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Johannes Full

»Techno-Economic Analysis of Hydrogen Production from Biomass with Carbon Capture and Storage«

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»Techno-Economic Analysis of Hydrogen Production from Biomass with Carbon Capture and Storage«

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zur Erlangung der Würde eines Doktor-Ingenieurs (Dr.-Ing.)
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Vorwort des Autors

Die vorliegende Dissertation entstand während meiner wissenschaftlichen Tätigkeit am Fraunhofer-Institut für Produktionstechnik und Automatisierung IPA in Stuttgart und am Institut für Energieeffizienz in der Produktion der Universität Stuttgart (EEP). Das anspruchsvolle, innovative und kollegiale Umfeld dieser Institutionen bildeten den idealen Rahmen für diese Arbeit.

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Inhaltsverzeichnis

Nomenclature

°C	Degrees celsius
BECCS	Bioenergy with carbon capture and storage
Biohydrogen	Hydrogen obtained from biogenic resources
BW	Baden-Wuerttemberg
CapEx	Capital expenditures
CCS	Carbon dioxide capture and storage
CDR	Carbon dioxide removal
CNH	Carbon-negative hydrogen
CO_2	Carbon dioxide
CRC	Carbon dioxide removal certificates
CS	Carbon dioxide storage
CU	Carbon dioxide use
DACCS	Direct air carbon dioxide capture and storage
DF	Dark fermentation
DIC	Direct and indirect costs
DP	Dark photosynthesis
FRG	Federal republic of Germany
GHG	Greenhouse gas
H_2	Hydrogen
HyBECC	Hydrogen bioenergy with carbon dioxide capture
HyBECCS	Hydrogen bioenergy with carbon dioxide capture and storage
HyBECCU	Hydrogen bioenergy with carbon capture and use
IPCC	Intergovernmental panel on climate change
KPI	Key performance indicator
LCA	Life cycle assessment
LCCNH	Levelized costs of carbon-negative hydrogen

LCNE	Levelized costs of negative emissions
LCOE	Levelized Cost of Energy
LCSC	Levelized costs of stored carbon dioxide
LHV	Lower Heating Value
NET	Negative emission technology
OpEx	Operational expenditures
R. rubrum	Rhodospirillum rubrum
SR	Steam reforming
TPC	Total plant costs
TRL	Technology Readiness Level

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Kurzfassung

Auf dem Weg zu klimaneutralen Systemen muss zukünftig neben der Reduktion von Treibhausgasemissionen auch Kohlenstoffdioxid (CO_2) aus der Atmosphäre entfernt werden. Eine vielversprechende Option dafür bieten Technologien, die Bioenergieerzeugung mit CO_2-Abscheidung und -speicherung koppeln (BECCS). In dieser Arbeit wird ein Technologiekonzept für BECCS vorgestellt, bei dem der Energieträger Wasserstoff aus biogenen Rohstoffen produziert wird: Biowasserstofferzeugung mit Kohlenstoffdioxidabscheidung und -speicherung (HyBECCS, engl. hydrogen bioenergy with carbon capture and storage). Für das HyBECCS-Konzept bestehen keine technologiespezifischen Möglichkeiten der techno-ökonomischen Bewertung. Standardisierte Bewertungsgrundlagen sind jedoch notwendig, damit potenzielle Anwender und Investoren bei ihren unternehmerischen Entscheidungsprozessen im Hinblick auf den Technologieeinsatz in der Praxis unterstützt werden können. Auch politische Rahmenbedingungen und Qualifizierungssysteme für öffentliche Subventionen können damit gezielt verbessert werden. Die in der vorliegenden Arbeit entwickelte Lösung stellt methodische Grundlagen für die techno-ökonomische Bewertung von HyBECCS-Technologien zur Verfügung. Dazu gehören einheitliche Systemgrenzen für ökologische und ökonomische Bilanzierungen und darauf aufbauende Kennzahlen. Diese können für Vergleiche mit anderen Wasserstoffproduktions- und Negativemissionstechnologien eingesetzt werden. Eine Besonderheit dabei ist, dass die Kennzahlen neben konventionellen betriebswirtschaftlichen Kriterien auch gesamtwirtschaftliche Auswirkungen integrieren, die aus den Treibhausgasemissionen und -reduktionen der zu bewertenden Technologien resultieren. Anhand eines exemplarischen Anschauungsbeispiels wird eine techno-ökonomische Analyse mit Hilfe dieser Kennzahlen durchgeführt. Dabei wird gezeigt, dass die erarbeiteten theoretischen Grundlagen in der Praxis einsetzbar sind.

Abstract

In addition to reducing greenhouse gas emissions, it is inevitable to remove carbon dioxide (CO_2) from the atmosphere to achieve climate-neutrality. Promising options for this purpose are negative emission technologies (NETs) that couple bioenergy production with carbon capture and storage (BECCS). In this paper, a novel technology concept for BECCS is introduced with the peculiarity that the energy carrier hydrogen is produced from biogenic sources: hydrogen bioenergy with carbon capture and storage (HyBECCS). For the HyBECCS concept, no possibilities for technology-specific assessment exist. However, standardized evaluation fundamentals are necessary to support potential users and investors in their entrepreneurial decision-making processes. They are of great importance with regard to the technical implementation of HyBECCS technologies. Additionally, political framework conditions and qualification systems for public subsidies could also be improved in a more targeted way. The solution developed in this doctoral thesis provides a methodological basis for techno-economic assessment of HyBECCS technologies. It includes uniform system boundaries for ecological and economic balancing and key performance indicators (KPIs). The KPIs can be applied to compare HyBECCS technologies with other hydrogen production technologies and NETs. In addition to conventional economic criteria, these indicators integrate macroeconomic effects resulting from the GHG emissions and reductions as a special feature. On the basis of an exemplary HyBECCS implementation project, a techno-economic analysis is carried out with the help of these KPIs. It is shown that the theoretical principles developed can be applied in practice.

1 Introduction

1.1 Initial Situation

Human-induced climate change and related rise in weather and climate extremes have already led to irreversible impacts on ecosystems and infrastructure. These impacts are related to socioeconomic consequences like reduced food and water security (IPCC 2022a, p. 9). Near-term actions that limit global warming to close to 1.5°C above pre-industrial levels would substantially reduce further damages related to climate change (IPCC 2022a, p. 13).

Without deep reductions in carbon dioxide and other greenhouse gas emissions in the coming decades, global warming of 1.5°C will very likely be exceeded during the 21st century (IPCC 2021a, p. 14). Considering the reduction of GHG emissions, there are feasible and effective mitigation measures. Within energy system transitions, decentralized renewable energy generation is among the options (IPCC 2022a, p. 25). In this area, hydrogen (H_2) can play a key role. Renewable generation possibilities as well as a wide range of applications in different sectors like heavy-duty transport and heat or power supply make H_2 a promising option (Kovac et al. 2021). It can be generated with low GHG emissions, for example, by water electrolysis using renewable electrical energy or from organic residual and waste materials using thermochemical or biotechnological conversion technologies (Turner 2004, Nikolaidis & Poullikkas 2017). Hydrogen obtained from biogenic resources can be referred to as biohydrogen (Bhatia 2014).

In addition to GHG emission reductions, carbon dioxide removal (CDR) from the atmosphere in the order of 100-1000 GtCO_2 over the 21st century will very likely be unavoidable to limit global warming to 1.5°C (IPCC 2018a, p. 17). CDR aims to compensate for residual emissions to reach net zero CO_2 or net zero GHG emissions (IPCC 2021a, p. 29). This is a requirement for stabilizing GHG-induced global temperature increase (IPCC 2021a, p. 30). Carbon dioxide capture and storage (CCS) technologies make this possible, but only if the CO_2 is of biogenic or atmospheric origin. CCS alone does not remove CO_2 from the atmosphere (IPCC 2021b, p. 2218). Biogenic carbon dioxide can be obtained from biomass conversion, i.e. during bioenergy production (BECCS). Atmospheric CO_2 can be captured directly from ambient air using direct air carbon capture and storage (DACCS) approaches. Besides BECCS and DACCS, there are different CDR measures. Among them are afforestation, reforestation, soil carbon management and biochar (IPCC 2021b, p. 242). Known storage options for CO_2 include geological storage in salt rock formations or depleted natural gas and oil fields. Storage of CO_2 in deep, onshore or offshore geological formations has been proven economically feasible under specific conditions for oil and gas fields and saline formations (IPCC 2005, p. 6).

The concept of BECCS rests on the premise that bioenergy production is carbon neutral. This means that as much CO_2 is captured from the air when growing biomass as is released by combustion or conversion. If this biogenic CO_2 is captured and stored, the net effect is a removal of CO_2 from the atmosphere or negative emissions (IPCC 2021b, p. 763). BECCS is constrained by sustainable biomass availability, but it is estimated to have a worldwide potential to remove 1–85 $GtCO_2$ from the atmosphere in 2050 (IPCC 2018b, p. 342-343). This range can be narrowed to 0.5–5 $GtCO_2$ per year (Fuss et al. 2018, p. 31). In Europe, the potential for CDR through BECCS is estimated at 200 $MtCO_2$ per year (Rosa et al. 2021) and for the Federal Republic of Germany (FRD), a potential of approx. 62 $MtCO_2$ per year is estimated (Borchers et al. 2022, p. 19). As stated in the Climate Change Act of the FRD, the annual greenhouse gas emissions have to be reduced by 88 percent compared to 1990 until 2040 and reach net neutrality in 2045 (FOJ 2021). Looking at the last step towards GHG neutrality from 2040–2045, an annual amount of about 130 $MtCO_2eq$ of remaining GHG emissions would, therefore, need to be able to be reduced or removed from the atmosphere within five years.

In this work, a new concept for BECCS is introduced with the special characteristic that hydrogen is produced. Biohydrogen production technologies generating biogenic CO_2 as a by-product are suitable for CDR and generate negative GHG emissions. The co-generation of biogenic CO_2 applies to most of the known biohydrogen technologies, e.g. photofermentation (Singh et al. 2017, p. 14, p. 106), dark fermentation (Singh et al. 2017, p. 59, p. 212), pyrolysis (Singh et al. 2017, p. 219-220), microbial electrolysis (Singh et al. 2017, p. 215) and biomethane steam reforming (Singh et al. 2017, p. 272).

The HyBECCS negative emission technology concept introduced in this work combines biohydrogen production from renewable biomass, preferential biogenic residual and waste materials, with CCS. A basis for techno-economic assessment of technologies related to this concept is elaborated. The assessment allows the comparison of HyBECCS technologies among themselves and to other hydrogen production technologies or NETs. It is applied to the example of a specific HyBECCS technology implementation project. This is an important step for the understanding of the HyBECCS concept and its impacts and, therefore, supports its potential transfer into broad implementation.

1.2 Problem and Objective

Individual technology combinations for biohydrogen production with carbon capture and storage have already been described. Examples are based on biomass gasification (Susmozas et al. 2016) or biomethane reforming (Antonini et al. 2020), for instance. However, a comprehensive technology concept that generically describes technical implementation options, peculiarities and prerequisites for HyBECCS has not yet been specified.

Further, because there is no description basis, individual HyBECCS technologies are not yet sufficiently comparable and assessable from a techno-economic point of view. Techno-economic assessments should enable the analysis of monetary costs and benefits of a particular technology or process to determine the economic feasibility and to compare different options. For HyBECCS technologies, there are no specific assessment fundamentals available for this purpose. Abstractions, standardizations and uniform system boundaries have not yet been elaborated. However, private and public investments depend on objective techno-economic comparability. Hence, there is a lack of conceptual techno-economic assessment fundamentals and guidelines for HyBECCS technologies that could serve as an important basis for their transfer to wider application.

Appropriate and standardized key performance indicators (KPIs) are necessary to techno-economically compare individual technologies with competing ones in the market environment. They are inevitable for analyzing and specifically improving the relative economic performance of upcoming and existing technologies. However, to depict the added value for society, it should further be possible to include societal costs in the assessment. This is particularly important in the case of technology concepts that promise additional socioeconomic benefits. As the HyBECCS concept intends to generate such benefits through avoiding economic damage related to climate change, it is particularly important to assess these technologies. Possibilities to integrate the impacts of HyBECCS technologies through GHG emission reductions or removals into techno-economic KPIs do not yet exist. However, this is an essential precondition for understanding the economic impacts holistically. The realization of the socioeconomic potentials of future technologies can be supported by comprehensive and holistic assessment metrics, which serve as a necessary basis for designing policy frameworks and qualification systems for public funding.

Hence, the objective of this work is to establish a basis for techno-economic assessment of HyBECCS processes. This basis should enable a comparison of HyBECCS technologies with each other and with other hydrogen production technologies and NETs in terms of their techno-economic performance. It thus should serve technology providers and investors as a basis for decision-making. Moreover, it should be possible to consider aspects of climate protection and resulting economic impacts to serve as a guideline for political and societal decision-making. For this purpose, technical abstractions and prerequisites, suitable system boundaries and KPIs are intended to be identified or defined in this scientific work.

According to Kubicek, a central aspect of science is formulating research questions. The legitimacy of research questions is based on the knowledge that can be gained by answering them (Kubicek 1977, p. 14-16). Hence, the following central research question and the associated five sub-questions are derived from the objectives described above:

How can HyBECCS technologies be assessed techno-economically?

1. What is the HyBECCS concept?
2. Which requirements have to be fulfilled to qualify as HyBECCS technologies?
3. Which system boundaries are suitable for HyBECCS technologies to balance monetary, mass and greenhouse gas emission flows?
4. How can the economic impact of the greenhouse gas balance be incorporated into the techno-economic evaluation of HyBECCS processes?
5. Which key performance indicators are suitable for techno-economic assessment of HyBECCS technologies?

The sub-questions build on each other in the sequence shown. The main research question can be answered conclusively from the results of the answers to the sub-questions.

1.3 Structure of the Work

The research conducted as part of this dissertation can be assigned to the research process according to Ulrich, as shown in Figure 1-2 below (Ulrich 2001, p. 195). The seven single steps of this process are linked to the chapters of this thesis, as illustrated. Since this is a cumulative dissertation, essential contents have already been published in the five scientific papers (A-E) listed below.

- **Paper A:** Full, Johannes; Merseburg, Steffen; Miehe, Robert; Sauer, Alexander, 2021. A new perspective for climate change mitigation – introducing carbon-negative hydrogen production from biomass with carbon capture and storage (HyBECCS). In: Sustainability 13.7 (2021): 4026. doi:10.3390/su13074026
- **Paper B:** Full, Johannes; Hohmann, Silja; Ziehn, Sonja; Gamero, Edgar; Schließ, Tobias; Schmid, Hans-Peter; Miehe, Robert; Sauer, Alexander, 2023. Perspectives of Biogas Plants as BECCS Facilities: A Comparative Analysis of Biomethane vs. Biohydrogen Production with Carbon Capture and Storage or Use (CCS/CCU). In: Energies 2023, 16, 5066. doi: 0.3390/en16135066
- **Paper C:** Full, Johannes; Ziehn, Sonja; Geller, Marcel, Miehe, Robert; Sauer, Alexander, 2022. Carbon-negative hydrogen production: Fundamentals for a techno-economic and environmental assessment of HyBECCS approaches. In: GCB Bioenergy 14.5 (2022): 597-619. doi:10.1111/gcbb.12932
- **Paper D:** Full, Johannes; Trauner, Mathias; Miehe, Robert; Sauer, Alexander, 2021. Carbon-Negative Hydrogen Production (HyBECCS) from Organic Waste Materials in Germany: How to Estimate Bioenergy and Greenhouse Gas Mitigation Potential. In: Energies 14.22 (2021): 7741. doi: 10.3390/en14227741
- **Paper E:** Full, Johannes; Geller, Marcel; Ziehn, Sonja; Schließ, Tobias; Miehe, Robert; Sauer, Alexander, 2023. Carbon-Negative Hydrogen Production (HyBECCS): An Exemplary Techno-Economic and Environmental Assessment In: International Journal of Hydrogen Energy, doi: 10.1016/j.ijhydene.2023.09.252

The basic chapter structure and the interconnections to the research process are explained in the following. References to the research questions are made in each case, and the contributions made in the respective research publications (A-E) are described briefly.

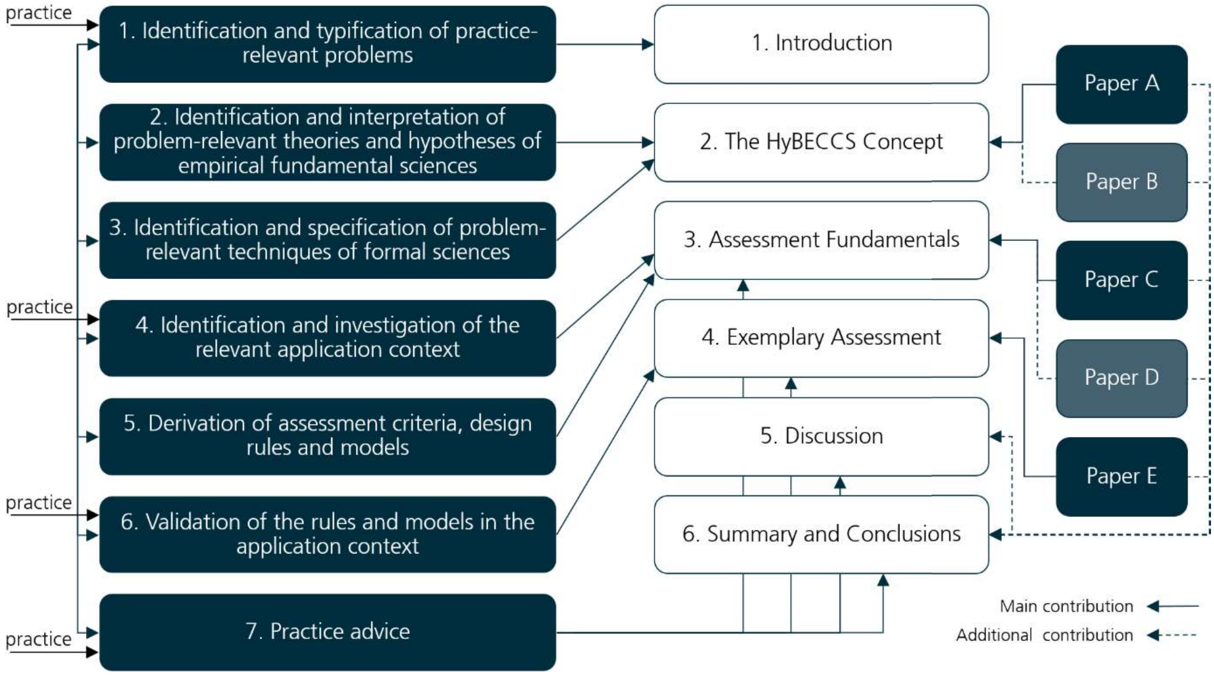

Figure 1-1 Seven steps of the research process according to (Ulrich 2001, p.195) and connecting points of this work.

The work begins and ends in practice and is mainly focused on investigating of the application context (Ulrich 1981, p.19). In chapter 1, the practice-relevant problems are identified first. This starts with a description of the initial situation and motivation for the research to be conducted. Problems resulting from human-induced climate change and the novel technological HyBECCS approach to support its mitigation are derived. Moreover, the research gap of insufficient assessability for this approach is explained briefly. This is followed by the elaboration of the philosophy of science assigning the work in a scientific-theoretical context to the applied sciences in general, and to technical sciences in particular. A more detailed specification of the research gaps is conducted thereafter and objectives are deducted. These serve to derive the research questions to be answered in this work. The main question of how to assess HyBECCS technologies from a techno-economic perspective is thereby divided into five sub-questions. The respective answers lead to a holistic view of the answer to the superordinate question.

In the second chapter, the HyBECCS concept is introduced, and its associated scientific foundations are defined and described from a technological point of view. Following the first step of the research process according to Ulrich, theories and techniques from the fundamental and the formal sciences are identified (Ulrich 2001). These include, in particular, physical and biological knowledge. Significant generic contributions to this part are covered in Paper A (Full et al. 2021a). It summarizes the state of the art in science and technology for biohydrogen production as well as for NETs focusing on BECCS and carbon dioxide sequestration options. Further, the HyBECCS technology concept is defined generically and subdivided into four basic process steps to be implemented with different technology options. It further provides initial estimates of the technological potential for climate protection and considerations of the economic viability of the HyBECCS concept. An additional contribution on specific application peculiarities is made in Paper B (Full et al. 2023a). Herein, the focus is laid on retrofitting existing biogas plants using biogas steam reforming technology. The technical implementation is described and trade-offs for this approach are discussed. The first and second research sub-questions (cf. Section 1.2) are addressed in chapter 2, introducing and describing the HyBECCS technology concept and defining basic requirements for technological implementation options.

In the third chapter, the fundamentals for techno-economic assessment of HyBECCS technologies are elaborated. Referring to the research process, the relevant application context for this purpose is identified first. As summarized in section 1.2, the results are intended to support investors, technology providers and policy makers in their decision-making processes. Assessment criteria, design rules and models are derived and advices for application in practice are elaborated. The main contributions to this part are covered in Paper C (Full et al. 2022b). Results are uniform system boundaries and KPIs enabling comparison of HyBECCS technologies with other hydrogen production technologies and NETs. Additional contributions are made in Paper D (Full et al. 2021b), outlining terminologies for waste classification and giving methodological advice for substrate selection and bioenergy potential estimation for HyBECCS technologies. Research sub-question 2 is intended to be conclusively answered in this chapter by providing an in-depth understanding of the state of the art for the HyBECCS concept and concretizing the verification of the technical requirements defined. Sub-questions 3, 4 and 5 are addressed, providing basic fundamentals for techno-economic assessment of HyBECCS technologies. These include uniform system boundaries with standardized material, monetary and GHG emission flows as well as KPIs. Impacts on global climate and their economic correlations are particularly considered.

