Civil engineering	0.30
<i>Fab</i>	Additional buildings	0.20
<i>Fpnc</i>	Painting and coating	0.10
<i>Fepe</i>	Equipment edification	0.30
<i>Fobl</i>	Outside battery limits	0.40
<i>Fde</i>	Design and engineering	0.30
<i>Fcn</i>	Contingency charges	0.10
<i>Fmso</i>	Management and salary overhead	2.13
<i>Fmnc</i>	Maintenance costs	0.05
<i>Fplc</i>	Property and land costs	0.03

Table A.3.: Material factors (Dimian et al., 2014; Sinnott and Towler, 2009).

Material	Material factors of equipment (F_{mi})
Carbon steel	1.00
Aluminum	1.07
Bronze	1.07
Cast steel	1.10
SS304	1.30
SS316	1.30
SS321	1.50
Hastelloy C	1.55
Monel	1.65

To estimate the annual cash flows (CF_n) of every year n during the life span, equations (A.4) and (A.5) were followed. Where P_n stands for annual profit (Rev_n) from selling bioproducts, minus the fixed and variable OPEX (OF_c and OV_c). Dn stands for the annual depreciation, which is linearly the same for every year, and t for the tax rate, fixed at 25%.

$$CF_n = P_n - (P_{n-1} - D_{n-1})t \quad (A.4)$$

$$P_n = Rev_n - OF_c - OV_c \quad (A.5)$$

For the depreciation, the straight-line approach was followed, which divides the fixed capital costs (FCC) with the plant's total years (equation A.6)).

$$Dn = \frac{FCC}{DP} \quad (A.6)$$

where DP is the depreciation period in years, which was set at 25 years.

The net present value (NPV), which will indicate if the project is profitable or not, was estimated using equation (A.7) considering the cash flow of year n (CF_n), the project life of 25years (t) and an interest rate i of 6.00%.

$$NPV = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n} \quad (A.7)$$

Moreover, the internal rate of return (IRR) which in essence is the interest rate that makes NPV equal to zero is estimated using equation (A.8).

$$0 = \sum_{n=1}^{n=t} \frac{CF_n}{(1+IRR)^n} \quad (A.8)$$

Payback time (*PBT*) was also estimated following the equation (A.9):

$$PBT = \frac{\text{Total Investment}}{\text{annual average cash flow}} \quad (\text{A.9})$$

The return on investment, *ROI*, is estimated using equation A.10.

$$ROI(\%) = \frac{\text{annual average cash flow}}{\text{Total Investment}} \quad (\text{A.10})$$

The total annualized costs (*TAC*) is a combination of annualized capital and operational costs fixed (*OPEX_{fix}*) and variable (*OPEX_{vr}*) (Equation A.11).

$$TAC = AF * CAPEX + OPEX_{fix} + OPEX_{vr} \quad (\text{A.11})$$

where *AF* is the annualized capital factor which is investment expressed as a recurrent annual cost (Equation, A.12).

$$AF = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (\text{A.12})$$

Table A.4. provides the raw materials, utilities and operating cost parameters employed in the economic calculations.

Table A.4.: Cost parameters for utilities, raw materials and operating labors.

Utilities	MWh/year	€/MWh	Source
Electricity	126,655.00	150.00	(Endesa S.A., 2023)
Heating with BECCS	6,978,545.00	160.00	(Cabral et al., 2019;
Heating with natural gas	6,978,545.00	89.70	(Eurostat, 2023)
Raw materials	ton/year	€/ton	
Water	3,480,895.00	2.00	(Team, 2023)
OTP biomass feedstock	547,500.00	44.70	(Romero-García et al., 2016)
Bacterias	328.50	1,300	(InterMesh., 2023)
Enzymes	6,351.00	2,850.00	(InterMesh., 2023)
Resin	30,536.00*	4,650.00*	(Alibaba Group, 2023)
Ethyl acetate	4,293.00	1,255.00	(Analyst, 2023)
Phosphoric acid	1,825.00	2,345.00	(Analyst, 2023; IndexBox, 2023; InterMesh., 2023)
Potassium hydroxide	292.00	450.00	(Analyst, 2023; IndexBox, 2023; InterMesh., 2023)

Sulfuric acid	219.00	58.00	(Analyst, 2023; IndexBox, 2023; InterMesh., 2023) d
Calcium hydroxide	1,971.00	322.00	(Analyst, 2023; IndexBox, 2023; InterMesh., 2023)
Tripotassium phosphate	255.50	1,424.00	(Analyst, 2023; IndexBox, 2023; InterMesh., 2023)
Operating labor costs	Operator's median salary per month	Annual operating labor costs for all workers in €	
28 operators working in the plant	2,270.00	762,720.00	(Salary team, 2023; Sánchez et al., 2013)

*Resin is washed and regenerated to be reused. Resin is replaced after 2 years of operation.