Chapter 4 is a conclusion chapter summarizing the outcomes of the previous chapters and applying the techno-economic assessment fundamentals. Following the research process according to Ulrich (2001), the rules and models are validated in the context of application. An exemplary HyBECCS implementation project is defined for this purpose. Further practice advice can be derived from the validation example by concretizing the procedures to determine and analyze the relevant KPIs on the basis of the practical application example. The contributions to this part are described in Paper E (Full et al. 2023b). Research sub-questions 2, 3, 4 and 5 are considered to be answered conclusively in this chapter through application validation. The system boundaries with standardized material, monetary and GHG emission flows defined in Paper C are applied for this purpose. The KPIs are derived and analyzed. The example technology can be compared with other hydrogen production technologies and NETs considering the economic effects resulting from GHG emissions and removals.

In chapter 5, the interrelationships between the single contributions (Paper A-E) are outlined, and the common thread of the work is described for a better understanding of the overall context of the results.

In chapter 6, all results elaborated in chapters 2-4 are discussed, and the limitations for their application are explained. This contributes to the seventh step in the research process, providing practice advice. It contributes to answering research sub-question 5, especially in terms of applicability constraints.

Chapter 7 summarizes the results of the work and explains its core findings. The significance of the results for scientific advancement and practice application is outlined. With regard to the research process, concluding advice for practice in terms of holistic application possibilities of the findings is provided. This advice, however, does not represent a temporal end point. It must be understood as a constantly recurring phase, as envisaged by Ulrich (Ulrich 1981, p. 21). In the sense of this iterative character of the overall research process, advice for further scientific development of the results obtained is given. All substantial results are explained in terms of their contributions to answering the five research sub-questions. The main research question defined for this thesis can finally be answered by recapitulating the essential findings and resuming the answers to the sub-questions in a superordinate overall context.

1.4 Philosophy of Science

In the common understanding, science intends to explain states and events of reality by attributing them to the validity of general laws (Ulrich 2001, p. 169). However, it can also be applied to the systematic derivation of recommendations for human action (Ulrich 2001, p. 170). In general, the science process can be defined as systematic thinking that takes place according to specific rules. As there are no common criteria for those rules, they result in a consensus problem. However, this consensus problem can be addressed by science systematics. Science systematics provide classifications into science categories. These allow guidance to examine the rules attached to individual science categories more specifically. Figure 1-1 shows the essential fundamentals of science systematics according to Ulrich and Hill (Ulrich & Hill 1976, p. 305). In the following, these systematics are explained and related to the present work to understand the objectives and its position in the context of science philosophy.

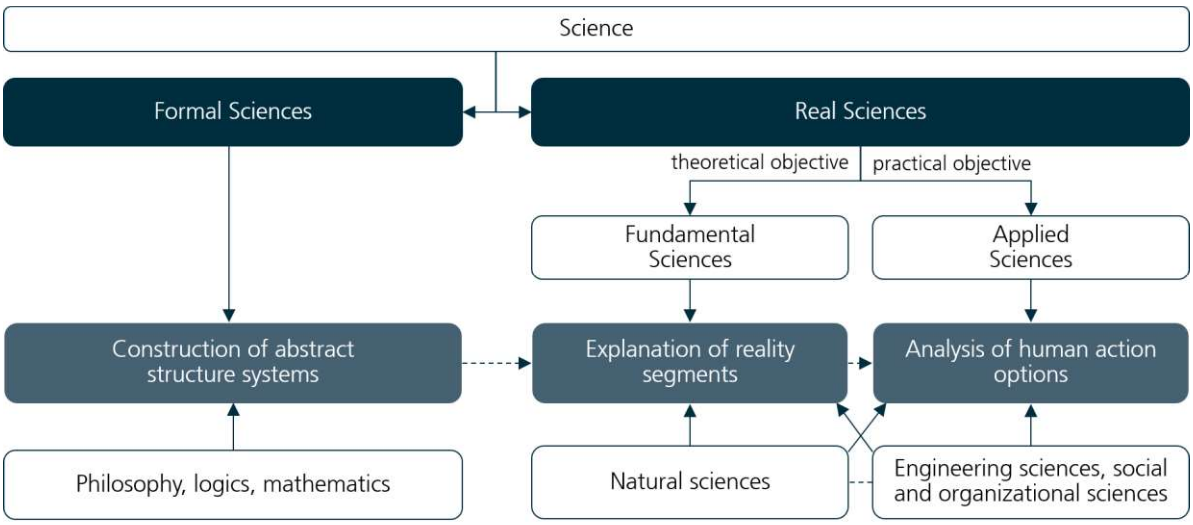

Figure 1-2 Science systematics (Ulrich & Hill 1976, p. 305)

As illustrated in Figure 1-2, science can generically be subdivided into formal and real sciences. In formal sciences, constructing languages or character systems with rules for their use is the objective. Thereby, no reference to reality exists and the findings can only be checked for their logical truth. Real sciences describe, explain and shape empirically perceivable sections of reality. The findings must be checked for their truth from a logical and a factual point of view. Real science precisely describes new forms of thinking according to certain rules and generalizes them. Hence, they always need formal sciences as a prerequisite. (Ulrich & Hill 1976, p. 305-306)

Among real sciences, a distinction can be made between fundamental and applied sciences. In fundamental sciences, the explanation is their key focus and explanatory models are formed. The applied sciences analyze human action alternatives for the design of social and technical systems. For this purpose, decision models or processes are developed. An applied science must be able to provide appropriate design models and rules for changing social reality in complex social systems (Ulrich 2021, p. 192). Problems of applied research originate outside of science in practice. The problem to be investigated is not the validity of theories but the applicability of models and rules to support human behavior in practice (Ulrich 2001, p. 2020).

Therefore, the central task of the applied sciences is the study of the application context. It expresses itself in practice, since that is where problems arise, and their solutions are realized. Practice can be defined as human action or, more broadly, their behavior and the effects that result from it. The application of scientific knowledge, as it also takes place in this work, deals with human action or behavior and impacts and provides solutions for changing social reality. (Ulrich 1981, p. 7)

The technical sciences can be located between fundamental and applied sciences. They aim at the research and development of artificial artifacts with the goal of testing a practical functionality (Ropohl 2009, p. 161-162). In a broader sense, the artifact and the actual and possible actions associated with it and their forms of organization must be encompassed (Kornwachs 2011, p. 140).

Due to the practical relevance and the main outcome of an applicable basis for technology-specific assessment of a novel technology concept, the present work can be assigned to the applied sciences. It aims to provide appropriate design models and rules for changing social reality in a complex social system. A generalizing abstraction of the novel technology concept is derived to test and support the practical implication of individual cases within this concept through the provision of a standardized assessment basis. In particular, the work is also linked to technical sciences as the actual and possible actions associated with the technology concept belong to the application context.

2 The HyBECCS Concept

The HyBECCS (hydrogen bioenergy with carbon capture and storage) technology concept combines biohydrogen production from renewable biomass, preferential waste and residues, with carbon dioxide capture and storage. In this chapter, the technological fundamentals are explained, and implementation options are described.

In Paper A, the basic concept is introduced and the state of the art from a technical point of view is explained. The technology concept is divided into four generic process steps, for each of which different technology options can be selected. Technical requirements for the suitability of the options are established and peculiarities are analyzed. The state of the art on biohydrogen production and NETs is elaborated. Additionally, general perspectives for HyBECCS from economic and ecological points of view are outlined.

Paper B emphasizes a technical implementation option of the HyBECCS concept based on modifying existing biogas plants with biogas steam reforming.

2.1 Summary of Paper A: Conceptualization of the technology approach

Paper A (Full et al. 2021a) introduces the basic approach of the HyBECCS concept. It starts with deriving the role of negative emissions and hydrogen in energy transition and climate change mitigation activities. Thereafter, the state of the art in science and technology for hydrogen technologies and NETs is elaborated. A special focus is placed on biohydrogen production technologies and BECCS approaches. It is made clear that the HyBECCS concept can be implemented in various technological ways.

For better understanding, it is divided into four steps: biomass pretreatment (1), biohydrogen production (2), product gas separation (3), and their processing (4). All steps are interdependent and can be performed by different technology options. For the selection of the substrate biomass, it is suggested to use residual and waste materials. However, their suitability depends on the technology choices for the pretreatment and biohydrogen production steps. Considering biohydrogen production, it is a necessary condition that carbon dioxide is produced as a by-product. This applies to most of the biohydrogen production technologies known. CO_2 storage options include geological storage in salt rock formations or depleted natural gas and oil fields, for instance.

As HyBECCS is introduced as a NET concept, the entire HyBECCS process chain, including biomass supply, the use of hydrogen and storage of CO_2, must have a negative GHG balance. This is an essential basic requirement for HyBECCS technologies, which is explained in more detail in chapter 3. If this prerequisite is fulfilled, the hydrogen produced can be referred to as carbon-negative hydrogen (CNH).

In comparison to other NET approaches, the potential advantages of HyBECCS from a technical point of view are derived. Compared to direct air carbon capture and storage (DACCS), the main advantage of HyBECCS and BECCS in general is the energy-efficient capture of CO_2 from a highly concentrated point source. A disadvantage, however, are ecological and social problems that can arise from biomass recovery. Compared to other BECCS approaches that produce hydrocarbon-based energy carriers, the theoretical relative carbon dioxide removal potential of HyBECCS technologies is higher. For example, in biogas or biomethane production with carbon capture and storage (CCS), a stoichiometric fraction of the carbon from the biomass remains in the energy carrier methane (CH_4). This carbon is usually distributed, e.g. as fuels for transport applications or heating, and emitted as CO_2 during biogas or biomethane combustion. The distribution complicates the capturing of the GHG. In HyBECCS projects, the carbon-free energy carrier H_2 is produced (and distributed), and CO_2 can be captured centrally at the biohydrogen plant site as a point source. Thus, the main technical advantage of HyBECCS is the thermodynamically efficient capture of a large share of CO_2 from biomass.

Further, the role of HyBECCS in future energy systems is analyzed. Key societal and technological drivers are discussed. At the example of the FRD, ecological impacts on GHG emissions for Germany are estimated briefly. The determination is based on the example of dark fermentation (DF) as the biohydrogen production technology choice. A theoretically possible annual production capacity of hydrogen in the amount of about 9.9–19.9 TWh/a is therefore adopted from Weide et al. (2020, p. 6) for the reference year of 2030. This assumption is based on estimates for theoretically available biogenic residual materials in Germany derived from Brosowski et al. (2016, p. 266-268) and shows how high the theoretical H_2 potential through DP would be if all available waste streams were used. The average value for the theoretical hydrogen yield per ton of residual materials is therefore assumed to be 90 - 180 litres of hydrogen per kilogram of organic dry matter according to Weide et al. (2019, p. 24114-24117). Based on this data, an initial estimation of the theoretical maximum emission reduction potential through substituting natural gas could be made, resulting in an amount of 2.0–4.0 Mio. tCO_2eq/a. However, alternative uses and competition for biomass are not taken into account in this analysis. Since all types of biomass are limited and can have multiple end uses, as analyzed by the European Environment Agency (EEA 2023, pp. 19-21), for example, this leads to resource conflicts and trade-offs. These are not taken into account in this example, thus these results can only be considered and classified with these limitations in mind, as explained further in chapter 6. Refinement of the theoretical potential to a sustainable potential through further work is strongly recommended by the author of this thesis. In addition, GHG emissions from biomass production, transport and pretreatment, the biohydrogen production process and hydrogen distribution and usage, as well as for the carbon dioxide capturing, transport and storage are neglected. Based on stoichiometric conditions, the same amount of biogenic CO_2 (in moles) as hydrogen produced is assumed to be generated through dark fermentation. This number leads to the potential estimation for capturable and storable biogenic CO_2. It also represents the maximum possible potential for negative GHG emissions, which is determined at 6.4–13 Mio. tCO_2/a. The total ecological potential in terms of GHG emissions sums up to 8.49 – 17.06 Mio. tCO_2eq/a of maximum possible CO_2 reduction and capture potential. Additionally, the maximum production costs for CNH to be competitive in Germany are estimated, considering hydrogen market forecasts. They would have to be below 4.30 EUR per kg H_2 in a worst-case scenario and below 10.44 EUR per kg H_2 in a best-case scenario.

In conclusion, an outlook from a technical point of view discusses a concept for biorefineries based on the HyBECCS concept. The main gas fractions of HyBECCS technologies, H_2 and CO_2, could therefore be used in a combinatorial way. For example, using H_2 as a reducing agent for CO_2 could serve as a basis for the production of hydrocarbons.

2.2 Summary of Paper B: Exemplary implementation characteristics

Paper B (Full et al. 2023a) is a supplementary contribution describing and analyzing a specific technological implementation approach for the HyBECCS concept, retrofitting existing biogas plants: Biohydrogen production via steam reforming of biogas with carbon dioxide capture and storage (HyBECCS process, process option 2). This option is compared to biomethane production from biogas with carbon dioxide capture and storage (process option 1). Technical, economic, and environmental aspects are considered. The aim is to provide insights into the technical configuration of the HyBECCS process and the tradeoffs that must be considered when retrofitting biogas plants.

First, the technical implementation particularities of the options are described. The focus is laid on the biogas steam reforming process step. Relevant reaction equations and a flow diagram for producing biohydrogen and biogenic carbon dioxide are provided and discussed. The exemplary comparisons for the two process options are carried out based on these technological descriptions.

Considering the energy efficiency, the results indicate that the HyBECCS approach in process option 2 leads to an energy loss of approximately 37% compared to process option 1. This is estimated in terms of the absolute lower heating value (LHV) of the products hydrogen and methane per kg of biomass or biogas input. Expanding the observation system to compare usable driving energy for heavy-duty transport applications, using H_2 produced in process option 2 still results in a comparable energy loss of approximately 4.2%.

To determine the theoretical negative emission potential, the maximum amount of storable biogenic CO_2 was calculated for both process options. In comparison, process option 1 results in a maximum amount of 1.65 kg CO_2 per kg of CH_4 produced, while the HyBECCS approach (process option 2) shows a maximum of 4.4 kg CO_2 for the same quantity of biomass input. This corresponds to about 2.7 times the amount of storable biogenic CO_2, assuming an average composition of the biogas of 37.5 vol% CO_2 and 62.5 vol%.

In the context of this dissertation, the results of Paper B serve to understand technical aspects of the HyBECCS concept better using the example of retrofitting biogas plants with steam reforming technology aiming to provide an application-oriented basis of understanding for the assessment fundamentals described in the following chapter.

3 Assessment Fundamentals

Fundamentals for techno-economic assessment of HyBECCS processes are elaborated in this chapter. Mathematically verifiable prerequisites for the qualification as HyBECCS technologies, uniform system boundaries, key performance indicators (KPIs) and guidelines for GHG emission reduction, GHG removal and bioenergy potential estimations are the main outcomes of this part.

In Paper C, the main contributions regarding techno-economic assessment fundamentals for HyBECCS technologies are made. A transferable definition of system boundaries is developed with associated material, emission and monetary flows. Economic influences and interrelationships between subsystems are specified, and suitable techno-economic KPIs are derived. These include, for example, the levelized costs of carbon-negative hydrogen (LCCNH) and levelized costs of negative emissions (LCNE). A particular characteristic of these indicators is the possibility to include the environmental impact costs due to GHG emissions and removals. Climate change related damage and damage prevention effects can thus be considered in the techno-economic analysis.

Additionally, a methodological approach to support the evaluation of bioenergy potentials for HyBECCS technologies is described in Paper D. A four-step methodical approach dealing with available waste materials, uncertainties of early-stage processes, and calculation aspects provides information on the estimation of usable energy.

3.1 Summary of Paper C: Techno-economic and environmental assessment

Paper C (Full et al. 2022) provides fundamentals for the techno-economic assessment of HyBECCS technologies. It first summarizes and concretizes the characteristics of the HyBECCS concept outlined in Paper A. For this purpose, the state of the art for CCS, NET, CDR and BECCS, to which the HyBECCS concept can be assigned, is presented. Further, an overview of the regulatory status quo of these concepts is given to understand the techno-economic peculiarities of HyBECCS better.

The main outcome of the paper is to provide assessment fundamentals for HyBECCS technologies. Therefore, uniform system boundaries are elaborated first. An overall system boundary, B3, and two subsystem boundaries, B1 and B2, are defined. System elements are assigned to each of the two subsystem boundaries. For B1, the production of biohydrogen and capturing of CO_2 (HyBECC) and for B2, the transport and storage of CO_2 (CS) are determined. In contrast to the four process steps distinguished on a technical basis in Paper A, the HyBECCS process is subdivided with regard to its ecological and economic balancing. As the two system elements, HyBECC and CS, are likely to be spatially and economically separated, they are considered individually. Both system elements combine to the overall HyBECCS technology. Further, mass flows, monetary flows and GHG emission flows are defined for each of the system boundaries. Connections and interrelations between the flows are described in detail. Mass flows can be linked to monetary flows and also to GHG emission flows in the case of CO_2, for instance. GHG emission flows can also be linked to monetary flows. This occurs in the case of economic systems that provide for internalizing the environmental impacts resulting from the GHG emissions.

With this in mind, interrelationships between ecology and economics are discussed. Through internalization mechanisms, the HyBECCS concepts could benefit economically in two different ways. On the one hand, low process GHG emissions throughout the entire HyBECCS value chain would result in a relative cost reduction compared to other processes with higher process emissions. On the other hand, (net) negative emissions would be a source of revenues through internalization approaches like carbon removal certificates (CRC). Accordingly, negative emissions can be considered a product of HyBECCS technologies alongside hydrogen. A simplified basic model for regulatory systems in net-zero emission economies is proposed to translate positive and negative GHG emissions into costs and revenues. This model is based on the assumption that the external costs and benefits for the climate are entirely internalized.

As the next step, requirements for HyBECCS technologies are detailed based on the system boundaries and associated flows. As a first prerequisite, the overall GHG emission flow of system boundary B3 must be negative. To ensure this, all GHG emission flows must be calculated following the ISO standards 14040/44. Considering monetary flows, the overall profit must be positive (P>0) for the HyBECCS technology to be economically viable.

To finally assess HyBECCS technologies, eligibility checks are elaborated at first. These could lead to the exclusion of technologies that cannot meet the requirements for HyBECCS. To check the theoretical ability on a technological level, permanent removal of CO_2 must be ensured. It is recommended to review experience values from literature as they are the only available reference points. Further research is proposed, for example, to create a positive list of appropriate CS technologies. By ensuring negative emissions through calculating the total GHG emission flow in B3, eligibility can be checked on a project level. Eligibility checks on both project and technology levels are recommended in the planning phase of HyBECCS technologies (ex-ante). After implementation, they must be validated in reality (ex-post).

Specific KPIs for the assessment of HyBECCS technologies are elaborated further. They are also based on the system boundaries and flows determined. First, the GHG removal efficiency is examined by introducing the emission factor (EF). The EF (in $tCO_2eq/tCO_2stored$) constitutes the ratio between process GHG emissions emitted within the overall system boundary B3 and the amount of non-fossil CO_2 physically stored. It can be used to quantify the GHG removal efficiency of NETs. For HyBECCS, the EF has to be smaller than one, which is always given if the total emission flow in B3 is negative according to the prerequisite defined. An EF of less than 1 in the case of HyBECCS or BECCS generally means that more biogenic CO_2 is stored than GHG emissions are caused by its extraction and storage. The closer the EF is to zero, the better the GHG removal efficiency of the NET.

To determine techno-economic KPIs, capital expenditures (CapEx), operational expenditures (OpEx), and revenue flows must be obtained for all subsystems. To calculate the CapEx, a decision tree is provided to choose a suitable cost estimation method. The OpEx can be estimated based on the planning status or on experience values. For the internalization costs and revenues, the amounts of the different GHG emission flows are required. They can be adopted using standardized databases for life cycle assessments according to ISO standards 14040/44 and literature values for leakages. Stoichiometric estimation approaches or literature values can be used for estimating biogenic CO_2 production. The translation of positive and negative GHG emission flows into internalization cost and revenue flows can be carried out using the defined basic model for regulatory systems in net-zero emission economies. For this purpose, prices can be assumed that reflect the total societal costs due to GHG emissions.

Both internal and internalized costs and revenues are included in the calculation of two central techno-economic KPIs: The levelized costs of carbon-negative hydrogen (LCCNH) and the levelized costs of negative emissions (LCNE). The costs for the production of the core products (hydrogen and negative emissions) are considered under the assumption of an ideal neutralization of the GHG emissions. Those KPIs allow the comparison of different HyBECCS approaches with other hydrogen production technologies and NETs in terms of their economic competitiveness and environmental performance in terms of GHG emissions. The key points of the KPIs are summarized as follows:

- The LCCNH (in EUR/kWhH_2) constitute the costs incurred to produce 1 kWh (net calorific value) hydrogen with net-negative emissions in a climate-neutralized way.
- The LCNE (in EUR/tCO_2removed) are the costs that occur to achieve one ton of negative CO_2 emissions, i.e. to remove one ton of CO_2 from the atmosphere, in a climate-neutralized way.

Additionally, the levelized costs of stored carbon (LCSC) are defined as follows.

- The LCSC (in EUR/tCO_2stored) are defined as the costs that occur to permanently store one ton of CO_2 with a climate-neutralized process.

Climate-neutralized means, in all cases, that the entire external economic damage or damage avoidance through GHG emissions and removals is internalized according to the basic model for regulatory systems in net-zero emission economies defined.

3.2 Summary of Paper D: Bioenergy and greenhouse gas mitigation potential

In the supplementary contribution Paper D (Full et al. 2021), guidelines to support the determination of bioenergy potential of HyBECCS technologies are presented. It provides information on the amount of usable energy from waste and residue materials after conversion. For this purpose, a four-step methodical conduct is elaborated dealing with available waste materials, uncertainties of early-stage processes, and calculation aspects. Only material flows that do not compete with established, high-value utilization routes such as animal feed are considered. The work focuses on the utilization of waste streams in order to maximize ecology and value creation. As a consequence, particular biomass flows theoretically utilizable for biohydrogen production are discarded, as more sustainable or higher-value utilizations are possible.