Note that, for the calculations, an additional 25% discount was applied on raw materials and utilities due to bulky orders for industrial use.

Table A.5 shows the uncertainty range for the main cost parameters that were used to conduct the sensitivity analysis of the economic results.

Table A.5: Uncertainty ranges of inputs for the sensitivity analysis for the main cost parameters

Inputs	Optimistic scenario	Base case scenario	Pessimistic	Source
Electricity [€/kWh]	0.13	0.15	0.21	(Directorate-General for Energy et al., 2018)
Transferred (cooling) water [€/m ³]	0.12	0.15	0.20	(Secretaria General Técnica and Centro de Publicaciones, 2004)
Ethyl Acetate [%]	-3.30	0	+3.30	(IndexBox Inc., 2024)
OPTB [€/tone]	20.00	44.70	60.00	(Romero-García et al., 2016)
BECCS [%]	-6.67	0	+6.67	(Saharudin et al., 2023)
Various chemicals for processes [%]	-10.00	0	+10.00	(Berger et al., 2022)

A4. Inventory data

For the life cycle assessment (LCA), three inventories were developed, retrieving data from the literature (Fernández-Lobato et al., 2021; Romero-García et al., 2016; Sánchez et al., 2013), and filling the gaps with Ecoinvent 3.8 (Wernet G. et al., 2016). For all activities, the APOS – U system model was chosen, as it distributes some of the waste impact on the products by enabling recycling

and therefore results in less impact. For the dataset, those for Spain ([ES]), Europe ([RER]), and global ([GLO]) or the Rest of the World ([RoW]) were selected when the former were unavailable.

For the biomass input, the OTPB, we account for the impacts associated with the pruning, including all relevant processes of growing olive trees, including fertilizers, pesticides, nutrients, land occupation techniques, and irrigation among others. For this, the ‘Olive fruit production – ES’ dataset from Ecoinvent v3.8 was used, and modified the original inventory by removing the wood waste entry. Then, all inputs and outputs between the olive fruit and the prunings were allocated based on an economic factor estimated according to Equation (A.14). Chipping and mulching pretreatment activities were also considered as well as transportation using a lorry for a 100 km distance from the olive groves. The inventory per 1 kg of OTPB is shown in Table A.6. Note that this OTPB entry is used as raw material for the biorefinery to obtain the bioethanol and the antioxidants but also in the BECCS system to be combusted to meet the heating need in the BIOR CCS scenario.

$$EI = \frac{(EV * M)}{\sum_n (EV_n * M_n)} * 100 \quad (A.14)$$

where EI is the allocation factor, EV is the economic value for the products (olive fruit and prunings) and M is the mass of the products. Market costs were assumed for the olive fruit of 3 €/kg (Trenda, 2023) and for the OPTB of 0.0447 €/kg (Servian-Rivas et al., 2022). For the mass, it is assumed that 0.26 kg of pruning is generated as waste per 1 kg of olive fruit according to the ‘Olive fruit production – ES’ dataset.

Tables A.6 present the OPTB and biorefinery life-cycle inventories.

Table A.6. Inventory of 1 kg on olive tree pruning biomass.

Output	
Olive tree pruning biomass	1.00 kg
Inputs from nature	
Carbon dioxide, fossil	-1.52 kg*
Inputs from technosphere	
Olive olive production	0.015 kg**
Wood chipping, industrial residual wood, stationary electric chipper [GLO], APOS U	1.05 kg
Transport, freight, lorry 3.5-7.5 metric ton [GLO] market for APOS, U	0.10 tkm

* Biogenic CO₂ embodied in the biomass was estimated considering a water content of 27.60% and carbon content, on a dry basis, of 49.40%, according to the Phyllis2 database (TNO Biobased and Circular Technologies, 2024).