At first, the state of the art regarding the legal framework for renewable energy as well as biomass utilization and disposal in Germany is outlined. Moreover, common treatment processes for biomass are presented, briefly touching upon their advantages and disadvantages. The state-of-the-art for biohydrogen production and the HyBECCS technology concept (cf. Paper A) are concretized with regard to the use of the various residues and waste materials. Furthermore, the essential basics of bioenergy potentials are explained. The different levels of utilization pathways, corresponding potential terms and system boundaries for bioenergy potential derivation are summarized.

The four-step methodological guideline elaborated in the main part is suitable to support the determination of the bioenergy potential and negative emission potential of HyBECCS technologies. The first step elaborates a procedure to select relevant biomass categories for hydrogen production. This procedure is divided into six sub-steps and applied through an exemplary biotechnological process. The selected waste types can be translated into technical feedstock potentials using values from further literature. Secondly, suggestions are made for making assumptions and defining framework conditions. Regarding biomass pretreatment, suitable methods or method combinations for the selected waste types are identified, and estimation approaches for their respective energy demands are provided. Further, suggestions for process energy demands are made, and peculiarities for logistics, substrate storage, and handling of residues and produced gases are discussed. In the third step, the equation for determining the bioenergy potential of HyBECCS processes is derived starting from the fuel potential of hydrogen and considering the energy efficiencies of the conversion steps. The energy demands for substrate pretreatments, as elaborated in the work, and for process operation are included. Both reduce the overall potential bioenergy output. The resulting bioenergy potential represents the utilizable amount of energy after conversion, reduced by the amount of energy consumed throughout the value chain. Finally, potentials for climate change mitigation are discussed in step four. A calculation equation to estimate the maximum potential for GHG reduction through substituting fossil energy carriers is derived. Subsequently, the calculation of the theoretical amount of storable biogenic carbon dioxide representing the theoretically achievable negative emission potential is outlined. Therefore, the product gas flow in the respective biohydrogen process and its CO_2 content must be known or estimated. However, process GHG emissions, leakages and risk deductions must be considered from this maximum potential, as described in detail in Paper C.

Concluding, in Paper D, guidelines for estimating bioenergy potentials specifically tailored for biohydrogen production and HyBECCS processes in the German energy and waste system are elaborated. It helps to establish a generally accepted method to determine bioenergy potentials to make their quantification more accessible and consistent. It can also support technology selection based on the suitability of different substrates for HyBECCS approaches, taking into account the available biomass potential in the respective area.

4 Exemplary Assessment

In this chapter, the assessment fundamentals elaborated in Paper C are summarized and applied by means of an exemplary HyBECCS implementation project. The key performance indicators EF, LCCNH, LCNE and LCSC are determined to compare the HyBECCS process with competing hydrogen production technologies and NETs. The main objective of this chapter is to validate the applicability of the techno-economic assessment fundamentals in practice.

4.1 Summary of Paper E: Exemplary techno-economic assessment

In Paper E (Full et al. 2023b), a techno-economic and ecological assessment is carried out at the example of a theoretical HyBECCS implementation project. The example process created for this purpose combines the microbiological biohydrogen production process "dark photosynthesis" (DP) with the capture and long-term storage of CO_2 in saline formations. The substrate for DP in the example process is fructose-containing waste from fruit processing. The assessment is based on the methodological fundamentals described in Paper C and was conducted primarily to validate them.

At first, the example project is described and the assumptions and framework conditions for the assessment are outlined. These involve the technical plant designs for the process steps, peculiarities for the life cycle assessment (LCA), product yields, economic parameters and surcharge factors for cost estimations. Further, the methodology is described. It strictly follows the guidelines defined in Paper C.

As a first assessment step, eligibility on the technology level is checked for the example project. Waste or residues from fruit processing is assumed as substrate. As fruits are a renewable, fast-growing biomass, the CO_2 in the substrate can be considered to be of biogenic origin. The theoretical permanence of CO_2 storage is given due to the technology choice made for CS. CO_2 storage in saline formations can be considered to be permanent for over 1000 years in the case of a careful site selection (IPCC 2005). Thus, the projects´ eligibility on a technology level is given.

The system boundaries described in Paper C are applied to the example project and are used for the calculation of the GHG emission flows. The results of their balancing (carbon footprint) show that the exemplary HyBECCS project would be capable of generating negative GHG emissions under the assumptions made. It would remove 17.72 $kgCO_2$ from the atmosphere for every kilogram of H_2 produced. Thus, the analyzed exemplary project qualifies to produce carbon-negative hydrogen (CNH) and as a HyBECCS and NET approach. Eligibility on a project level is given. The main share of 74.7 percent of the process GHG emissions within the HyBECC system element is due to the provision of heat for hygienization. Electricity from the German grid accounts for another 15.66 percent. Emissions from the CS system element contribute for a 9.38 percent share. The construction and CO_2 transport remain at 0.24 percent and 0.01 percent, respectively.

In the main section, the KPIs are analyzed and discussed. Compared to other NETs, the GHG removal efficiency represented by the EF (cf. Paper C) of the exemplary HyBECCS project (0.12 $tCO_2eq/tCO_2stored$) is at the lower end of the EF range of both other BECCS and of DACCS approaches. In relation to the resulting process GHG emissions, this indicates a high CO_2 capture potential of the considered HyBECCS example project.

CapEx estimations result in a total of 9,871,401 EUR for the example project. They can be split into 55 percent on the system element HyBECC and 45 percent on the system element CS. Total plant costs (TPC) and direct and indirect costs (DIC) of system element HyBECC account for 28 percent and 27 percent of the total CapEx respectively. The substrate management has the largest share of the TPC with 43 percent, and third largest share of total CapEx with 12 percent. Total OpEx sum up to 2,188,964 EUR per year. Heat accounts for the largest share of OpEx with 32 percent, followed by personal expenses with 22 percent, process water with 14 percent and CS (incl. transport and monitoring) with 12 percent.

The LCCNH were calculated, based on the assumptions made, to be 0.013 $EUR/kWhH_2$. Compared to grey hydrogen from natural gas (0.12 $EUR/kWhH_2$) and green hydrogen from electrolysis using renewable electricity (0.18 $EUR/kWhH_2$), this indicator points to a clear advantage of the HyBECCS project. Even without the assumed internalization of GHG impacts, the calculations of internal LCOE indicate an economic advantage of the exemplary project (0.12 $EUR/kWhH_2$) over green hydrogen from electrolysis (0.17 $EUR/kWhH_2$).

The LCSC of the exemplary project was calculated at -260 $EUR/tCO_2stored$ and the LCNE at -297 $EUR/tCO_2removed$. This means that the exemplary project generates an income of 297 EUR per ton of CO_2 removed from the atmosphere due to the sales of the co-product biohydrogen. For BECCS, literature shows a LCNE cost range of approx. 39-367 $EUR/tCO_2removed$ and for DACCS of approx. 25-1,127 $EUR/tCO_2removed$. This indicates a high level of economic viability and competitiveness of the exemplary HyBECCS project with other NETs.

A sensitivity analysis is performed to identify the parameters that affect the results most significantly. It shows that the GHG internalization costs and revenues, H_2 and CO_2 yield and the total OpEx have the greatest impact on the LCCNH. The H_2 and CO_2 yields have the greatest effect on the LCCNH, when being reduced. A reduction of the yields causes the LCCNH to converge to infinity. Increasing the total OpEx and decreasing the GHG internalization costs and revenues also have a comparatively high impact driving up the LCCNH. The highest value for LCCNH was calculated at 0.1417 EUR/kWh for reducing the H_2 and CO_2 yield by 50 percent. The lowest value for LCCNH was calculated at -0.0384 EUR/kWh for increasing the GHG internalization costs and revenues by 50 percent. The influences of the parameters on the LCNE show that the H_2 sales price has the greatest impact. While a 50 percent reduction would lead to a cost increase of 91 percent to -25.89 EUR/tCO_2removed, a 50 percent increase would reduce the LCNE by 91 percent to -567.48 EUR/tCO_2removed. Similar to the influences on LCCNH, the H_2 and CO_2 yield and the OpEx have a considerably high impact on the LCNE.

In conclusion, the HyBECCS technology could be evaluated and compared with other hydrogen production methods and NETs. In addition to classical techno-economic evaluation approaches, the economic consequences due to the impact on the global climate were taken into account. Therefore, the validation of the assessment fundamentals at the exemplary project was successful.

5 Contributions Overview

The publications (Paper A-E) on which this work is based are connected, as illustrated in Figure 5-1. The core results developed within those publications are presented in the chapters 2-4. As described in section 1.3, two publications contribute to the HyBECCS concept (chapter 2) and the assessment fundamentals (chapter 3), respectively. In each case, one of the papers constitutes the main contribution and the other one provides additional findings, as depicted in Figure 1-2. The exemplary assessment (chapter 4) is covered by a single publication (Paper E). The connections between the chapters and contributions are discussed in the following.

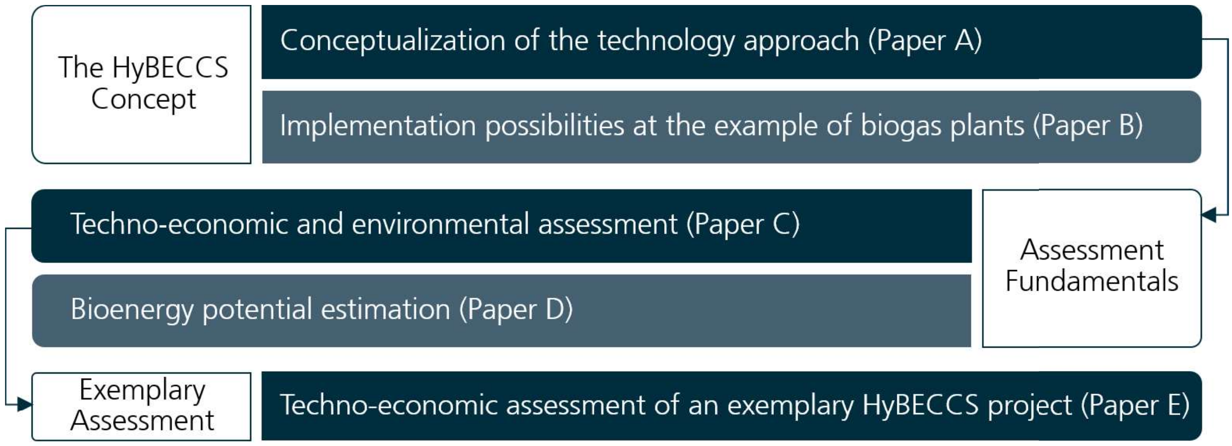

Figure 5-1 Structure and connections of the results of the work

Chapter 2 mainly provides for a better understanding of the technical basis, characteristics and prerequisites of the HyBECCS concept. The work starts with the introduction and conceptualization of the approach. It comprises a modular-based combinatory system. This consists of four sub-processes with respective technology options, as outlined in Paper A. Additional information is given in Paper B considering opportunities for biogas plant retrofits as a specific, application-oriented implementation area.

The fundamentals for techno-economic assessment are elaborated in chapter 3. With regard to the creation of standardized techno-economic assessment guidelines and KPIs, the HyBECCS concept is further abstracted. The most important contributions to this are derived in paper C. Essential outcomes of this work are uniform system boundaries with respective monetary, mass and GHG emission flows. Based on this framework, the key performance indicators EF, LCCNH, LCNE and LCSC are defined. They serve as a benchmark to compare price scenarios and cost forecasts. The LCCNH can be used to compare HyBECCS technologies to other hydrogen production technologies. The LCNE and LCSC serve to compare NETs in terms of their cost efficiencies. Paper D supplements the assessment fundamentals with a special look at biomass residues and waste materials to be utilized by HyBECCS technologies. Basic instructions for selecting suitable waste materials and estimating the respective bioenergy potentials are laid out. It raises awareness of the high importance of biomass substrate selection for HyBECCS technologies.

The exemplary techno-economic assessment conducted in chapter 4 focuses on applying the results derived in Paper C. The work carried out in Paper E aims to validate the suitability and applicability of the methodological guidelines and KPIs developed. For this purpose, an exemplary process combination is defined and described in detail. Based on this process combination, an exemplary HyBECCS implementation project is defined. All associated assumptions relevant to the techno-economic assessment are derived and described. The system boundaries proposed in Paper C are applied and the related monetary, mass and GHG flows are determined. The KPIs EF, LCCNH, LCNE and LCSC are calculated and discussed. It is shown that the theoretical fundamentals elaborated can be implemented in practice. A comparison of the exemplary HyBECCS project with other NETs and hydrogen production technologies is carried out successfully in this work.

Additionally, the publications on which this thesis is based contain partial results that are not directly related to each other. Paper B and Paper D, in particular, contain additional findings that contribute to a better understanding of the work but are not essential to the overall context. However, they have relevance for the entire work as additional contributions to the overall thread of the thesis. This mainly runs through Paper A, Paper C, and Paper D.

6 Critical Reflection and Limitations

In this chapter, various aspects that limit the applicability of the results are discussed, and further issues that significantly influence their practical application are outlined.

First, it has to be clearly stated that this work focuses on providing fundamentals for techno-economic assessments but does not make specific recommendations for individual technologies, such as dark fermentation (Paper A), biogas steam reforming (Paper B), or dark photosynthesis (Paper E). It is important to acknowledge that HyBECCS technologies are at an early stage of development, which introduces considerable uncertainties in their evaluation. Practical implementations may yield widely varying results, making it challenging to predict the precise ecological impacts and economic outcomes of these technologies. Hence, although the HyBECCS concept´s peculiarities and fundamentals for techno-economic assessment have been elaborated in the best possible view of technical realization, they must not be misinterpreted as results for the evaluation of specific technological approaches. All assumptions are solely made to demonstrate the applicability of the assessment fundamentals provided.

Second, deep and critical evaluations of the biomass substrate used for HyBECCS processes are essential for their assessment. In this work, the focus lays on the value chain parts after the biomass supply. However, the choice and production pathways of biomass for use in bioenergy processes profoundly impacts their sustainability. In general, when assessing the role of biomass supply in climate impacts, it is crucial to consider the overall greenhouse gas emissions in agriculture, forestry and other land use (AFOLU) and the food system by examining the links between production, consumption and trade (Blandfort & Hassapoyannes 2018, p. 34). According to the IPCC (2023, p. 44), AFOLU contributed to approximately 22% of total anthropogenic GHG emissions in the reference year of 2019. Within this, biomass generation impacts climate change directly through emissions of N_2O, CO_2 and CH_4. Further, agricultural activities can affect the capacity of soils to absorb and store carbon (soil carbon sequestration). Therefore they additionally contribute indirectly through their impact on land use and land-use change. Significant influences of the biomass production on bioenergy processes have been shown in many cases. For example, Lask et al. (2018) analyzed the environmental impacts of ethanol production from miscanthus grown on marginal land in an average-yield site in Germany. They show that biomass cultivation and harvest accounts for 16.5-18.0 kg CO_2eq per GJ, which corresponds to about 33-62 % of the GHG emissions of the ethanol production pathways considered (Lask et al. 2018, p.276-277). A further aspect is the transportation of biomass to the processing sites. It can contribute significantly to the overall GHG emissions of the value chains. At the example of the production, storage, (un)loading and transportation over 100 km of baled and chopped miscanthus analyzed by Smeets et al. (2009), the transport by truck contributes up to 20% of the total GHG emissions (Smeets et al. 2009, p. 1239). Understanding these impacts is crucial for the overall assessment of all bioenergy processes, including HyBECCS. Against this background, it must also be clearly stated that it is not enough to rely on the use of organic residual and waste materials, as their sustainability is not guaranteed. The varying effects of the biomass substrates used for bioenergy production are outlined by Tonini et al. (2016), for example. They compared greenhouse gas emission factors (EFs) for bioelectricity, biomethane, and bioethanol produced from various biomasses, including manures, wood residues, and food waste. The EFs show wide ranges for the various options. For example, in biomethane production through anaerobic digestion, the EFs differ widely for specific substrates, such as manures or household food wastes (-104 to -44 g CO_2eq / MJ), straw/stover, wild grass or seaweed (20–51 g CO_2eq / MJ), perennial crops like miscanthus or willow (10–40 g CO_2eq / MJ), annual energy crops like wheat grain (100 g CO_2eq / MJ), and agro-industrial residues like potato pulp (200 g CO_2eq / MJ) (Tonini et al. 2016, p. 129). Further, the availability of biomass sources is also strictly limited and subject to resource conflicts. For example, increased competition for waste and residues may occur in countries with developed economies due to a growing demand for bioenergy (Muscat et al. 2020, p. 4). As highlighted by the European Environment Agency (EEA 2023), many trade-offs must be considered for biomass use in terms of food and energy supply, nature conservation, pollution reduction and climate change mitigation. They conclude that, due to the different roles envisaged for biomass and a potential shortage of biomass supply in the future, decisions are pending on how and for what purposes biomass should be prioritized (EEA 2023, p. 9). Many studies deal with the uncertainties that arise e.g.

from these open decisions by using assumptions or idealizations in their scenarios. For example, Paper A in this work refers to an estimate of the theoretical potential for biohydrogen production from Weide et al. (2020, p. 6) which is based on theoretically available biogenic residual materials in Germany derived from Brosowski et al. (2016, p. 266-268). They assume that all available waste streams were used for biohydrogen production without considering alternative uses. However, the advantages and disadvantages of HyBECCS processes must be compared with other utilization methods for the restricted biomass available. Hereby, the manifold mechanisms that drive competition for biomass use and their interactions should be considered from the perspective of different disciplines like ecology, social science and agro-economy (Lewandowski 2015, p. 39). One prerequisite for the production of biomass for energy use, for example, is that priority is given to the demand for food, industrial roundwood and traditional wood fuel (Smeets et al. 2007, p. 95).

Third, considering the ecological effects of HyBECCS technologies as a part of the techno-economic assessment, a focus is set exclusively on the impact category of global warming potential. For instance, the EF aims to serve as a basis to compare NETs regarding their GHG removal efficiencies. The LCCNH, LCNE and LCSC also integrate solely GHG footprints. This is due to the main objective of the considered technology concept for climate protection. However, other ecological impact categories remain unconsidered. These include, for example, acidification and eutrophication potential or photochemical oxidant formation, ozone layer and abiotic depletion. In a broader view, since HyBECCS represents a BECCS technology, this novel approach is subject to all sustainability criteria of BECCS technologies. Therefore, all potential issues coming from biomass use should be carefully considered. Secure food supply, avoidance of land degradation and land use conflicts, conservation of water resources, as well as preservation of biodiversity should be taken into account (Fajardy 2019). Moreover, additional ecological risks and side effects related to carbon dioxide storage have to be considered. For instance, overpressure at CS could lead to the pollution of potable water, seismic activity or leaks, which could not only rapidly reverse positive mitigation effects but cause environmental and health damage at the leakage sites, are further potential issues to be addressed (Fuss et al. 2018, p. 14).

Moreover, economic influences from GHG balances are integrated into the key performance indicators LCCNH, LCNE and LCSC, following an idealized exemplary basic model for HyBECCS regulatory systems in carbon-neutral economies. This leads to all of those KPIs only being valid as long as no GHG emission internalizations are part of the internal cost calculations or if they are vanishingly small. Internalizations could be included, for example, with the costs for electricity, heat or fuels for transport. Additionally, internalizations already contained in the values of the LCOE of the comparative technologies must be considered. In this work, the internalizations are negligible in contrast to the assumed internalization prices based on the societal costs of carbon. Those are included in the KPIs separately, as defined. However, GHG emission internalizations would have to be considered and deducted from the internal cost calculations, especially in the case of future increases in internalization costs.

As described by Ulrich and Hill, scientific thinking is characterized by a conscious willingness to constantly test the correctness of the assumptions made (Ulrich & Hill 1976, p. 305). Considering the HyBECCS concept introduced in chapter 2, many of the related technology options for the sub-processes are already known and tested individually. However, a coherent HyBECCS process chain has never been implemented in reality. The concept´s technical feasibility has, therefore, only been demonstrated for individual approaches of the respective sub-process steps. The demonstration of a complete process chain is still pending. Further, there is no claim to completeness of the technology options under consideration. The possibilities and combinations are numerous and not defined conclusively. Moreover, further technology options are likely to be developed in the future, expanding the range of technical implementation possibilities. In particular, the exemplary HyBECCS project used as a validation example in chapter 4 has also not been implemented. The results strongly depend on the assumptions made and their respective uncertainties. Although this is demonstrated and discussed in the paper through a sensitivity analysis, further unconsidered characteristics may arise during implementation in reality. Moreover, the exemplary process analyzed in this paper is only one technological HyBECCS approach, amongst many others. It was used to achieve the primary objective of applying and validating the assessment fundamentals described in Paper C. It provides a better understanding of the theoretical basics and thus a better applicability in practice. However, the exemplary HyBECCS project and analysis results are not representative of HyBECCS technologies in general. They only apply to the technology combination considered under the assumptions made.

In conclusion, this work provides techno-economic assessment fundamentals for HyBECCS processes. There is a multitude of external factors that greatly influence the assessment results. These have been considered but cannot be fully covered in a single work. Calculating greenhouse gas footprints for substrate biomass, considering further environmental impact categories, limitations in sustainable biomass availability, and the technical uncertainties surrounding emerging technologies all play pivotal roles. Further research is essential to address these crucial aspects comprehensively and refine the assessment fundamentals of HyBECCS processes provided within this dissertation.