**Own activity modeled from the ‘Olive fruit production – ES’ dataset from Ecoinvent v3.8 by removing the wood waste entry. The input amount is estimated considering the economic allocation to the OTPB.

Secondly, the biorefinery activity in SimaPro v9.0, with a FU of 1 kg bioethanol and 0.15 kg antioxidants (Romero-García et al., 2016) was developed. It was estimated that around 6.07 kg of OPTB are needed to produce 1 kg of ethanol and 0.15 kg of antioxidants, respectively.

Finally, the BECCS inventory was developed based on literature data (Galán-Martín et al., 2021a). The results were modified due to the biomass and efficiency considered. BECCS inventory was scaled to the biorefinery’s total heating demands (280 MJ per FU). Out of those, only 30.50% was provided by OPTB or natural gas, while the other 69.50% was provided by residual biomass of the biorefinery, whereas, both of them were covered by the CCS system

Table A.7 shows the inventory of the biorefinery plant derived from the mass and energy balance from the simulations scaled to the functional unit of 1 kg of bioethanol and 0.15 kg of antioxidants.

Table A.7.: Inventory of the biorefinery for the production of 1 kg of bioethanol and 0.15 kg of antioxidants (functional unit).

Outputs			
Bioethanol	1.00 kg	-	
Antioxidants	0.15 kg	-	
Inputs from nature			
Air	0.048 kg	Antioxidant (SS2)	
Air	0.98 kg	WWT (SS4)	
Inputs from technosphere			
OPTB biomass	6.07 kg	Antioxidant (SS2)	
Ethyl acetate	4.76 kg	Antioxidant (SS2)	
Sulfuric acid	0.0018 kg	Antioxidant (SS2)	
Non-ionic hydrophobic resin	0.138 kg	Antioxidant (SS2)	
Phosphoric acid	0.0227 kg	Bioethanol (SS3)	
Calcium hydroxide	0.024 kg	Bioethanol (SS3)	
Potassium hydroxide	0.0036 kg	Bioethanol (SS3)	
Enzymes	0.079 kg	Bioethanol (SS3)	
Nutrients	0.047 kg	Bioethanol (SS3)	
Nutrients	0.004 kg	WWT (SS4)	
Sulfuric acid	0.0009 kg	Bioethanol (SS3)	
Tap water	70.30 kg	Antioxidant (SS2)	
Tap water	39.60 kg	Bioethanol (SS3)	
Tap water	1.88 kg	WWT (SS4)	
Electricity/Heat			
Electricity, high voltage, production mix	1.15 kWh	Antioxidant (SS2)	
Electricity, high voltage, production mix	0.38 kWh	Bioethanol (SS3)	
Electricity, high voltage, production mix	0.029 kWh	WWT (SS4)	
Heating*	84.00 MJ*	(SS5)	
Heating*	196.00 MJ*	Cogeneration Unit (CHP)(SS5)	
Emissions to air			
Carbon dioxide	0.95 kg	Bioethanol (SS3)	
Carbon dioxide	0.01 kg	WWT (SS4)	
Methane	0.0068 kg	WWT (SS4)	
Waste to treatment			
Waste wood	0.39 kg	Antioxidant (SS2)	
Waste gypsum	0.041 kg	Bioethanol (SS3)	
Ash	0.35 kg	Bioethanol (SS3)	

*The heating needs could be met by either natural gas or BECCS (BIOR NG and BIOR CCS)

scenarios, respectively. The BECCS inventory was developed based on an activity from the literature by modifying the biomass input with the OTPB (Galán-Martín et al., 2021).

A5. Life cycle assessment

All the LCIs data were built in SimaPro v9.5.0.0 software taking the background data from Ecoinvent v3.8 (Wernet et al., 2016). To assess the environmental footprint of the biorefinery scenarios were employed 18 midpoint categories from the ReCiPe 2016 (H) methodology. For the Global Warming (GW) category (expressed in kg of CO₂ eq), the biogenic CO₂ in the biomass OTPB is modeled as a negative entry of fossil CO₂ fossil, contributing as a carbon-negative component in the overall emissions accounting. To calculate the final balance all upstream and downstream greenhouse gas emissions are accounted for.

Table A.8. shows the absolute values for the 18 ReCiPe 2016 midpoint categories.