7 Summary and Outlook

Negative emission technologies are very likely to be inevitable to limit global warming to 1.5 °C above pre-industrial levels (IPCC 2018, p. 17). In this doctoral thesis, a concept for a negative emission technology is introduced that combines hydrogen production from renewable biomass, preferential biogenic residues or waste, with carbon capture and storage. This concept is referred to as HyBECCS (hydrogen bioenergy with carbon capture and storage). HyBECCS is not a single technology but can be implemented with many different technological options. The objective of the work is to establish a general and comprehensive basis for techno-economic assessment of these individual technologies. This basis should enable technology comparisons with other hydrogen production technologies and NETs regarding their techno-economic performance. A special focus is placed on the integration of climate protection aspects and resulting impacts on the economy. Figure 6-1 illustrates the basic structure of the work, as outlined in section 1.3. The contributions made to answer the research sub-questions derived in section 1.2 are explained below.

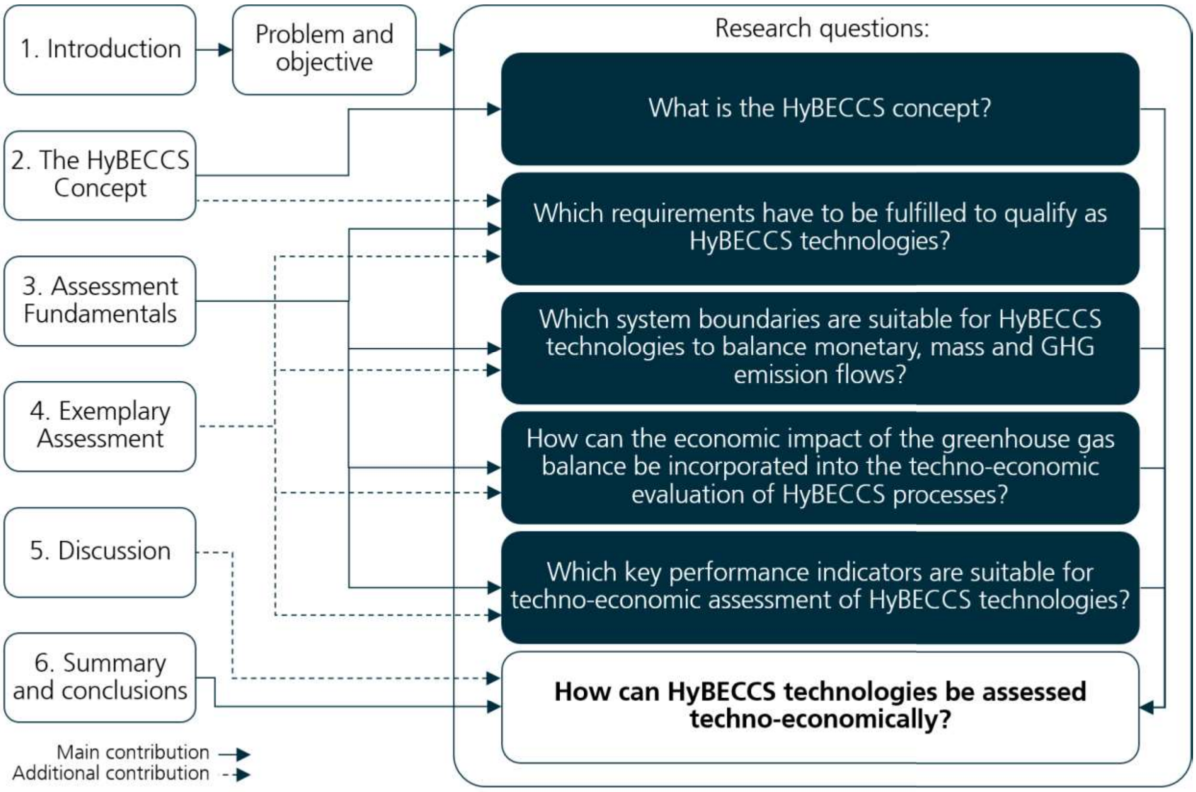

Figure 7-1 Summary of the work: Main structure, paper contributions and connecting points to the research sub-questions.

In the first chapter, the initial situation is described in section 1.1, starting with the problems arising from climate change. The role of carbon dioxide removal (CDR) in limiting global warming to 1.5 °C above pre-industrial levels is explained and technical options for NETs are discussed. They include bioenergy with carbon capture and storage (BECCS) approaches like HyBECCS and direct air carbon capture and storage (DACCS), among others. The important factor for NETs is the carbon dioxide source. It must be either of atmospheric or biogenic origin. CCS alone or based on CO_2 from fossil origin does not remove CO_2 from the atmosphere.

Furthermore, the objective of the work is derived in section 1.2. The research gap of a missing basis for the techno-economic assessment of HyBECCS technologies is outlined. It leads to the derivation of research questions. Hereby, the main question on how HyBECCS technologies can be assessed techno-economically is further subdivided into five sub-questions, as depicted in Figure 6-1.

In section 1.3, the research process and the basic structure of the work are explained. The interconnections between the single contributions are explained and references to the research questions derived in 1.2 are made. The contributions to the research process according to Ulrich as well as the research questions addressed in the respective chapters and publications (A-E) are described briefly (Ulrich 2001, p. 195).

Moreover, the philosophy of science is explained in section 1.4, assigning the work to the applied sciences. This is due to the practical relevance of the outcomes. They aim to provide appropriate tools for changing reality in a complex social system through methodological advice for private and political decision-making. In particular, the work is also linked to technical sciences as the actual and possible actions are associated with a novel technology concept introduced in this work.

The first research sub-question *„What is the HyBECCS concept?"* is answered in chapter 2 introducing the definition of HyBECCS and outlining the peculiarities of the concept. Preparatory to answering the second sub-question *„Which requirements have to be fulfilled to qualify as HyBECCS technologies?"*, a definition of basic requirements is paved by the technical abstraction and classification of HyBECCS as a NET and CDR option.

For this purpose, the HyBECCS technology concept and the associated scientific foundations are introduced and explained first. Significant contributions to this part are covered in Paper A. It summarizes the state of the art in science and technology for hydrogen technologies and NETs to derive the basic HyBECCS concept. The HyBECCS concept is introduced as a novel option for BECCS. It is based on the physical-technical fact that large shares of highly concentrated biogenic CO_2 are produced as a by-product during most biohydrogen production processes. The combination of biohydrogen production with CCS results to the HyBECCS technology concept as a new perspective for CDR.

The concept is further abstracted into four basic technical process steps: biomass pretreatment, biohydrogen production, product gas separation and its processing and use or storage. Different technological options can be selected for all steps. As a prerequisite for every HyBECCS technology, the GHG balance of the overall process chain must be negative. To calculate the GHG balance, the amounts of physically captured and stored biogenic CO_2 can be subtracted from the GHG emissions resulting from all sub-processes. After the deduction, the total process GHG emissions must be negative for the produced hydrogen to qualify as carbon-negative hydrogen (CNH). Moreover, technical advantages of HyBECCS technologies in comparison with other NETs are indicated in Paper A. Potentially high capture capabilities for biogenic CO_2 with comparatively low energy inputs are highlighted as the main technical benefits of the approach. Additionally, based on further literature, a theoretical maximum amount of GHG emissions to be avoided through the substitution of natural gas with biohydrogen produced by dark fermentation, as well as the maximum amount of sequestrable biogenic CO_2, is estimated for the geological and political area of the FRG and the reference year 2030.

Additional contributions on more specific application possibilities are made in Paper B, considering the technology option of retrofitting biogas plants to HyBECCS facilities. The technical process of biogas steam reforming is described and discussed considering technical and economic aspects.

In chapter 3, the basis for techno-economic assessment of HyBECCS technologies is introduced. Research sub-question 3 *„Which system boundaries are suitable for HyBECCS technologies to balance monetary, mass and greenhouse gas emission flows?"* is answered by separating the overall concept into two system elements: Biohydrogen production with carbon dioxide capture (HyBECC) and carbon dioxide transport and storage (CS). For both system elements, separate subsystem boundaries B1 and B2 are determined. Monetary, mass and GHG emission flows are defined for each subsystem boundary. They combine to the overall HyBECCS system boundary B3.

These abstractions allow the basic prerequisites for HyBECCS technologies to be substantiated from a mathematically accessible point of view and the definition of specific KPIs. An important value for validating the prerequisite of negative emissions is the emission factor (EF). It relates the process emissions caused over the entire process chain to the physically stored amount of biogenic CO_2. This value must be less than 1 for the HyBECCS approach to qualify as NET and the hydrogen produced as CNH. If the value exceeds 1, more GHG emissions are released over the entire process chain than are removed from the atmosphere. From an economic point of view, it is required to make a profit P. The correlations for the value P are described in the work. It must be above zero for HyBECCS technologies to be economically viable. The mathematical evaluation correlations for both the basic requirements of HyBECCS technologies profitability (P<0) and qualification as a NET (EF<1) are thus completed in this paper, answering research question 2 conclusively.

Sub-question 4 *„How can the economic impact of the greenhouse gas balance be incorporated into the techno-economic evaluation of HyBECCS processes?"* is answered by discussing the correlations between GHG emissions and economic effects of HyBECCS technologies. Internalization of economic damages caused by GHG emissions or benefits that occur through avoiding the damages are identified and described as a link between ecology and economy. Negative emissions, as one of the main products of HyBECCS processes, and emission reductions do not represent an individual, internal benefit but an overall societal, external benefit. Conventional market-based mechanisms and tools are, therefore, not sufficient to make such processes economically viable. The answer to the question lies in the instrument of internalization. Through internalization mechanisms, the HyBECCS concepts could benefit economically in two different ways: Relative cost reductions against competing technologies with higher process emissions and revenues for generating negative emissions. Internalization mechanisms are described specifically for the HyBECCS concept in chapter 3.

Sub-question 5 *„Which key performance indicators are suitable for techno-economic assessment of HyBECCS technologies?"* is answered by defining and applying appropriate KPIs. The LCCNH, LCNE and LCSC are introduced as key KPIs. The LCCNH constitute the costs incurred to produce 1 kWh (net calorific value) hydrogen with negative emissions in a climate-neutralized way, i.e. fully internalize the economic impacts of GHG emissions and removals. The LCNE are the costs that occur to remove one ton of CO_2 from the atmosphere in a climate-neutralized way, and the LCSC are defined as the costs that occur to permanently store one ton of CO_2 in a climate-neutralized way. All of these KPIs assume ideal internalizations of GHG emissions and reductions. This means that the entire external economic damage or damage avoidance through GHG emissions and removals is assumed to be internalized. For this assumption, a basic model for regulatory systems in net-zero emission economies is defined.

In chapter 4, the assessment fundamentals derived in Paper C are applied using an exemplary HyBECCS technology. By successfully performing the techno-economic assessment, research sub-questions 2-5 are answered conclusively, evaluating the applicability of the assessment tools provided. The contributions to this part are described in Paper E. At the example of a

HyBECCS technology approach based on the „dark photosynthesis“ process and carbon dioxide storage in saline formations, the EF, LCCNH, LCNE and LCSC are determined and discussed. The exemplary assessment leads to a better understanding of the assessment principles and serves as a guide for application in practice. The results show that the exemplary project would be capable of generating CNH, removing 17.72 kgCO_2 from the atmosphere for every kilogram of H_2 produced. Capital expenditures are estimated at 9,871,401 EUR, and operational expenditures at 2,188,964 EUR per year. The LCCNH are estimated to be 0.013 EUR/kWhH_2. Compared to grey hydrogen from natural gas (0.12 EUR/kWhH_2) and green hydrogen from electrolysis using renewable electricity (0.18 EUR/kWhH_2), the results indicate a high level of economic viability. Even without the assumed internalization of GHG impacts, the calculations point to an economic advantage of the exemplary HyBECCS project (0.12 EUR/kWhH_2) over green hydrogen from electrolysis (0.17 EUR/kWhH_2). Converted to EUR/kgH_2, the internal LCOE of the HyBECCS project amounts to approx. 4 EUR/kgH_2. These costs are below the estimated maximum total costs to be competitive in Germany of 4.30 EUR/kgH_2 in the worst-case scenario of Paper A. Compared to other NETs, the GHG removal efficiency represented by the emission factor (EF) of 0.12 tCO_2eq/tCO_2stored is at the lower end of the EF range of both other BECCS and DACCS approaches. The LCSC of the exemplary project was estimated at -260 EUR/tCO_2stored, and the LCNE at -297 EUR/tCO_2removed. This can be interpreted for the exemplary project to be capable of generating a respective income per ton of biogenic CO_2 stored (LCSC) or removed from the atmosphere (LCNE). The income is mainly due to the sales of the co-product biohydrogen. For BECCS, the LCNE cost range is estimated at approx. 39-367 EUR EUR/tCO_2removed and for DACCS approx. 25-1,127 EUR/tCO_2removed. This indicates a high level of economic viability and competitiveness of the exemplary project with other NETs.

It is shown that the theoretical assessment fundamentals elaborated in this doctoral thesis can be implemented in practice. A comparability of the exemplary HyBECCS project with other NETs and hydrogen production technologies in terms of their techno-economic performance was achieved. It was also possible to specifically evaluate the economic influences for society coming from GHG emissions for the technologies under consideration. The analysis shows that the findings can support technology providers and investors in decision-making. In addition, especially through the integration of climate protection aspects and resulting impacts on the economy, the assessment fundamentals can also serve as a guideline for political decision-making. The objectives of the work, as stated in section 1.2, are thus fulfilled

However, the results are discussed in chapter 5. Core findings and limitations are derived to give further practice advice for the techno-economic assessment of HyBECCS technologies. For this purpose, parts from all five papers are included in the discussion. Important limitations include the fact that the assumptions made have yet to be validated ex-post based on a real example process. Further, the exclusive consideration of GHG emissions when integrating environmental effects into the assessment is discussed, and the limits of applicability of the defined KPIs are stated. If GHG emission or removal internalization cannot be separated from or neglected within cost and revenue calculations, the KPIs are not applicable.

In conclusion, the central research question on how HyBECCS technologies can be assessed techno-economically has been answered delivering the main outcomes of the work, as summarized in the following bullet points:

- A comprehensive technology concept that describes different process combinations for HyBECCS has been elaborated.
- Requirements and prerequisites for their suitability as NET have been defined, and fundamental assessment tools for their verification have been provided. They make sure that the technologies are economically viable and actually provide negative emissions.
- Standardized rules, system boundaries and key performance indicators for HyBECCS technologies have been derived. They serve to compare HyBECCS technologies with other hydrogen generation technologies (LCCNH) and NET (EF, LCNE, LCSC)
- The added value for society, including economic effects resulting from climate change mitigation, can be depicted analyzing the KPIs. The connection between economic sustainability and the impact on the global climate is thus made tangible.
- A techno-economic assessment of an exemplary HyBECCS implementation project has been conducted to validate the applicability of the elaborated fundamentals in

practice. It has been shown that decision-making for private investments and public subsidies can be supported with the fundamentals provided.

Both the HyBECCS concept and the assessment fundamentals elaborated in this doctoral thesis should be further developed. Considering the HyBECCS concept, in this work, the focus is placed on the use of hydrogen and the storage of biogenic CO_2. However, possibilities for biohydrogen production with CO_2 capture and utilization (HyBECCU) could further increase the economic perspectives. As outlined in Paper A, a coupled use of biohydrogen for the chemical reduction of CO_2 aiming to create higher-value products is a promising approach for HyBECCU. Yet, higher risk of reversals, insecurity concerning the time horizon of storage, and challenges such as monitoring the permanence should be taken into account considering CU (Otto et al. 2017). It has to be clearly stated that CO_2-based products from HyBECCU with short lifetimes before re-emitting the CO_2, such as fuels or disposable plastic products, are not capable of achieving negative GHG emissions.

Further investigations should also be conducted to improve and extend the techno-economic assessment basis. For example, as CS technologies and NETs are associated with different time horizons of storage and risks of reversal, these factors have not been considered yet. They should be taken into account within further research activities to raise the comparability of different NETs and CS technologies. Respective advancements of the KPIs derived in this work are advisable.

Social and political framework conditions should also be adapted. Establishing a certification system for carbon-negative hydrogen, which can ensure that the product has a negative carbon footprint, could help to ensure widespread and long-term acceptance. This could be based on the assessment fundamentals elaborated within this work.

8 Literature

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Appendix A: Paper A

Contributions to the work

Title: A New Perspective for Climate Change Mitigation - Introducing Carbon-Negative Hydrogen Production from Biomass with Carbon Capture and Storage (Hybeccs)

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A New Perspective for Climate Change Mitigation—Introducing Carbon-Negative Hydrogen Production from Biomass with Carbon Capture and Storage (HyBECCS)

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Abstract: The greatest lever for advancing climate adaptation and mitigation is the defossilization of energy systems. A key opportunity to replace fossil fuels across sectors is the use of renewable hydrogen. In this context, the main political and social push is currently on climate neutral hydrogen (H_2) production through electrolysis using renewable electricity. Another climate neutral possibility that has recently gained importance is biohydrogen production from biogenic residual and waste materials. This paper introduces for the first time a novel concept for the production of hydrogen with net negative emissions. The derived concept combines biohydrogen production using biotechnological or thermochemical processes with carbon dioxide (CO_2) capture and storage. Various process combinations referred to this basic approach are defined as HyBECCS (Hydrogen Bioenergy with Carbon Capture and Storage) and described in this paper. The technical principles and resulting advantages of the novel concept are systematically derived and compared with other Negative Emission Technologies (NET). These include the high concentration and purity of the CO_2 to be captured compared to Direct Air Carbon Capture (DAC) and Post-combustion Carbon Capture (PCC) as well as the emission-free use of hydrogen resulting in a higher possible CO_2 capture rate compared to hydrocarbon-based biofuels generated with Bioenergy with Carbon Capture and Storage (BECCS) technologies. Further, the role of carbon-negative hydrogen in future energy systems is analyzed, taking into account key societal and technological drivers against the background of climate adaptation and mitigation. For this purpose, taking the example of the Federal Republic of Germany, the ecological impacts are estimated, and an economic assessment is made. For the production and use of carbon-negative hydrogen, a saving potential of 8.49–17.06 $MtCO_{2,}eq/a$ is estimated for the year 2030 in Germany. The production costs for carbon-negative hydrogen would have to be below 4.30 € per kg in a worst-case scenario and below 10.44 € in a best-case scenario in order to be competitive in Germany, taking into account hydrogen market forecasts.

Keywords: negative emission technologies; carbon dioxide removal; HyBECCS; hydrogen bioenergy with carbon capture and storage; biohydrogen; carbon-negative hydrogen; climate positive hydrogen; CCS; BECCS; DACCS; NET; CDR

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1. Introduction

The Paris Accord was adopted in 2015 to significantly limit the risks and impacts of climate change. The participating nations committed themselves to keeping the increase in the global mean temperature well below 2 K compared to pre-industrial levels and to making efforts to limit the increase even to 1.5 K. To achieve these agreements, measures are to be taken that will lead to a balance of greenhouse gas (GHG) emissions and sinks, i.e., greenhouse gas neutrality, in the second half of the 21st century [1]. Therefore, laws and policies have been introduced worldwide. For example, the European Union (EU) resolved the European Green Deal in 2019, which includes several key measures to reach greenhouse gas neutrality by 2050 within the EU [2]. Numerous resolutions and legislations were also passed at national levels. The Federal Republic of Germany, for example, has set the Climate Protection Program 2030 and the Climate Protection Act, which came into force in December 2019 [3,4].

Burning fossil fuels for gaining energy has the greatest impact on climate change in industrialized nations. Energy-related emissions account for about 81% of greenhouse gas emissions across Europe [5] and about 85% in Germany [6]. The steady expansion of renewable energy is therefore considered a key lever for reducing greenhouse gas emissions. These efforts currently take into account mainly climate-neutral electrical energy by wind power and solar plants [2,7]. However, some of the greenhouse gas emissions cannot be avoided through electrification and expansion of renewable electricity generation. For example, sectors such as the steel, chemical, and cement industries are particularly difficult to defossilize, because electrification is not sufficient [8–10]. Moreover, in the transport and mobility sectors, complete electrification is hardly feasible, especially for large commercial vehicles or in aviation and shipping, due to the limited gravimetric energy density of currently existing battery technologies [11–15]. Renewable chemical energy carriers with high energy densities, generated either via electrochemical, so-called power-to-x processes or from renewable biomass, are better suited for this purpose [7,16]. In this context, sustainably produced green hydrogen is seen as a key chemical energy carrier of the future [7,10,17,18]. Green hydrogen can be produced through electrolysis using renewable electricity or from renewable biomass, either through thermochemical processes or by using microorganisms and biotechnological methods. Hydrogen produced from biomass is also referred to as biohydrogen and can lead to a more efficient use of biogenic raw materials exploiting residual and waste materials.

However, even with a complete conversion of the electrical energy supply to renewable power generation and a successful defossilization of the heat and transport sectors, residual emissions remain in areas such as agriculture and waste management. These emissions must be compensated to net zero GHG emissions by 2050 [7]. GHG emissions in the earth's atmosphere are therefore to be actively reduced using negative emission technologies (NET). The latest special report by the Intergovernmental Panel on Climate Change (IPCC) outlines development scenarios that could limit global warming to less than 1.5 K. In all success scenarios, NET are essential components that will play an increasingly important role in climate adaptation and mitigation by 2050 [19]. Known NET include technologies that achieve a negative carbon footprint by capturing the greenhouse gas CO_2 and permanently storing (CCS—Carbon Capture and Storage) or using (CCU—Carbon Capture and Utilization) it [19]. The most relevant NETs are the direct capture of CO_2 from ambient air (DACCS) and Bioenergy with Carbon Capture and Storage (BECCS), where energy sources are extracted from the biomass and the resulting co-product CO_2 is captured [19,20].

This paper introduces a new NET concept combining biohydrogen production with carbon capture and storage, referred to as HyBECCS. HyBECCS couples the sustainable production of hydrogen from renewable biomass, for example from residual and waste streams, with efficient CO_2 capture and subsequent storage. The hydrogen produced has a negative carbon footprint and is therefore referred to as carbon-negative hydrogen or climate-positive hydrogen. The technological advantages of this new concept can support climate adaptation and mitigation in the future by approaching the GHG emission problem from two sides. On the one hand, it contributes to the defossilization, bringing more emission-free hydrogen into use, especially for sectors that are difficult to electrify, and, on the other hand, it contributes to the compensation of the remaining residual emissions through the active CO_2 extraction from the atmosphere. The availability and suitability of organic feedstocks, microorganisms, and process technologies, as well as the economic relations and ecological impacts of the HyBECCS approach need to be investigated to be able to solve societal and environmental problems. This paper gives the basics for this purpose through defining the new approach and describing related technologies, discussing technological properties, and assessing ecological and economic benefits for climate adaptation and mitigation using the example of Germany.

2. Objectives and Enablers

The HyBECCS concept describes technology combinations that merge the production of hydrogen from renewable biomass with subsequent carbon dioxide capture and storage or use. The main objectives of the HyBECCS concept introduced in this section are given by climate adaptation and mitigation goals. Hydrogen has a key role to play in this context, as it can greatly contribute to the defossilization of critical industrial areas that are difficult to electrify, such as steel production, chemical industry, cement production, or heavy-duty transport industry. Therefore, many countries have already adopted national strategies to establish sustainably produced green hydrogen as a basic energy carrier. These include, for example, the US, Canada, Japan, France, Norway, the Netherlands, Australia, and Chile [21–28]. The use of carbon-negative hydrogen produced with HyBECCS concepts can additionally compensate for residual emissions by achieving a reduction of the GHG concentration in the atmosphere through active CO_2 capture and storage. For companies, the use of carbon-negative hydrogen offers an opportunity to improve their carbon footprint. Its use can have a positive impact on their GHG emission balances and can make a direct and effective contribution to climate change mitigation. Besides, HyBECCS can contribute to a more efficient use of existing raw materials by residual and waste exploitation. However, to provide sustainable value creation, carbon-negative hydrogen must be competitive and have undergone a holistic ecological analysis to ensure positive environmental impacts. The HyBECCS concept must therefore be ecologically as well as economically analyzed and optimized. Therefore, the most important basis is a technical understanding of the underlying processes, the fundamentals of which are explained in the following sections.

Furthermore, societal, political, and scientific developments that could encourage the dissemination of carbon-negative hydrogen and the application of HyBECCS technologies can be observed. One societal factor that has gained momentum in science and politics in recent years is the so-called biological transformation of the industry and society toward a biointelligent value creation which is closely interlinked with the global efforts of building a sustainable bioeconomy [29–31]. The process of biological transformation describes an increasing use of biology and its materials, principles, and organisms to create new and sustainable value creation systems. This development is enabled by the increasing interconnection of biotechnology, production technology, and information technology. The creation of a sustainable energy supply system is a major field of action and objective of this transformation process, which can lead to a sustainable bioeconomy in the form of a technology-based subsistence economy [32,33]. Key characteristics of these activities are efficient and coupled material and energy carrier cycles as well as utilization cascades which result in energy recovery [29,31,34,35]. Accordingly, the introduced HyBECCS concept can be seen as part of the biological transformation and bioeconomy developments and is likely to be strengthened from the momentum they generate.

3. State of the Art

This section introduces hydrogen usage as an energy carrier and raw material and its particular importance for achieving climate protection targets (Section 3.1). A special focus is placed on the sustainable production of biohydrogen from biomass, as it is the key subprocess for the HyBECCS approach presented (Section 3.2). Further, existing technology approaches for NET are explained, and the respective advantages and disadvantages are discussed (Section 3.3).

3.1. The Future of Hydrogen

Hydrogen as an energy carrier has many advantages and will play an important role in the energy infrastructure and circular economy of the future [36,37]. Since hydrogen can be produced in a climate-neutral manner, and only water is released during its use, it is considered a climate-friendly energy carrier [36–39]. Hydrogen that is produced from renewable sources is generally referred to as "green hydrogen". It is contrasted with the so-called "grey hydrogen", which is referred to as hydrogen produced from fossil, non-renewable sources [18]. Currently, most of the global hydrogen production consists in grey hydrogen produced by steam reforming of fossil natural gas [8,37]. Grey hydrogen can be made carbon-neutral by applying carbon capture and storage (CCS) technology and is then called "blue hydrogen", but it stays a non-renewable source [18,40]. We introduced "carbon-negative hydrogen" to distinguish between carbon-neutral green or blue hydrogen. Due to the high gravimetric energy density and good storage and transportability, there are many possible applications for hydrogen [37]. Fuel cells can be used to generate electric power as well as heat from hydrogen. Hydrogen can also be used as a reducing agent in the steel industry [8]. It is considered an inevitable basic building block in sectors that are difficult to electrify [37].

In addition to electrolysis using renewable electricity, green hydrogen can be produced from biomass, e.g., from organic residual and waste streams referred to as biohydrogen. A distinction is made between thermochemical and various biotechnological generation pathways for biohydrogen, which will be discussed in the following.

3.2. Biohydrogen Production

Biohydrogen production technologies can be divided into thermochemical and biotechnological approaches. On an industrial scale, biohydrogen can be produced from biomass (wood, straw, grass cuttings, etc.) but also from other bioenergy sources (biogas, bioethanol, etc.) using thermochemical processes. Thermochemical processes can be subdivided into gasification and pyrolysis. Depending on the feedstock used, the synthesis gas formed during gasification or pyrolysis gas consists of varying proportions of hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and other components such as nitrogen, water vapor, light hydrocarbons, hydrochloric acid, alkali chlorides, sulfur compounds, biochar, or tar [41,42]. Using subsequent steam reforming and/or water gas shift reactions, the following chemical reactions take place, resulting in the production of CO_2 and hydrogen [43,44].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

Biotechnological biohydrogen production processes using suitable microorganisms in adequate production facilities can be divided into three main categories: biophotolysis, photofermentation, and dark fermentation [45,46]. Dark fermentation is particularly promising because it is easier to scale up without exposure due to its simpler structure [47–50]. Moreover, technological maturity is the most advanced among the biotechnical processes and thus also relevant knowledge, for example about process parameters such as product gas compositions, is known. Therefore, in this paper, a special focus is given to dark fermentation, knowing that there are alternative processes or process combinations with even higher potential. These include, for example, combinations, e.g., of dark fermentation and photofermentation [51–53]. Sugars and starchy products are particularly suitable feedstocks for dark fermentation [48]. However, with pretreatment, a variety of feedstocks such as food waste, wood, or wastewater can be used for biological hydrogen production [46,49,54,55]. In dark fermentation, the contained glucose is decomposed into hydrogen, carbon dioxide, and the byproducts acetic acid (3), propionic acid (4), or butyric acid (5) [39,48,49,56,57]. The following reaction equations form the basis of these syntheses and take place enzymatically catalyzed via metabolic processes of the microorganisms used.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (3)$$

$$C_6H_{12}O_6 \rightarrow CH_3COOH + CH_3CH_2COOH + CO_2 + H_2 \quad (4)$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 2CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (5)$$

The net energy ratio (NER) of biohydrogen production of 1.9 is significantly better than conventional hydrogen production with methane steam reforming, which has a NER of 0.64 [58]. Utilizing the resulting byproducts in one- or two-stage processes [48,56,58] can further improve the NER. For example, coupling dark fermentation with photofermentation can further decompose the acetic acid components producing hydrogen and increase the NER to 3.1 [58]. Both single organisms and mixed bacterial cultures can produce other byproducts in a biohydrogen plant such as acetone, ethanol, or butanol [48]. Furthermore, adding nanoparticles of various metal oxides can also result in a better hydrogen yield [56]. Thus, further improvements of the processes can be expected through continuous research [39,49–51,53,56]. The product gas of biohydrogen production consists of 30–65% H_2 and 70–35% CO_2, depending on the process parameters, such as the type of microorganism, temperature and pH [52,59–65]. Hydrogen sulfide, water, and nitrogen are also possible by-products [66,67].

3.3. Negative Emission Technologies

NET create greenhouse gas sinks through anthropogenic activities. Sinks that are not directly influenced by humans are not included [19]. Most prominent NET are also known CCS technologies which include, for example, BECCS and DACCS. They can be classified as NET if CO_2 is removed from the atmosphere and negative emissions are generated. However, if the carbon comes from fossil sources, the net emissions are at best zero. In this case, it cannot be classified as NET. In general, CCS technologies can be divided into two steps: first, the capture and sequestration; and second, the storage of CO_2. To capture and sequester CO_2 from gas mixtures in the first step, technologies are needed that separate CO_2 from gas mixtures. Four approaches (absorption, adsorption, cryogenic separation, and membrane separation) have already been tested and are used for CCS technologies [68–76]. The differences between those options in their effectiveness, robustness, energy requirements, and costs regarding their potential use for HyBECCS concepts are discussed below.

Absorption uses a solvent such as water or polyethylene glycol in which CO_2 is first dissolved and then released by changing the conditions [68]. Pressurized water scrubbing, for example, is used in biogas plants to separate CO_2 and H_2S from methane. In this process, water serves as an absorber for CO_2 through increased pressure. This absorber technology is considered comparatively robust and cost-effective [69,70]. Adsorption, in contrast, occurs at the surface of solids [76]. Again, CO_2 remains on the solid sorption material under certain conditions and can be regenerated by a change in temperature, pressure, or humidity [74]. A technically mature adsorption process is pressure swing adsorption on activated carbon. At a low temperature, of about 5 °C, and increased pressure, of about 2–7 bar, CO_2 accumulates on the surface of the activated carbon. The gas must first be free from impurities such as sulfur or dust for the activated carbon to achieve long lifetimes of up to 20 years [72]. Cryogenic separation takes advantage of the different condensation temperatures of the gases. For example, CO_2 condenses at −78.5 °C and hydrogen at −252 °C [77]. At very low temperatures the liquified CO_2 can easily be separated from other components still in a gaseous state. A very high purity of the recovered CO_2 fraction of 99.9% can be achieved, but this requires a comparatively high energy input. Membrane technology, in which the selective permeability of gases through certain material is exploited, is particularly suitable for gas mixtures that already contain a very high CO_2 content, of more than 90% [72–74]. Membrane technologies are considered to be more environmentally friendly and cost-effective than the other options described [67,78]. This is due to the simpler modular design and lower energy requirements [76,78]. Challenges include selectivity, permeability, and sensitivity to sulfur compounds [68,74,79]. Further, the comparatively low purity of the CO_2 fraction after separation is to be mentioned. The difference in purity, however, moves in a wide range, from 80–99.9999%, and depends on the membrane technology chosen and the materials used [78,80,81].

In general, gas mixtures with a relatively low CO_2 concentration require technologies with higher selectivity to effectively separate CO_2 [82]. It is thermodynamically advantageous if the gas mixture to be separated already contains a large amount of CO_2 [83]. Thus, the CO_2 source has a strong influence on the choice of the separation process and the costs per captured tonnes of CO_2. In this context, the initial situations are differentiated between the separation of CO_2 from ambient air or from so-called point sources, which already have a significantly higher CO_2 concentration than the ambient air. The possibility to capture CO_2 from ambient air is known as Direct Air Capture (DAC). The obvious advantage of DAC is that the CO_2 concentration in the atmosphere can directly be lowered and does not require point sources [84,85]. However, because the ambient air has a relatively low CO_2 concentration, of about 400 ppm, on average, the capture of CO_2 is thermodynamically less favorable than using point sources [83]. This is a reason why BECCS outperform, e.g., DACCS in terms of the primary energy required per tonne of carbon sequestered [86]. Chemical absorbers or adsorbers that undergo a chemical reaction with CO_2 are often used for DAC [71,72]. Because of the strong binding and selectivity, even the small amount of CO_2 in the air mixture can be filtered out. However, more energy must be expanded for the regeneration of the CO_2, and a large volume of air must be passed through the equipment to capture CO_2 in appreciable quantities. This results in high energy requirements and high costs for DAC [20,82,87]. If the high energy requirement for DAC is not carried out exclusively with renewable excess energy that does not compete for other uses, this can even lead to a positive emission balance instead of net negative emissions [20]. The second option is to capture CO_2 at point sources that already contain a higher concentration of CO_2. These include, for example, exhaust gases from coal or gas-fired power plants, bioenergy plants, or other industrial facilities. The higher CO_2 concentration of the gas mixture allows a higher energy efficiency of gas separation [87]. However, if the gas mixture has a complex and pollutant composition, the separation can be very costly and technologically complex [69]. Therefore, post-combustion carbon capture (PCC), in which combustion exhaust gases are filtered, is in many cases cost-ineffective, because the heterogenous gas composition is harmful to the separation technology [72]. Additionally, it cannot be classified as NET if the carbon originates from fossil sources, as in the case of PCC at coal-fired power plants.

The second step of CCS technology is the permanent storage of the captured CO_2. This can be done, for example, in geological formations such as aquifers [88]. Furthermore, there is the possibility to upgrade and use CO_2 for new products like plastics or lithium carbonate for accumulators. If the captured CO_2 is used, this is referred to as CCU technologies [89]. However, there is no consensus on whether this is a NET because of the limited lifetime of the products. It may only be a delay in emission [90]. But not only CO_2 can be used to achieve negative emissions. Residues from processed biomass can increase the carbon content of soil in so-called soil carbon sequestration and therefore lead to negative emissions [91,92]. Beyond the described CDR technologies, naturally occurring processes that can be influenced by humans, such as reforestation or enhanced weathering, also fall under the term NET. However, these are not relevant to the derivation of the introduced HyBECCS approach and are therefore not considered in this paper.

BECCS is highlighted in the IPCC Special Report as one of the key NET on achieving the 1.5 K target [19]. Additionally, the presented HyBECCS concept can be classified as a new BECCS technology approach. Therefore, BECCS technologies are discussed in more detail in the following paragraph.

With BECCS technologies, plant-based biomass is used for energy generation, and the CO_2 that is released can be captured and permanently removed from the atmosphere [93,94]. Regarding BECCS, three basic ways of generating energy from plant biomass are distinguished: the thermochemical conversion, the physicochemical conversion, and the biological conversion of biomass to solid, liquid, or gaseous energy sources [95]. One example of thermochemical conversion is incomplete combustion or pyrolysis. In this process, wood and stalk-type biomass are converted into coal, pyrolysis oil, and various gases [69]. The relative proportions of solids, liquid, and gas depend on the combustion parameters and residence time in the combustor [96]. Depending on the feedstock and process conditions, gas mixtures are produced that contain H_2, CO, CH_4, and CO_2 as well as water vapor, nitrogen, particles, tar, hydrochloric acid, alkali chlorides, and sulfur compounds, as described in Section 3.2 [97,98]. The gas mixture must then be separated and processed for use as fuel [69,95–100]. Physicochemical conversion can be used for energy recovery from plant-based oils. They can be mechanically pressed or extracted from plants and then be chemically upgraded, for example by transesterification [101]. The resulting so-called biodiesel is a well-known product from physicochemical conversion processes, but research is also being conducted on the production of kerosene substitutes for aviation from algae oil, for example [102,103]. In biological conversion, biomass is decomposed by microorganisms and converted to methane, hydrogen, or alcohol, for example. A well-known biological conversion process is agricultural biogas production [94]. In conventional biogas plants, microorganisms produce a mixture consisting of 40–75% methane and 15–60% CO_2. Impurities such as H_2S are other possible components that can occur [57,75]. To use it as biogas, this mixture is separated. Biogas with high methane contents can be transported better, and its calorific value increases [68,75]. The CO_2 can be captured and permanently removed from the atmosphere in storage facilities, thus causing negative emissions. Moreover, the digested residue can be used as fertilizer, potentially leading to a further increase of the negative emission effect [92]. However, when the methane biogas is used, CO_2 is released into the atmosphere unless another CCS measure is implemented.

4. Basic Considerations for the HyBECCS Concept

In this section, the HyBECCS concept is described in detail, deriving main technological advantages that lead to lower costs and energy efficiency compared to competing technologies, such as DACCS and other BECCS processes.

The HyBECCS concept summarizes modular process combinations that can be split into four basic process steps (cf. Figure 1): the biomass pretreatment, the biohydrogen production, the product gas separation, and its processing. The authors suggest drawing the system border for economic and ecological classification and balancing around this four steps. Using a consistent system border will make it easier to compare different HyBECCS process combinations. For each of the four steps there are variable sub-processes which have either already reached market maturity or whose functionality has been demonstrated and tested at laboratory scale or prototype scale. Many of them are described in Section 3. However, a HyBECCS process combination has never been experimentally implemented as a whole process linking all of the four steps. Respective technological peculiarities, challenges, and opportunities in all of the four steps are discussed below. The subsequent processes of transportation and storage or utilization of CO_2 and options of hydrogen usage are not in the focus of consideration in this paper, since they have already been discussed and compared in other publications [104–107]. In addition, biomass production and transportation is not included in this work. The following diagram outlines the modularity of the HyBECCS approach described in the following.

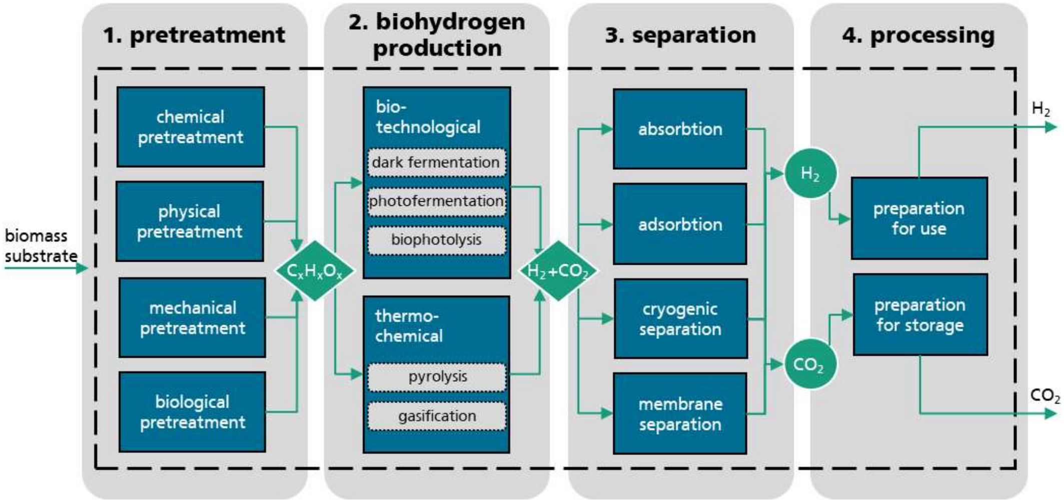

Figure 1. Process diagram for carbon-negative hydrogen production using the Hydrogen Bioenergy with Carbon Capture and Storage (HyBECCS) approach.

For the key step of all HyBECCS approaches to biohydrogen production, the possible feedstocks are very diverse, as described in Section 3.2. However, upstream pretreatment processes (step 1) are required in most cases. For example, to be able to apply biotechnological fermentation processes, residual and waste materials containing sugar are usually pre-filtered and woody biomasses have to undergo a saccharification process. Substrates containing starch, fats, or proteins are subjected to hydrolysis pretreatment releasing single sugars, amino acids, and fatty acids for further microbial metabolism, as is common, for example, in most existing biogas production plants [108–113]. In addition, mechanical comminution or physical digestion methods are necessary. They are also needed for many thermochemical biohydrogen production processes. Moreover, thermochemical processes often require preparatory drying. One challenge of the pretreatment step is therefore the efficient processing of the widest possible range of residual and waste materials for use in biohydrogen processes. For the biohydrogen production (step 2), there is a choice of different thermochemical or biotechnological process options or combinations, as described in Section 3.2, that must be selected according to the specific characteristics of the available biomass streams and pretreatment options. Relevant for subsequent steps and the overall efficiency of the HyBECCS approach is the product gas composition resulting from the biohydrogen production process. In most cases, hydrogen and carbon dioxide are the main outputs [52,59–65]. The proportions of these two components should be maximized to exploit the ecological and economic potential and prepare for efficient gas separation (step 3). The lower the heterogeneity of the gas mixture to be separated and the higher the proportions of the main fractions H_2 and CO_2, the better the conditions for efficient gas separation. Using biotechnological biohydrogen production processes, for example, the mixture usually does not contain combustion residues or other harmful gases that can negatively affect the downstream gas separation, as is the case with PCC or some thermochemical biohydrogen production processes [87]. To fractionate the product hydrogen for use and the carbon dioxide for downstream storage or use, a suitable gas separation process which can be carried out in various options is to be chosen, as described in Section 3.1. To separate H_2 and CO_2, the physical and chemical prerequisites of an efficient separation are given, for example, due to the different polarities and molecular sizes. Membrane technologies, for example, are an attractive alternative to conventional processes, such as pressure swing adsorption or cryogenic distillation, due to their comparatively high separation quality and energy efficiency [67]. As described in Section 3.1, the disadvantage of DAC regarding the gas separation step is the low content of CO_2 in the ambient air, leading to higher energy consumption and high plant investment compared to the point source resulting from, e.g., biohydrogen production processes [83]. In the final step of processing (step 4), the separated CO_2 has to be compressed or otherwise prepared for storage or use, and hydrogen has to be compressed or liquefied and purified so that it can either be fed into the natural gas network or transported to users, e.g., in composite pressure tanks. The carbon-negative hydrogen produced can be used materially for chemical processes or by means of fuel cells as energy carriers to generate heat and electricity or to power vehicles, as described in Section 3.1. Using fuel cells, the reaction with oxygen from the ambient air produces only water. In contrast to hydrocarbon-based e-fuels or bio-fuels such as biogas, no greenhouse gas emissions are emitted during its use. This results in an inherently higher CO_2 capture potential for HyBECCS, leading to a decisive advantage over BECCS technologies that aim to produce hydrocarbons as energy carriers. However, to use hydrogen in fuel cells, purity requirements must be met, which are specified in European standards, for example. The purity of hydrogen for its use in hydrogen fuel cells is specified therein at the value 3.7, which corresponds to a purity of 99.97% [114]. The following three points summarize the key advantages of HyBECCS concerning their environmental and economic potential:

1. The product gas composition of biohydrogen processes consisting mainly of H_2 as the main product and CO_2 as a co-product makes the capturing of CO_2 energy- and cost-effective compared to low concentrated CO_2 sources like ambient air [52,59–65,83,87,115].
2. The possibility to use biotechnological methods for biohydrogen production within HyBECCS approaches leads to carbon sources that are not polluted with combustion residues. In comparison to PCC, there is no risk to impair the subsequent separation or further processing [66,67,69,87].
3. Hydrogen is a carbon-free energy carrier. Since there is no carbon remaining in the product, HyBECCS approaches have a comparatively high cumulative CO_2 capture rate and thus a larger specific GHG emission reduction potential compared to, e.g., BECCS technologies producing hydrocarbon-based biofuels [36–39].