Table A.8: Absolute values for the 18 ReCiPe 2016 midpoint categories.

Impact category	Unit	BIOR NG	BIOR CCS
Global warming	kg CO ₂ eq	28.22	-84.37
Stratospheric ozone depletion	kg CFC11 eq	$9.18 \cdot 10^{-5}$	$0.24 \cdot 10^{-3}$
Ionizing radiation	kBq Co-60 eq	0.96	2.33
Ozone formation, Human health	kg NO _x eq	0.30	0.69
Fine particulate matter formation	kg PM _{2.5} eq	$0.80 \cdot 10^{-1}$	0.17
Ozone formation, Terrestrial ecosystems	kg NO _x eq	0.30	0.70
Terrestrial acidification	kg SO ₂ eq	0.27	0.56
Freshwater eutrophication	kg P eq	$0.79 \cdot 10^{-2}$	$0.14 \cdot 10^{-1}$
Marine eutrophication	kg N eq	$0.17 \cdot 10^{-2}$	$0.11 \cdot 10^{-1}$
Terrestrial ecotoxicity	kg 1,4-DCB	253.26	633.22
Freshwater ecotoxicity	kg 1,4-DCB	1.18	2.17
Marine ecotoxicity	kg 1,4-DCB	1.69	3.28
Human carcinogenic toxicity	kg 1,4-DCB	1.63	2.78
Human non-carcinogenic toxicity	kg 1,4-DCB	81.50	179.98
Land use	m ² a crop eq	1.99	16.67
Mineral resource scarcity	kg Cu eq	$0.85 \cdot 10^{-1}$	0.18
Fossil resource scarcity	kg oil eq	9.44	14.05
Water consumption	m ³	0.43	1.13

A6. Nomenclature

BECCS = Bioenergy and Carbon Capture and Storage

BIOR_CCS = Biorefinery with Carbon Capture and Storage

BIOR_NG = Biorefinery with Natural Gas

CDR = Carbon Dioxide Removal

DACCS = Direct Air Carbon Capture and Storage

ETEA = Environmental Techno-economic Analysis

LCA = Life Cycle Assessment

OTP = Olive Tree Pruning

OPTB = Olive Pruning Tree Biomass

CCS = Carbon capture and storage

CCU = Carbon capture and use

EA = Ethyl Acetate

TAC = Total annualized cost

CAPEX = Capital expenditure

OPEX = Operational expenditure

AF = Annualized factor

NPV = Net present value

ROI = Return on investment

PBT = Payback time

LCI = Life cycle inventory

LCIA = Life cycle inventory and analysis

IBL = Inside battery limits

OBL = Outside battery limits

GW = Global warming

GWP = Global warming potential

F_p = Piping

F_{mi} = Material factor of equipment

F_{inc} = Instrumentation and control

F_{ei} = Electrical infrastructure

F_{cve} = Civil engineering

F_{ab} = Additional buildings

F_{pnc} = Painting and coating

F_{epe} = Equipment edification

F_{obl} = Outside battery limits

F_{de} = Design and engineering

F_{cn} = Contingency charges

F_{mso} = Management and salary overhead

F_{plc} = Property and land costs



UNIVERSITAT ROVIRA I VIRGILI

Exploring the economic and environmental implications of integrating carbon capture in biorefinery systems

Climate change-related natural disasters are more profound and intense than ever before in the history of humankind. There is an urgent need to act immediately to save future generations from experiencing unpleasant disasters and potential threats to their well-being, safety, health, and economy. Governments around the world, develop regulatory frameworks to control and reduce greenhouse gas emissions, by investing in decarbonization policies.

The thesis focuses on one of the many carbon dioxide removal technologies, to facilitate carbon-negative emissions, in a cycle production of bioproducts from an olive pruning tree biomass biorefinery. Bioenergy with carbon capture and storage (BECCS) technology shows promising results in reducing carbon footprint when retrofitted into the biorefinery, but this comes with a set of adverse effects both in terms of environmental and economic implications. This thesis sheds light on this direction by identifying parameters that cause the burden-shifting effect and suggesting alternative solutions to mitigate unintended environmental impacts. Finally, addresses the high financial cost of BECCS systems by investigating financial aids that are designated by governments to offset the high investments and support such initiatives.