Due to these advantages, the HyBECCS concept can be seen as a new promising perspective within BECCS methods. However, to be able to make conclusive statements on process ecology and economics, more in-depth techno-economic analyses and ecological assessments must be carried out. The following section gives an insight into these assessments using the example of Germany.

5. General Perspectives for HyBECCS Approaches

Due to the advantages described in Section 4, HyBECCS offers a perspective for sustainable and efficient production of hydrogen as well as climate adaption and mitigation. Associated political regulatory measures such as CO_2 pricing and emissions trading could result in monetary credits from which the HyBECCS concept could benefit. Further, the global political and societal push toward establishing green hydrogen as a sustainable basic energy carrier across several sectors will have a positive effect for carbon-negative hydrogen production by better meeting the resulting demand. Furthermore, the increasing efforts of companies to leverage its externalities through carbon footprint improvements for business purposes in so-called social or green marketing concepts are also potential drivers of the HyBECCS concept [7,10,18,116,117]. An important basis for further development and industrial application of HyBECCS is a fundamental understanding of their economic and ecological impacts. In the following, from the example of Germany, possible impacts for climate adaptation and mitigation (Section 5.1) and the economic viability of HyBECCS concepts are discussed (Section 5.2).

5.1. Ecological Classification

The amount of sustainably available biomass is limited and should therefore be used as efficiently as possible. One promising way to do so is carbon-negative hydrogen production. The main ecological advantage of this possibility in terms of climate adaption and mitigation is the removal of CO_2 from the atmosphere. Compared to other NET, this can be done particularly efficiently by HyBECCS, as described in Section 4. In the following, an estimate of the GHG emission reduction potential of HyBECCS in Germany is carried out, starting from bioenergy potentials already investigated for biohydrogen production through dark fermentation processes. Biohydrogen production as a stand-alone technology is already considered as a potentially climate-neutral process with a wide substrate spectrum. Among the options described in Section 3.2, biotechnological pathways allow for hydrogen production with less energy-consumption than thermochemical and electrochemical processes, which is due to lower process temperatures and pressures [46]. Besides, biotechnological hydrogen production has the advantage of offering a carbon source with high purity and no combustion residues, that could impair the subsequent separation or purification of CO_2, as described in Section 4. Thermochemical processes like pyrolysis or gasification are disadvantaged in these points. In the following, a special focus will therefore be placed on a biotechnological hydrogen production process as the basis for HyBECCS. In this investigation, the best-known and most widespread biotechnological approach, dark fermentation, is considered for the following ecological assessment. Further, the analysis is reduced to the environmental impact category global warming and to Germany as the spatial and systemic frame of reference.

The future potential of biohydrogen production from residuals through dark fermentation has been investigated in a recent study for Germany [118]. It should be noted that only biomass potentials from residues were taken into account in this consideration, which serves as a basis for the subsequent analysis. Social conflicts concerning land-use, for example through competitive situations with the production of food and feed, are thus not to be expected. For Germany, it was estimated that a theoretically achievable annual energy supply of 9.9 TWh/a up to 19.9 TWh/a will be possible in 2030 through dark fermentation of residual and waste materials. This is the same order of magnitude as that of Germany's targets for the production of hydrogen by electrolysis using renewable electricity. Within the national borders, these are set up to 14 TWh/a until 2030 [18]. Assuming that this energy amount of green hydrogen from dark fermentation substitutes an equal amount of energy provided by natural gas, this results in a saving of 2.0–4.0 $MtCO_{2,}eq$/a. In addition to natural gas, coal, and lignite, grey hydrogen or heating oil could also be substituted, which would lead to even greater savings due to higher specific GHG emissions related to the amount of energy produced [119]. Besides, the substitution of electricity from fossil sources is possible using hydrogen fuel cells. However, the replacement of natural gas serves as a plausible assumption, since hydrogen can be used directly in the mixture with natural gas in many cases without technological adjustments and can also be fed directly into natural gas distribution networks [18]. HyBECCS approaches further increase the GHG savings potential by creating negative emissions, as described in Section 4. Assuming that the entire amount of CO_2 produced as a by-product during dark fermentation processes were to be separated and stored, 6.4–13.0 $MtCO_{2,}eq$/a of negative GHG emissions could be achieved in Germany by 2030. This assumption was based on a realistic stoichiometric-based product gas composition of fermentative biohydrogen production through the dark fermentation of CO_2 and H_2 in equal quantities, as can also be seen in Section 3.2 and Equations (4) and (5) [64–70]. In total, the use of carbon-negative hydrogen, under the assumptions made, results in a saving potential of 8.49–17.06 $MtCO_{2,}eq$/a due to CO_2 avoidance through fossil energy source substitution and its active removal from the atmosphere. In Figure 2, the estimated emission reduction potentials using HyBECCS are summarized.

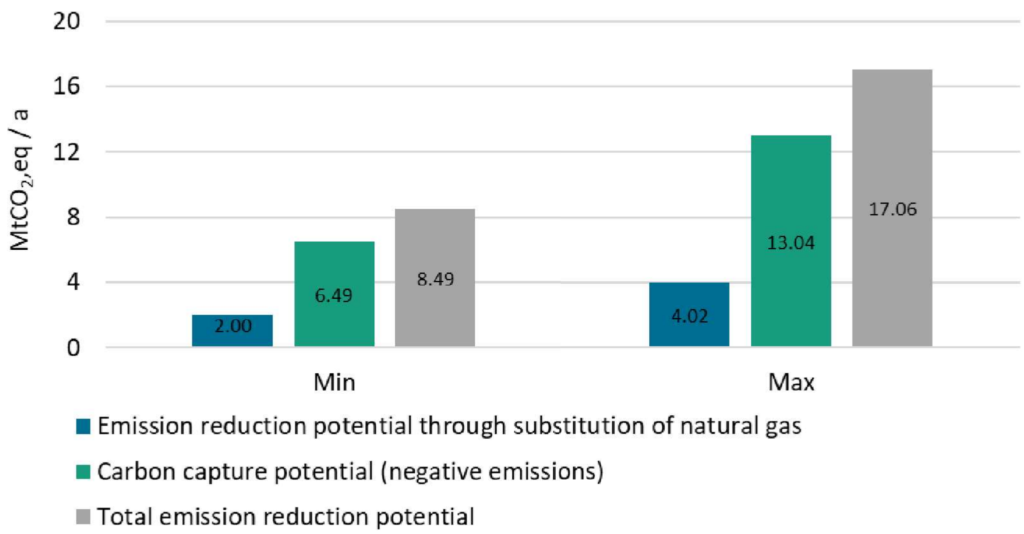

Figure 2. Emission reduction potential through HyBECCS in Germany based on carbon-negative hydrogen production from residual biomass using dark fermentation.

The most important challenge in tackling climate change at a global level is the reduction of GHG emissions. However, a sole consideration of the GHG balance is not sufficient to explore the sustainability of HyBECCS approaches [115,120]. Further impact categories within life cycle assessments (LCA) according to DIN EN ISO 14040/44 are to be considered. Based on EEA classifications 6 and 10 for the chemical industry and agricultural products according to Grosse-Sommer et al., this also includes resource depletion, acidification, consumptive water use, eutrophication, human toxicity potential, photochemical ozone formation, ozone depletion, and land use [121]. Furthermore, the impact categories biodiversity loss and ecosystem services should also be considered [122]. However, this paper cannot make a final assessment taking into account all relevant impact categories. For a holistic view and final assessment, further investigations are still needed.

5.2. Economic Classification

The use of carbon-negative hydrogen can be economically attractive for companies, as it can provide a way to improve their corporate image, reducing the company's carbon footprints, and contribute to social or green marketing concepts. However, to be broadly applied, carbon-negative hydrogen must also be price-competitive, and its production must be profitable. The profitability depends on many internal and external impact factors, some of which are summarized in Figure 3. The internal impact factors describe influences that emanate directly from the technical setup and equipment used for the HyBECCS process combination as described in Section 4, leading to differences in CO_2 separation rates, hydrogen yield, energy efficiency, or plant investment costs, for example. Internal factors are necessary information for comprehensive techno-economic analyses. However, they are very difficult to estimate for HyBECCS due to the low level of technological maturity of the central process step of biohydrogen production and the lack of corresponding industrial-scale production technologies as data sources. Although further research in this regard has already been initiated by the authors, the information situation is not yet sufficient for a comprehensive analysis.

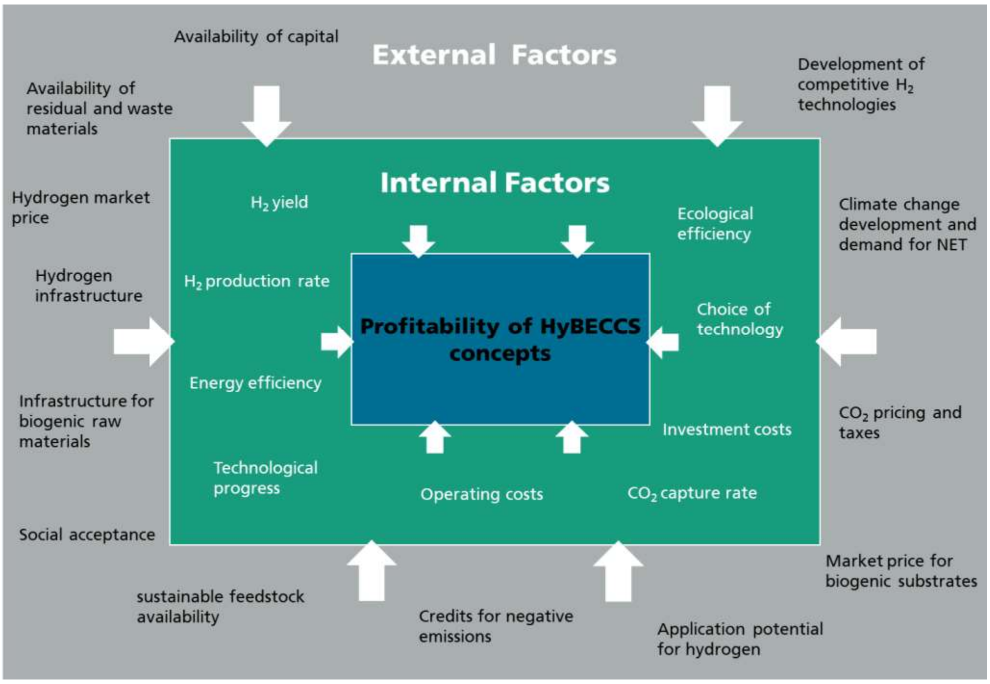

Figure 3. Impact factors on the profitability of carbon-negative hydrogen and HyBECCS.

External factors, in contrast, include forces that affect the competitiveness of carbon-negative hydrogen in the marketplace and are not directly dependent on the technical setup of the chosen process combination and technical setup. These include, for example, market or policy conditions affecting the price of hydrogen or the profitability of carbon-negative hydrogen production through financial incentives. A key external factor in this context are political regulatory measures from environmental and climate policies. Thereby, for the political regulation of GHG emissions via financial incentive systems, a distinction can be made between the taxation of CO_2 emissions and the incentivation of negative emissions establishing credits for NET. Both approaches have a fundamentally high impact on the economics of all NET [20] and carbon-negative hydrogen production. To provide a basis for initial quantitative assessments on economic prerequisites for HyBECCS, the maximum production costs required for competitive carbon-negative hydrogen are estimated in the following considering external factors. Therefore, the existing estimates of production costs for competing green hydrogen and expected incentives for the active removal of CO_2 from the atmosphere are carried out in the following, using the example of Germany.

The market price for hydrogen is a major external impact factor on the economics of carbon-negative hydrogen. HyBECCS plant operators must be able to produce at costs that are below this market price, which depends, among other things, on the general hydrogen demand and its supply situation. Forecasts predict a sharp increase in hydrogen demand in the coming decades [18,37]. Despite the extensive expansion of electrolysis capacities, there will be a large gap between demand and generation capacity in Germany that is to be closed by imports of green hydrogen according to their national hydrogen strategy, as described in Section 3.1. Therefore, a distinction regarding hydrogen prices in Germany can be made between imported green hydrogen and green hydrogen that is produced in the internal market. Since internal demand is very unlikely to be met by the production of green hydrogen by electrolysis within national borders [18], there will be no direct competition between green hydrogen and carbon-negative hydrogen within Germany. The production costs for carbon-negative hydrogen should therefore be measured against the price of imported green hydrogen. Accomplished studies have estimated the price for hydrogen produced in North Africa and transported to Germany either via pipelines or by ship at 3.10 € per kg in 2050. Despite the lower costs for renewable energy, this is more expensive compared to hydrogen produced in the domestic market (2.45 €). Average transport costs are estimated at 1.70 per kg H_2 [123]. Other studies come up with supply costs of up to 119 €/MWh with the example of importing green hydrogen from North Africa to Central Europe, which equals 3.97 € per kg H_2 [124]. Further studies predict production costs between 3.85 € and 4.81 € per kg H_2 from solar energy in Morocco [125], amounting to supply costs of 5.55 € and 6.51 € including transport costs, according to [123].

Additionally, credits for CCS should be considered to assess the economics of NET like carbon-negative hydrogen production. The introduction of policy instruments that incentivize NET deployment by generating revenues linked to the amount of CO_2 captured and safely stored is likely to be seen [20]. The expected potential credits per tonne of CO_2 taken from the atmosphere through HyBECCS are estimated in the following. Worldwide, the so-called social costs of carbon (SCC) serve as benchmarks for pricing or tax models. These correspond to the damage caused by an additional tonne of CO_2 to the economy and society and were first defined by Nordhaus [126]. In recent decades, numerous quantitative estimates of SCC have been made. Based on several available models, the National Academies of Sciences, Engineering, and Medicine quantify the SCC for one tonne of CO_2 at an average of 46 € in 2020 and 55 € in 2030 [127]. These figures are based on well-documented empirical assessments of climate damage and can be considered conservative [128]. However, there is uncertainty about the extent of the expected warming, damage, and risks. An expert survey on expected climate damage with 386 respondents from different disciplines placed the average estimate of SCC at 70–90 € per ton CO_2. Other investigations from the German Environment Agency (GEA) consider an SCC of more than 180 € per tonne of CO_2 realistic [129,130]. Governments around the world are basing their statutory CO_2 prices on these calculations. In Germany, for example, since January 2021, the emissions of carbon dioxide in the building and transport sectors have been affected by a fixed price of 25 € per tonne of CO_2, thus covering areas that are not yet affected by the European emissions trading system. This uniform price per tonne of CO_2 emitted is to rise gradually, to 30 € per tonne in January 2022, 35 € in 2023, 45 € in 2024, and 55 € in 2025 [131]. Switzerland, on the other hand, has been charging 96 Swiss francs per tonne of CO_2 since 2018, equivalent to 86.50 €, and has passed legislation that could raise the price to 210 Swiss francs per tonne of CO_2, equivalent to 189.22 € [132].

An estimate of the impact on the production of one kilogram of carbon-negative hydrogen in Germany is based in the following on the assumption that a credit per tonne of CO_2 actively extracted from the atmosphere is made at the level of SCC or existing CO_2 taxes. For this, a worst-case and best-case distinction is made. In the worst-case path considered, we use the agreed price in Germany of 55 € per tonne of CO_2, applicable from 2025 [131], and for the best-case scenario the proposed price of 180 € per tonne of CO_2 of the GEA [130] is assumed. Provided that the use of 1 mol (0.002 kg) of carbon-negative hydrogen is associated with the capture and storage of 1 mol of CO_2 (0.044 kg), the expected credits that could be paid per kg of carbon-negative hydrogen can be estimated. For the worst-case scenario, this results in an incentive of 1.20 €, and for the best-case scenario of 3.93 € per kilogram of carbon-negative hydrogen produced. Also for the supply price of competitive green hydrogen, a distinction is made between a minimum case of 3.10 € and a maximum case of 6.51 € [123,125]. In the figure below, the CCS incentive forecasts, together with the estimated production costs for imported green hydrogen, are shown.

As shown in Figure 4, the incentives for CO_2 capture and storage can have a major impact on the economics of the HyBECCS concept. The sum of the estimated target prize per kg of carbon-negative hydrogen and CCS incentives gives a basic value from which to draw initial conclusions about the maximum production costs of carbon-negative hydrogen to be competitive in the future hydrogen market in Germany. Under the assumptions made, the production costs would have to be below 4.30 € per kg of carbon-negative hydrogen in the worst case and below 10.44 € in the best case to be able to compete with imported green hydrogen. To date, no comparative estimates of the production costs of carbon-negative hydrogen have been available, but this first classification sets a target for cost-effectiveness analyses, which should consider both external and internal impact factors.

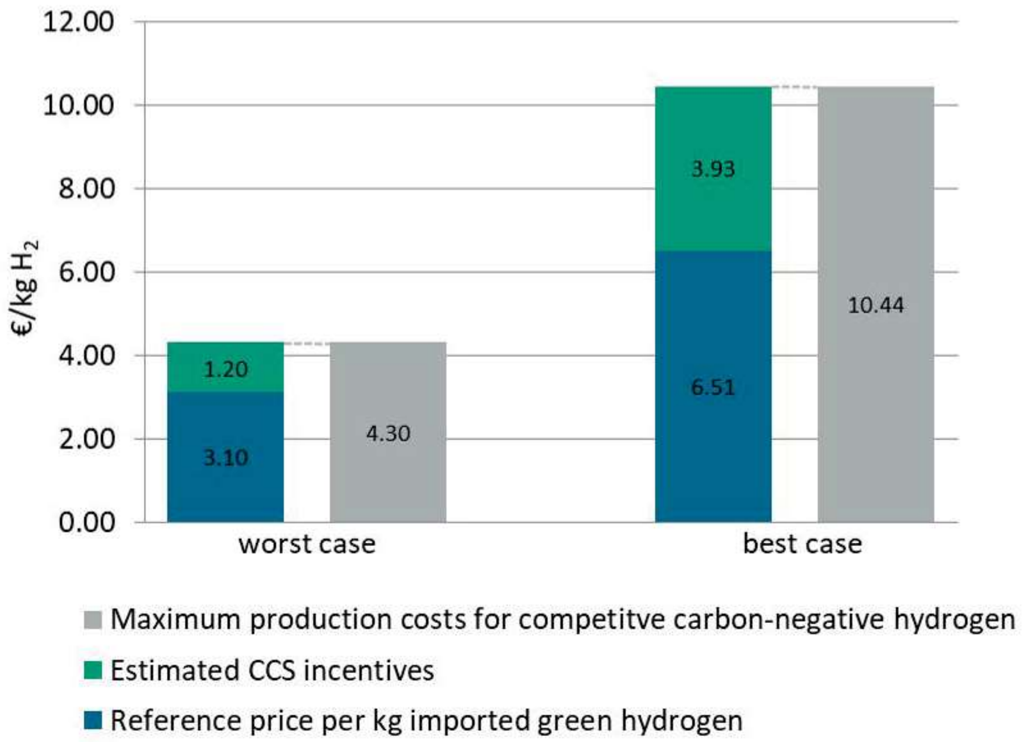

Figure 4. Pricing fundamentals for carbon-negative hydrogen considering the supply costs of competing imported green hydrogen and the expected incentives for CO_2 capture and storage in Germany.

6. Limitations

The HyBECCS concept described in this paper comprises a modular-based system consisting of variable sub-processes. Many of them are already known and tested. However, a complete HyBECCS process combination has never been implemented in a contiguous facility. Their testing in pilot and experimental facilities is still pending and could lead to new findings or process challenges that are not described in this paper. The concept's classifications of ecology (Section 5.1) and economics (Section 5.2) described in this paper are based on simplifications and assumptions made by the authors in an effort to make a conservative estimate. For the ecological assessment, only single-stage dark fermentation, the exclusive use of biogenic residues, a focus on the densely populated country (Germany), and the use of H_2 for the substitution of natural gas were assumed to give a realistic estimate and in order not to create unrealistic expectations. On the other hand, possible emissions connected to farming and the pretreatment of biomass, as well as during carbon storage, which would have an effect on the emission balance, were not taken into account in this paper. In the economic estimation, possible financial benefits through the use of CO_2 as raw material were excluded, as well as possible financial benefits from soil carbon sequestration. Furthermore, carbon-negative hydrogen was compared with imported green hydrogen, although a better carbon footprint of carbon-negative hydrogen is likely to lead to a market advantage over green hydrogen. Nevertheless, process-related peculiarities that are still unknown due to the low technology maturity can lead to negative effects on the economic viability of the HyBECCS approach. The assumptions made need to be reviewed and validated in further research. Additionally, a detailed techno-economic analysis of the process concepts, testing in pilot and experimental plants as well as holistic life-cycle assessments are needed. Then, more precise statements about the potential of carbon-negative hydrogen and the HyBECCS approach will be possible.

7. Summary

In this paper, the HyBECCS (hydrogen bioenergy with carbon capture and storage) concept was introduced as a new approach for NET. This concept combines hydrogen production from renewable biomass with downstream processes for CO_2 capture and storage or use. The hydrogen produced has a negative carbon footprint and is referred to as carbon-negative hydrogen. HyBECCS processes are described as modular process combination options that can be assigned to four basic steps: the pre-treatment of the substrate biomass, the biohydrogen production process, the separation of hydrogen and CO_2 from the product gas, and their treatment. All steps are interdependent and can be performed by different technology options, some of which are described in this paper. Although HyBECCS has never been technically implemented as a physically connected process combination, there are technology options for each of the four steps that have either already reached market maturity or whose functionality has been proven and tested on a laboratory or prototype scale. The main advantage of HyBECCS over competing NETs can be seen in the efficient capture of CO_2 with high purity produced as point source in a comparatively high concentration during the second step, biohydrogen production. Therefore, technological disadvantages arising either from the contamination of CO_2 with combustion residues or from the energy- and cost-intensive concentration of CO_2 from heterogeneous gas mixtures can be avoided. Further, hydrogen can either be used in the chemical industry, for steel production, or to generate emission-free heat and electricity, in contrast to GHG-emitting hydrocarbon-based energy carriers like biogas or other biofuels produced, for example, from biomass within BECCS approaches. Due to these advantages, the ecological and economic benefits of the HyBECCS concept can be concluded. These benefits were analyzed using the example of Germany. An ecological assessment was made estimating the GHG emission reduction potential through HyBECCS approaches. For the production and use of carbon-negative hydrogen, a theoretical saving potential of 8.49–17.06 $MtCO_{2,}eq/a$ was estimated for the year 2030 in Germany based on existing estimations of biohydron production through dark fermentation processes. This results from the potential combination of CO_2 avoidance by substitution of natural gas with hydrogen as an energy source (2.00–4.02 $MtCO_{2,}eq/a$) and the active extraction of CO_2 from the atmosphere (6.49–13.04 $MtCO_{2,}eq/a$). In addition, to provide a basis for initial estimates of the economics of the HyBECCS concept, the maximum costs for competitive carbon-negative hydrogen production were estimated for Germany in two scenarios. For this purpose, existing estimations for the production costs of the competing product green hydrogen were added to potential monetary incentives for the extraction of CO_2 from the atmosphere. According to these estimations, the production costs of carbon-negative hydrogen would have to be below 4.30 € per kg of carbon-negative hydrogen in the worst-case and below 10.44 € in the best-case scenario to be able to compete with imported green hydrogen in Germany. In this paper, the definition and differentiation of the HyBECCS concept for sustainable energy solutions as well as initial potential assessments have set the basis for a more in-depth consideration of this novel approach.

8. Outlook

In further investigations, the HyBECCS concept presented in this paper should be analyzed in more detail so as to identify particularly promising process combinations and prepare for experimental research and technological implementation. A holistic techno-economic and ecological understanding of the HyBECCS process's combination possibilities must therefore be gradually developed in order to drive their development and optimization in a targeted manner. To ensure the ecology of the processes, relevant environmental impacts must be identified and analyzed on this basis. A holistic life cycle assessment following DIN EN ISO 14040/44 for the production of carbon-negative hydrogen through HyBECCS should be established. In addition, cross-impact analyses and model calculations on the overall economic implementation in the energy system and industry should be carried out with a focus on intersectoral system developments, e.g., by means of material and energy flow system model analyses. However, to bring carbon-negative hydrogen into widespread use, not only economic and ecological optimization is needed. Social and political framework conditions must also be adapted. A robust quantification of negative emissions under international supervision is required. Further, social and environmental conflicts, in particular land and water use conflicts, must be prevented. Establishing a certification system for carbon-negative hydrogen, which can ensure that the product has a negative carbon footprint, could help to ensure widespread and long-term acceptance.

From a technical point of view, HyBECCS process combinations can be combined with bioeconomic biorefinery concepts in perspective. An expanded range of products and substrates could lead to higher value creation and improve economic efficiency. The main product gas fractions H_2 and CO_2 could therefore be used in a combinatorial way, for example by using H_2 as a reducing agent for CO_2, as outlined in Figure 5. Eco-efficient carbon cycles with high added value can thus be created based on the presented HyBECCS approach.

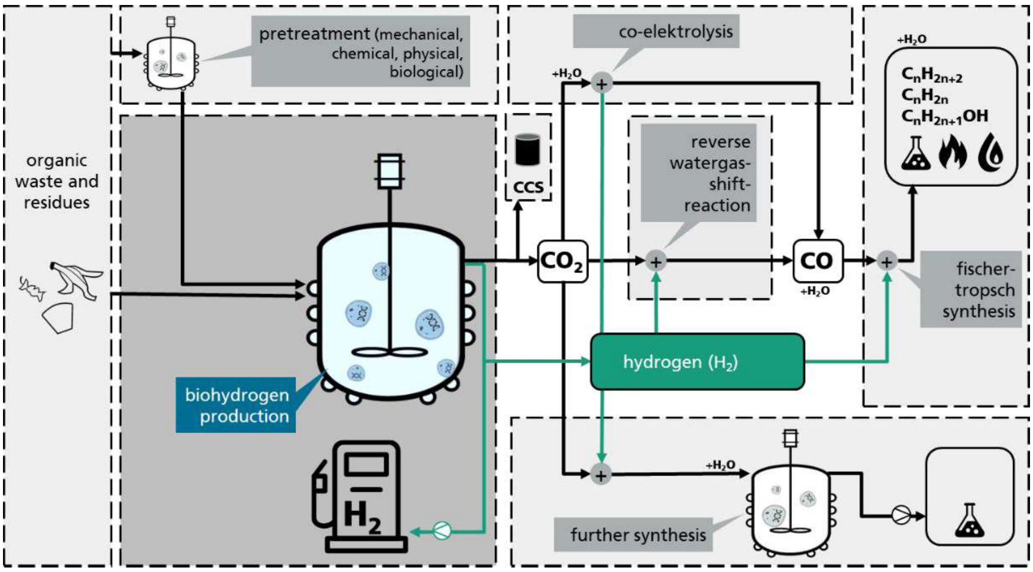

Figure 5. Exemplary scheme for the expansion of the product range to create a biorefinery concept.

However, the most important basis for both HyBECCS and bioeconomy approaches is a deeper techno-economic understanding as well as a comprehensive life-cycle assessment of the basic process step of biohydrogen production from biomass.

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Appendix B: Paper B

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Article

Perspectives of Biogas Plants as BECCS Facilities: A Comparative Analysis of Biomethane vs. Biohydrogen Production with Carbon Capture and Storage or Use (CCS/CCU)

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Abstract: The transition to a carbon-neutral economy requires innovative solutions that reduce greenhouse gas emissions (GHG) and promote sustainable energy production. Additionally, carbon dioxide removal technologies are urgently needed. The production of biomethane or biohydrogen with carbon dioxide capture and storage are two promising BECCS approaches to achieve these goals. In this study, we compare the advantages and disadvantages of these two approaches regarding their technical, economic, and environmental performance. Our analysis shows that while both approaches have the potential to reduce GHG emissions and increase energy security, the hydrogen-production approach has several advantages, including up to five times higher carbon dioxide removal potential. However, the hydrogen bioenergy with carbon capture and storage (HyBECCS) approach also faces some challenges, such as higher capital costs, the need for additional infrastructure, and lower energy efficiency. Our results give valuable insights into the trade-offs between these two approaches. They can inform decision-makers regarding the most suitable method for reducing GHG emissions and provide renewable energy in different settings.

Keywords: HyBECCS; hydrogen; BECCS; biogas; biohydrogen; biomethane; CDR; NET; carbon-negative hydrogen; steam methane reforming; SMR

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1. Introduction

The urgent need to mitigate climate change has led to the development of innovative technologies that can reduce greenhouse gas (GHG) emissions and promote sustainable energy production. Additionally, negative emission technologies (NETs), also known as carbon dioxide removal (CDR) technologies, are crucial for limiting human-induced global warming to less than 2 °C above pre-industrial times [1,2].

Biogas, a renewable energy source produced by the anaerobic digestion of organic waste, has emerged as a promising alternative to fossil fuels [3]. During the process of biogas production, microorganisms break down organic matter in an oxygen-free environment. The result is a gas mixture that is mainly composed of methane (CH_4) and carbon dioxide (CO_2) [4]. The CH_4 contained in biogas can be purified and is then referred to as biomethane [5]. Once the biogas has been purified to methane, it can be used in various ways, e.g., as a fuel for transportation or for industrial applications. It can also be injected into and transported through the natural gas grid. In biomethane production with carbon dioxide capture and storage (CCS), the biogenic CO_2 released during the anaerobic digestion is captured and permanently stored. However, biomethane is a greenhouse gas itself when emitted into the atmosphere, and its use in combustion engines or combined heat and power (CHP) units results in CO_2 emissions.

Alternatively, biogas can be processed by steam reforming to produce hydrogen (H_2) [6,7]. H_2 can also be used as a fuel for transportation or injected into the natural gas grid [8,9]. An advantage of H_2 over biomethane is that it can be used decentrally without emitting CO_2 or other greenhouse gases, as it is a carbon-free energy carrier. Furthermore, during the steam-methane reforming (SMR) process, in addition to the CO_2 in the biogas, biogenic CO_2 is generated as a product and can be captured and stored. This leads to a higher CO_2 removal potential compared to biomethane production with CCS. However, energy losses resulting from the conversion processes must be considered. Technologies that combine biohydrogen production with CCS are referred to as Hydrogen Bioenergy with Carbon dioxide Capture and Storage (HyBECCS) approaches [10].

Biogas reforming for hydrogen production is a promising area of research and development. Significant progress has been made in the efficiency and scalability of the technology [11–13]. Furthermore, several companies and research institutions are actively engaged in advancing biogas reforming processes, optimizing catalysts, improving reaction kinetics, and exploring their integration with CCS technologies. Some examples include the Canadian company Xebec Adsorption [14], the French Air Liquide [15], and WS Reformer in Germany [16]. Similarly, pilot projects and demonstration plants are being developed, indicating a growing interest in harnessing the potential of biogas reforming as a sustainable pathway for hydrogen production (see for example [17–19]).

For CO_2 storage, there are several options. One common method is injecting the CO_2 into underground geological formations, such as depleted oil and gas reservoirs, saline aquifers, or coal seams [2,20]. Furthermore, there are also several options for the long-term use of captured carbon dioxide (CCU) [21]. One example for CCU is the production of building materials, such as cement, concrete, and mortar, which can help reduce greenhouse gas emissions by replacing GHG-intensive materials in the building sector. As the captured and stored CO_2 is from biogenic sources, its storage or long-term use can lead to negative emissions, and the process can be considered a CDR approach or NET [22,23].

This paper compares biomethane production from biogas with CCS with biohydrogen production from biogas with CCS. The analysis considers the technical, economic, and environmental aspects of each approach. The aim is to provide insights into the trade-offs to be considered in terms of energy efficiency, their potential for negative emission generation and economic potentials. First, a general energy efficiency analysis is presented. For this, a use case is defined that involves the use of biomethane or hydrogen as a fuel in heavy-duty vehicles. Next, the negative emission potential (NEP) for each process option is calculated and compared. Finally, a discussion about the associated costs and profitability of both processes is presented.

2. Basics

2.1. Biomethane Production through Biogas Purification

Biogas is produced through the anaerobic digestion of organic waste [3,24]. It consists mainly of methane (CH_4) and carbon dioxide (CO_2). Typically, the amount of CH_4 in biogas is between 55 vol% and 70 vol% [4]. Other gaseous components like hydrogen sulfide (H_2S), hydrogen (H_2), and nitrogen (N_2) can be present in small quantities. Biogas can be purified to biomethane using various technologies such as pressure swing adsorption (PSA), membrane separation, or cryogenic distillation [5,25]. The purification process removes CO_2 and impurities such as water and trace gases to increase the CH_4 content of the gas [26]. In terms of physical properties, biomethane and methane are identical, as they are the same substance. The different name only refers to their origin and production process. While “methane” refers to any type of methane, including methane derived from fossil resources, biomethane specifically designates methane obtained from biogas [27].

2.2. Biohydrogen Production through Biogas Steam Reforming

Biogas steam reforming is a process used to produce H_2 from biogas. The process involves the conversion of CH_4 into gaseous H_2 and CO_2 through a reaction with steam and the parallel occurring carbon monoxide (CO) shift. According to Rostrup-Nielsen and Christiansen, the process is described by the following two reactions [28]:

$$n\ CO_2 + CH_4 + H_2O_{(g)} \leftrightarrow 3\ H_2 + CO + n\ CO_2;\ \Delta H = +206.15\ kJ/mol \tag{1}$$

$$CO + H_2O_{(g)} \leftrightarrow H_2 + CO_2;\ \Delta H = -41.2\ kJ/mol \tag{2}$$

where n describes the molar ratio of CO_2 to CH_4 in the feed gas. This ratio is between 0.43 and 0.82, as the molar amount of CH_4 is between 55% and 70% for typical biogas plants, assuming ideal gas conditions [4]. Assuming the complete conversion of the C feedstock into CO_2, the overall stoichiometric reaction, obtained by combining Equations (1) and (2), is [29]

$$n\ CO_2 + CH_4 + 2\ H_2O_{(g)} \leftrightarrow 4\ H_2 + (n + 1)\ CO_2;\ \Delta H = +\ 164.95\ kJ/mol \tag{3}$$

2.3. Carbon Dioxide Removal

NETs are essential to counterbalance exceedingly high GHG emissions and to limit global warming to 2 °C above pre-industrial levels [1]. NETs consist in removing CO_2 from the atmosphere and storing it for long periods, effectively reducing the overall concentration of CO_2 in the atmosphere. Negative emissions correspond to the amount of removed and stored CO_2 that exceeds the GHG emissions caused during the entire process of generating such carbon removals. This means that these GHG emissions must be deducted from the stored CO_2 to quantify the amount of negative emissions [30]. For process comparisons based on similar technologies, the maximum possible negative emissions can be estimated. For this purpose, all GHG emissions are neglected, and only the maximum captured amount of biogenic (or atmospheric) CO_2 is considered. This is a comparative value referred to as negative emission potential (NEP) [23].

CDR involves the capture and storage of atmospheric CO_2 from direct air carbon capture approaches (DACCS, direct air carbon capture and storage) and of biogenic CO_2, e.g., from the energetic use of biogenic waste (BECCS, bioenergy with carbon capture and storage). The most common method of CO_2 storage is geological storage, which involves injecting CO_2 into deep geological formations such as depleted oil and gas reservoirs, saline aquifers, and unmineable coal seams [2,31]. Another option for CO_2 storage is mineralization, which involves the reaction of CO_2 with naturally occurring minerals to form stable carbonates [32]. This process can occur naturally over long periods. However, it can be accelerated through various methods like mineral carbonation. This involves the reaction of CO_2 with magnesium and calcium silicate minerals to form stable carbonates. In addition to the permanent storage for CO_2, some carbon capture and utilization (CCU) approaches can be considered CDR, as long as the utilized carbon is durably stored in the respective product. Examples are the production of long-term materials like high-tech plastics or construction materials [33,34].

2.4. The HyBECCS Concept

HyBECCS is an umbrella term for processes in which H_2 is produced from biogenic residual and waste materials and the resulting CO_2 is captured and permanently stored. It can also be seen as a subsidiary branch of bioenergy with carbon capture and storage (BECCS) with the particularity that H_2 is produced as an energy source. The technical approach can be split into four basic process steps: 1. substrate biomass pretreatment, 2. the production of biohydrogen and biogenic CO_2, 3. the separation of the product gases CO_2 and H_2, and 4. their processing for the use of H_2 and long-term storage or the use of biogenic CO_2, including the permanent CO_2 storage or use itself [10]. For each of the four steps, there are different technology options. A main technological advantage of BECCS and HyBECCS approaches is the energy-efficient capture of biogenic CO_2 as it generally occurs as a point source. It provides a double effect on climate mitigation by providing GHG-free energy and the storage of biogenic CO_2 with the potential to provide negative emissions. The basic requirements are, however, the deduction of all GHG emissions occurring over the entire process chain to determine the amount of negative emissions, economic viability, and a reliable long-term CO_2 storage [30]. Considering biogas plants, there are several possibilities to retrofit existing plants to HyBECCS facilities [35]. The technical approach considered in this work combines biogas-steam reforming with CCS, as described in the following section.

3. Process Descriptions and Main Assumptions

This section defines and describes the two process options to be compared in this work: biomethane production with CCS (process option 1) and biohydrogen production through biogas-steam reforming with CCS (process option 2). The various stages of each process option with a focus on the differences are described and the main assumptions for their comparison are outlined.

An overview of the two process options is provided in Figure 1. The first stage of both process options involves the preparation of the feedstock, followed by biogas production through the anaerobic digestion of organic waste in large vessels that provide an oxygen-free environment for microorganisms to break down the organic matter [3]. Different types of organic waste can be used, including agricultural waste, food waste, and sewage [36,37].

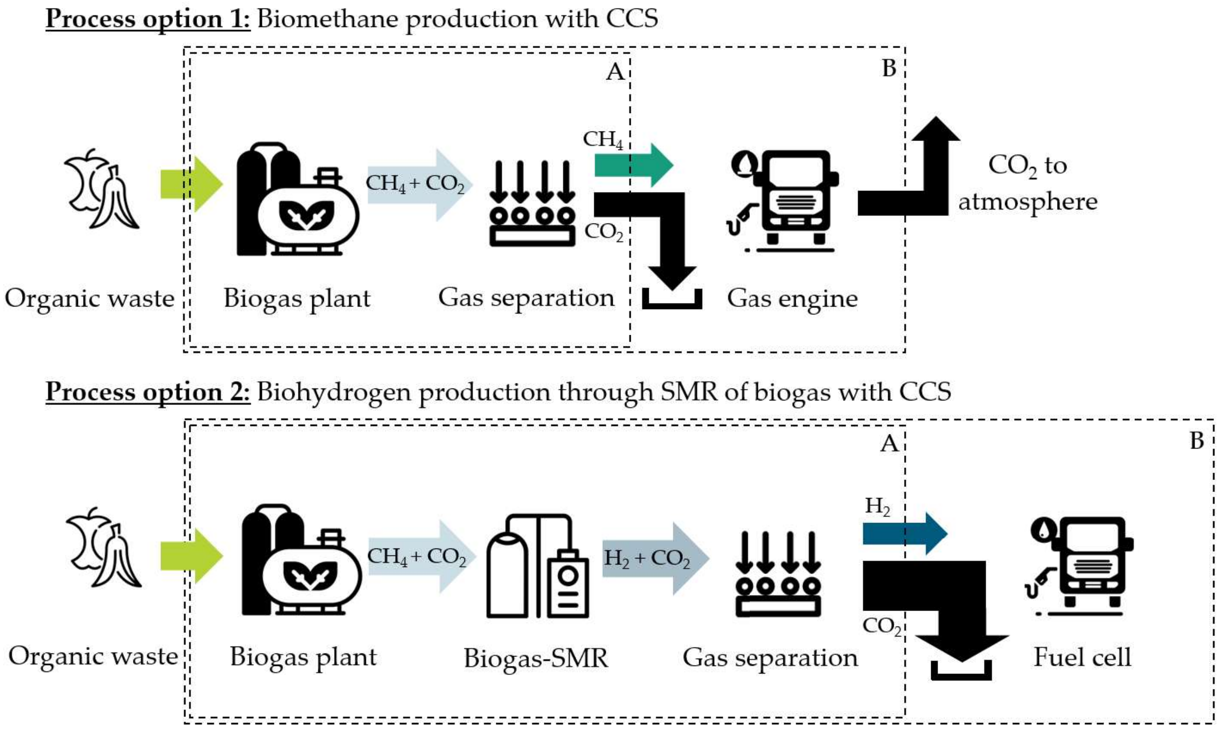

Figure 1. Process options and system boundaries (A and B) for biogas usage (own representation).

In process option 1, the second stage is separating the CH_4 from the other gas components in the biogas. This is typically performed by PSA that uses adsorbent materials to selectively adsorb CO_2 and impurities, leaving behind purified biomethane, as described in Section 2.1 [25,27,38]. Alternatively, membrane separation or water scrubbing can be used.

For process option 2, the biogas is fed into a steam reforming process, as described in Section 2.2. The resultant gas mixture is subjected to further treatment, including a water-gas shift to increase the H_2 and CO_2 concentration, and gas separation through PSA to gain the product fractions CO_2 and H_2. Relevant reaction equations for this process option are derived below.

The next step for both process options is CO_2 capture and storage. In process option 1, the biogenic CO_2 from the biogas supply is captured after the separation of the biomethane. In process option 2, biogenic CO_2 is present in the biogas fuel and feed and enriched during biogas burning, reforming and CO-shift steps. After the H_2 separation, the tail gas is redirected to the burner to be oxidized, resulting in further CO_2. The aggregated CO_2 can be captured from a single exhaust gas stream. The essential difference between the two process options is that in process option 1, only the CO_2 present in the biogas can be captured. Part of the carbon content of the original biomass is bound in the CH_4 and is released during the decentralized use of the methane. In contrast, in process option 2, the entire carbon content of the biogas is released during the SMR step and can be captured from the "Exhaust Gas" stream (cf. Figure 2) as CO_2.

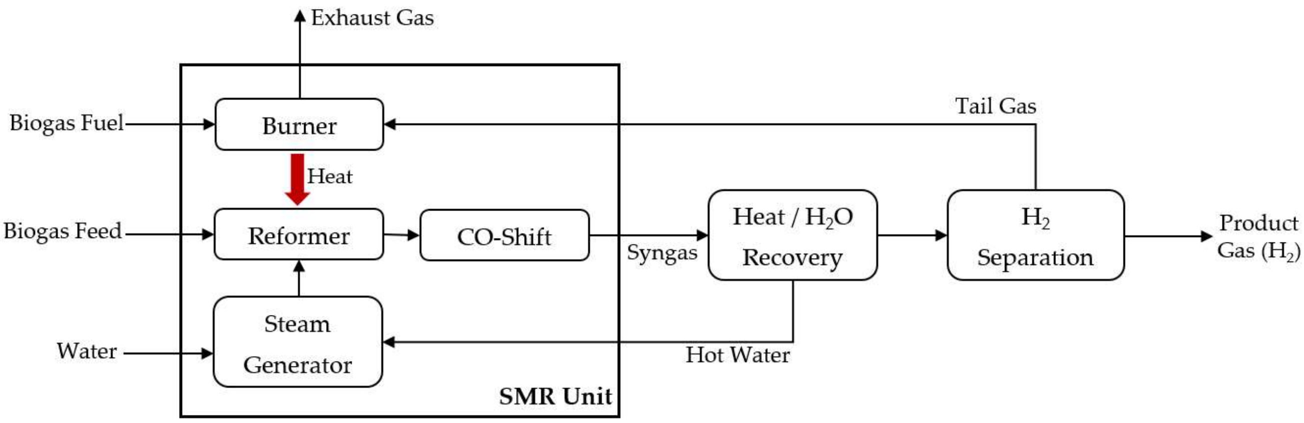

Figure 2. Flow diagram of the steam methane reforming process step within process option 2 (own representation).

After its separation, the CO_2 is compressed for transportation either via pipelines or in containers by truck. Storage sites are often located offshore, which may require additional transport by ship. Which option is more economically and environmentally viable must be decided for each case specifically. Transport over short distances can be carried out by truck and ship, while transport via pipeline involves higher expenditures, but becomes viable in the long term if CO_2 is transported over long distances and when the amounts of CO_2 transported are higher [39,40]. Finally, the CO_2 is stored to prevent its emission into the atmosphere, e.g., in geological formations, such as depleted oil and gas reservoirs or saline aquifers [2].

It is assumed that the use of both chemical energy carriers H_2 and CH_4 provided in process options 1 and 2 is decentralized and that no carbon capture occurs during their use. For example, vehicles can be fueled, or heat can be supplied. Two cases are defined for exemplification: Case A (see system boundary A in Figure 1) compares the biomethane from process option 1 to the biohydrogen produced via process option 2 in terms of their chemical energy content as secondary energy carriers, expressed by the lower heating value (LHV). As depicted in Figure 1, the system boundaries for case A range from the biomass supply to the biomethane and H_2 production.

Case B (see system boundary B in Figure 1) compares the useful energy generation potentials of both process options for heavy-duty transport applications. In process option 1, the useful energy from biomethane is generated by bio-liquefied natural gas (LNG) combustion engines. In process option 2, the energy from H_2 is generated with fuel cell power trains. Hence, the system boundary B is set from the biomass supply to the use of biomethane and H_2, respectively, for heavy-duty transportation (system boundary B in Figure 1). Burning liquefied biomethane in gas engines can reach efficiencies up to 44% [41]. State-of-the-art fuel cell systems for electric truck powertrains peak at efficiencies of 63% [42–44]. In the following, with regard to further technological development and optimization, high efficiencies of 44% (for bio LNG engines) and 63% (for H_2 fuel cell engines) are assumed for both process options.

Relevant reaction equations for Process option 2 are derived in the following: An average biogas composition of 37.5 vol% CO_2 and 62.5 vol% CH_4 is assumed [4]. By converting the units and referring to the product of 1 kg H_2, reaction Equation (3) can be written as follows:

$$3.3 \text{ kg } CO_2 + 2.0 \text{ kg } CH_4 + 4.5 \text{ kg } H_2O_{(g)} \leftrightarrow 1 \text{ kg } H_2 + 8.8 \text{ kg } CO_2; \Delta H = +5.73 \text{ kWh/kgH}_2 \quad (4)$$

This reaction is endothermic and, thus, energy must be provided to drive the reaction towards H_2 and CO_2 production Typically, this energy is supplied in the form of heat, generated by the oxidation of a part of the biogas and of the tail gas after H_2 separation. Figure 2 shows the schematic structure of the SMR process with the respective material and energy flows.

As depicted in Figure 2, the ΔH in reaction (3) representing the endothermic heat of the reaction has to be provided by the burner being part of the SMR unit. Additionally, there is heat demand for steam generation and preheating the feedstock to typical operation temperatures in the reformer of around 800 °C, as well as for compensating wall heat losses and latent heat of the products. The total heat energy supplied amounts to approx. 25 kWh per kg of H_2 produced. This value is based on empirical data from existing biogas SMR units and is taken as an assumption in this paper. The combustion of biogas with air is described by the following equation:

$$n\, CO_2 + CH_4 + 2\,(O_2 + m\, N_2) \rightarrow 2\, H_2O_{(g)} + (n+1)\, CO_2 + m\, N_2; \Delta H = -802.25 \text{ kJ/mol} \quad (5)$$

where n describes the molar ratio of CO_2 to CH_4 in the feed gas and m describes the ratio of N_2 to O_2 in air. Usually air contains around 79 vol% N_2 and 21 vol% O_2 [45]. By converting the units and referring to 1 kg CH_4, Equation (5) can be rewritten as follows:

$$1.65 \text{ kg } CO_2 + 1 \text{ kg } CH_4 + 4 \text{ kg } O_2 + 13.17 \text{ kg } N_2 \leftrightarrow 2.25 \text{ kg } H_2O + 4.4 \text{ kg } CO_2 + 13.17 \text{ kg } N_2 \quad (6)$$

It can be seen that 62.5% of the CO_2 in the exhaust gas originates from the combustion of methane, while 37.5% comes from the biogas.

Summing up, the two process options consist of several identical process steps but also show some differences: The preparation of the feedstock, the biogas production in the biogas plant and the product gas treatment are identical for both processes. To compare both processes from an ecological point of view, these identical process steps can be excluded from the comparison according to the so-called "black-box" approach [46,47]. Also, for the economic comparison, identical plant components can be neglected.

The main differences between the two process options are: (i) The additional biogas SMR step in process option 2. (ii) The higher amount of captured CO_2 leading to more CO_2 to be compressed, transported, and stored in process option 2. Both (i) and (ii) increase the investment and operational costs of process option 2. (iii) The different products with their respective technology options for heavy-duty transportation: biomethane and biogenic CO_2 in process option 1 versus biohydrogen and more biogenic CO_2 in process option 2. Further differences are the technological and cost differences between H_2 and biomethane in compression and transportation.

4. Technology Comparison

4.1. Considerations on Product Application

In this section, the two products, H_2 and CH_4, are compared regarding their product properties. This comparison is independent of the two use cases described in Section 3 and intends to give a broader view on possible applications.

CH_4 has a higher volumetric energy density than H_2, which means it contains more energy per unit volume [48]. This makes CH_4 generally more suitable for applications where space is limited. However, H_2 has a higher energy content per unit mass, which makes it more efficient for applications where weight is a concern [49]. CH_4 and H_2 are both flammable and explosive above certain concentrations [50]. However, H_2 has a wider flammability range and can ignite at lower concentrations. With proper handling and storage, both gases can be used safely [51].

Both biomethane and H_2 are considered to play key roles in future energy provision, e.g., as substitutes for natural gas [52,53]. They can be used for transportation, heating, power generation, and in industrial processes, as described briefly in the following.

CH_4 is commonly used as a fuel for vehicles, especially in the form of compressed natural gas (CNG) or LNG [54,55]. CNG is used in light-duty vehicles such as cars, while LNG is used in heavy-duty vehicles like trucks and buses [56,57]. H_2 can be used with fuel-cell vehicles (FCVs) as well as modified internal combustion engine vehicles [58]. Furthermore, CH_4 as well as H_2 can be used for heating and power generation in residential, commercial and industrial applications. H_2, however, generally requires a specific environment for combustion due to its lower volumetric energy density, faster laminar flame speed, and higher combustion temperatures (1600 °C) compared to CH_4 (1300 °C) [59]. Subsequently, conventional gas engines must first be either retrofitted or replaced with gas turbines that are H_2-ready and thus adequate for the use of 100% H_2.

4.2. Energy Efficiency

Comparing process options 1 and 2, as described in Section 3, the chemical energy contents of the produced gases are a critical factor for energy efficiency comparison. Therefore, the available thermal energy produced by a combustion of the gases, expressed by the mass-specific lower heating value (LHV), was considered. As described in Section 2.2, the reactions of biomethane to CO_2 and H_2 proceed under energy input. The thermal energy for the endothermic reaction is obtained via the oxidation of biogas. Since CO_2 is completely oxidized, the thermal energy is obtained via full oxidation of the CH_4 in the biogas.

For the following calculation, it is further assumed that biogas consists of 62.5 vol% CH_4 and 37.5 vol% CO_2. This is an average value based on existing biogas processes, as described in Section 2.2. Equation (7) is derived from Equation (4) under consideration of the 25 kWh thermal energy input required for the overall SMR process, as described in Section 3.

$$2.0\text{ kg } CH_4 + 4.5\text{ kg } H_2O_{(g)} + 25\text{ kWh}_{th} \rightarrow 1.0\text{ kg } H_2 + 5.5\text{ kg } CO_2 \quad (7)$$

The chemical energy content of CH_4 and H_2 was calculated with Equation (8) using the LHV for the quantities given. The LHV of CH_4 is 13.9 kWh/kg and of H_2 33.33 kWh/kg [60].

$$E_i = LHV \times m_i \quad (8)$$

E_i is the total chemical energy content for the considered mass of the species i [in kWh] and m_i the mass of the species i [in kg]. In this case, 2.0 kg of CH_4 has an energy content of 27.8 kWh. Thus, 52.8 kWh of energy input, divided into 2.0 kg CH_4 (LHV) and thermal energy of 25 kWh, leads to 33.33 kWh of chemical energy produced in the form of 1 kg H_2 (LHV), as shown in Table 1. Therefore, the efficiency of the considered steam-reforming process is 63% in terms of the chemically stored energy content of the product H_2 in relation to the overall energy input.

Table 1. Energy balance for the production of 1.0 kg H_2 by biogas steam reforming (process option 2, system boundary A).

	Energy Input	**Energy Output**
Chemical energy content CH_4	27.8 kWh	0.0 kWh
Chemical energy content H_2	0.0 kWh	33.33 kWh
Thermal energy	25.0 kWh	0.0 kWh
Total	52.8 kWh	33.33 kWh

To compare the energy efficiency of CH_4 and H_2 in the heavy-duty transportation sector (case B), the efficiencies of the corresponding technologies must be included. As listed in Section 3, gas engines for liquefied biomethane can reach efficiencies up to 44%, while fuel cell systems with batteries for H_2 peak up to 63% [42–44]. The efficiencies can be included using the following equation.

$$E_{in} = E_{out}/\eta \tag{9}$$

where E_{in} is the energy in kWh, E_{out} is the usable energy in kWh and η is the efficiency of the corresponding technology.

For biomethane, providing 1 kWh of usable energy for transport requires an energy input of 2.27 kWh at an efficiency of 44%. For H_2, the calculation must also take into account the energy efficiency of its production via steam reforming with a value of 63.1%, as shown above and in Table 2. Thus, for a 63% efficiency of the fuel cell system with a battery, the total efficiency of process option 2 for case B is 39.8%. This means that to supply 1 kWh of usable energy in the form of H_2, an energy input of 2.52 kWh is needed. Hence, using H_2 produced in process option 2 means a loss of approx. 4.2% of the usable energy in the form of propulsion energy for heavy-duty transport compared to process option 1.

Table 2. Required energy input for the production of 1.0 kWh usable energy (process options 1 and 2, system boundary B).

	Process Option 1	**Process Option 2**
Usable Energy	1.0 kWh	1.0 kWh
Efficiency (heavy-duty transport)	44.0%	63.0%
Relative Efficiency (production)	100%	63.1%
Total Efficiency	44.0%	39.8%
Energy Input	2.27 kWh	2.52 kWh

However, this is within the range of several uncertainties due to the assumptions made, e.g., assumed powertrain efficiencies and different driving behaviors. Furthermore, the compression of the two gases, CH_4 and H_2, are not considered. To convert CH_4 gas into LNG, an energy loss of 10–20% can be assumed (1.39–2.78 kWh/kg CH_4) [61]. For H_2 compression to 400 bar, an energy loss of about 10.8% (3.61 kWh/kg H_2) can be assumed [62]. Since the energy consumptions for both applications are associated with uncertainties and are in a similar order of magnitude, they can be neglected in the calculations.

In conclusion, however, it can be said that for Use Case B, the efficiency losses that occur in process option 2 due to the reforming process step (Use Case A) can be counterbalanced by better efficiency in the FCEV power train, leading to the useful energy for heavy-duty transport being in a similar order of magnitude for both process options.

4.3. Negative Emission Potential

The NEP represents the amount of negative emissions that are possible if all GHG emissions caused along the entire value chain up to the use or storage of the product gases are neglected, as described in Section 2.3. It can be used to compare the two process options described in Section 3 following the “black box” approach, where identical process steps are excluded from the comparison [46,47]. To determine the NEP, the theoretical maximum amount of storable biogenic CO_2 is calculated for the process options. Therefore, the amount of CO_2 generated via biogas production in the biogas plant is considered first. It is assumed, as described in Section 4.2, that biogas consists of CH_4 (62.5 vol%) and CO_2 (37.5 vol%). Thus, 1 Nm^3 biogas consists of 0.375 m^3 CO_2 and 0.625 m^3 CH_4. Furthermore, the biogas was considered an ideal gas. According to the ideal gas law [63], this leads to the following equation being applicable:

$$pV_k = n_k RT, \tag{10}$$

where p is the pressure in Pascal, V_k is the volume of the species k in m^3, n_k is the amount of the species k in mol, R is the general gas constant (in J/mol·K), and T is the temperature in K. From the ideal gas law, a molar ratio of 0.6 mol CO_2/mol CH_4 is obtained for the assumed average composition of biogas. This corresponds to a mass ratio of 1.65 kg CO_2/kg CH_4 and means that 1.65 kg of CO_2 is produced via the biogas plant per kilogram of CH_4 produced in process option 1. In process option 2, an additional 2.75 kg of CO_2 is produced from heat supply through biogas combustion and reforming, when the same amount of biogas containing 1 kg of CH_4 is supplied as input stream. Adding this amount to the biogenic CO_2 in the biogas leads to a total of 4.4 kg CO_2 to be captured in process option 2.

In summary, the biomethane production (process option 1) results in an NEP of 1.65 kg CO_2 per kg CH_4 produced, while the HyBECCS approach (process option 2) shows a NEP of 4.4 kg CO_2 for the same biomass input. This corresponds to about 2.7 times the amount of storable biogenic CO_2 of process option 2 compared to process option 1. Furthermore, depending on the biogas quality (CH_4 content), this ratio deviates, as shown in Figure 3. The NEP of process option 2 increases to up to 3.3 times the amount of process option 1 for a CH_4 content in the biogas of 70 vol%. For a CH_4 content in biogas of 55 vol%, the NEP for process option 1 is still 2.2 times higher than that of process option 1.

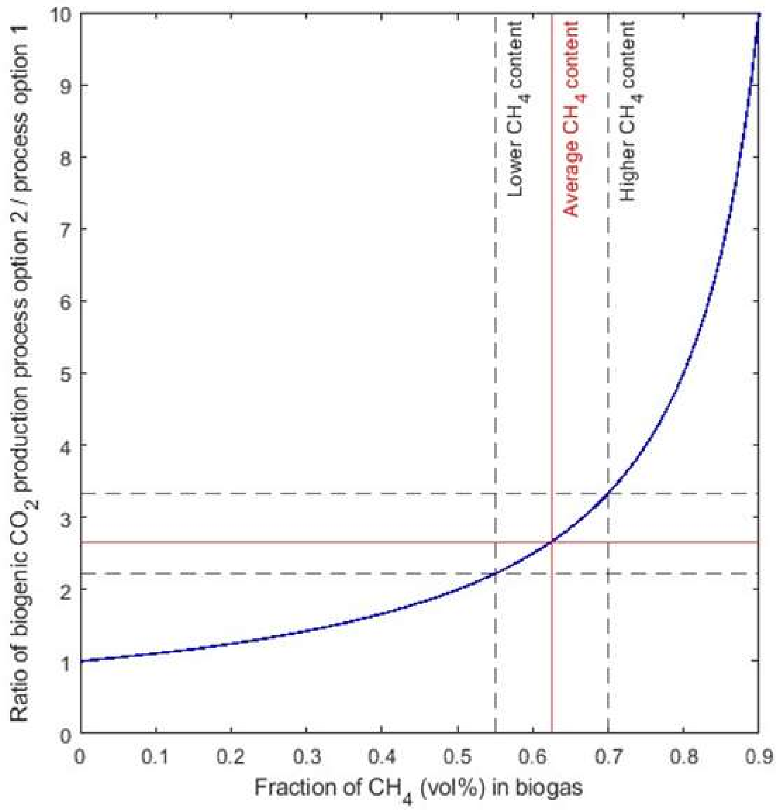

Figure 3. Ratio of biogenic CO_2 production of process option 2 vs. process option 1 for different CH_4 volume fractions in biogas (own representation).

4.4. Economic Comparison

The costs required and revenues to be expected for the two process options can vary significantly depending on the specific technology and scale of the project. However, some general considerations can be made.

Costs that arise in both process options can be neglected in the comparison, e.g., the main technologies used for upgrading biogas to biomethane are PSA and membrane separation [64]. This is also required for the purification of the biohydrogen and can therefore be neglected for the comparison [65]. Additionally, there may be costs associated with obtaining permits, certifications, and approvals for the biomethane as well as the biohydrogen production, depending on the regulations in the specific country or region. These costs can also vary depending on the project location and regulatory environment and are neglected in this work.

The costs for biogas steam reforming to produce H_2 include the capital costs of the reforming unit, which is the main equipment required for the process. Therefore, the capital costs for process option 1 are generally lower than for process option 2. This is primarily because additional plant components for the reforming process step are needed in process option 2. The costs for the SMR upgrade have to be analyzed specifically for each case. However, the additional costs for the SMR upgrade have to be compensated by a higher income from the sale of the products in order to be economically feasible. The income side is described in the following.

Furthermore, the different sources of income with their respective market prices, today and in the future, can be compared. In process option 1, the marketable products are CH_4 and negative emissions, whereas, in process option 2, the marketable products are H_2 and negative emissions. The total income for each process option depends on the market prices of the respective products today and in the future during the lifetime of the plant as well as the generated amount of each product. A total of 3.6 kg of CH_4 is necessary for the production of 1 kg of H_2, as described in Section 3. Process option 2 therefore requires 3.6 times the amount of biogas input per kg of produced energy carrier. Considering negative emissions, however, process option 2 has the potential to produce about 2.7 times the amount of storable biogenic CO_2 to be captured and stored, as shown in Section 4.3.

The current market prices of CH_4 and H_2 vary depending on the region and quality. However, some general price comparisons can be made based on available data. In the United States, the retail price of CNG for transportation ranges from USD 2–4 per gasoline gallon equivalent (GGE) (EUR 0.72–1.45 per kg natural gas [66]), whereas the retail price of LNG for transportation ranges from USD 2–5 per diesel gallon equivalent (DGE) (EUR 0.68–1.69 per kg LNG [66]), both depending on the location and the supplier. The retail price of H_2 for transportation ranges from USD 9.5–13.2 per kg (EUR 8.8–12.3 per kg), depending on the location and the supplier [67]. In Europe, the fuel prices for transportation vary from country to country. In the first quarter of 2022, the average fuel price range for CNG in Europe was EUR 5.23 to EUR 12.51 per 100 km travelled (average EUR 7.24 per 100 km), based on information submitted by nine member states [68]. Assuming an average consumption of 3.64 kg of CNG per 100 km [69], this corresponds to a price range of EUR 1.44 to EUR 3.43 per kg of CNG (Average: EUR 1.99 per kg). For LNG, the average retail price range for the same period was from EUR 0.45 to EUR 2.81 per kg of LNG, with an average price for Europe (EU-27) of EUR 1.86 per kg LNG [70]. With an average consumption of 2.14 kg LNG per 100 km for heavy trucks [56], this corresponds to a price range of EUR 0.96 to EUR 6.01 per 100 km (average: EUR 3.98 per 100 km). Average H_2 prices in the first quarter of 2022 ranged from EUR 9.00 to EUR 15.06 per 100 km (average: EUR 11.22 per 100 km), based on information submitted by six member states. Assuming an average consumption of 0.8 kg H_2 per 100 km [71], an average price range of EUR 11.25 to EUR 18.83 per kg of H_2 (average: EUR 14,01 per kg H_2) is obtained. An overview of the pump price ranges for different fuels in the European Union is shown in Table 3.

Table 3. Overview of price ranges for different fuels in the European Union (average for Q1 of 2022) [68,70].

Fuel	Price (EUR/kg)	Price (EUR/100 km)	Reference
CNG	1.44–3.43 Average: 1.99	5.23–12.51 Average: 7.24	[68]
LNG	0.45–2.81 Average (EU-27): 1.86	0.96–6.01 Average (EU-27): 3.98	[70]
H_2	11.25–18.83 Average: 14.01	9.00–15.06 Average: 11.22	[68,71]

Summarizing, the current market prices of CH_4 are clearly lower than those of H_2. This is due to H_2 being a downstream product predominantly produced from CH_4 obtained from natural gas [72]. However, the long-term price forecasts for H_2 indicate potential for lower prices due to cost reductions through technological alternatives like electrolysis as well as economies of scale [73].

Both process options generate negative emissions, when the biogenic CO_2 is not released into the atmosphere but captured, transported to a storage site, and permanently stored. However, generating negative emissions from biogenic CO_2 creates further costs and will, therefore, only happen when they are overcompensated by an income. One option is the sale of so-called carbon removal units (CRUs) issued for verified negative emissions (in tCO_2e) and can be sold to buyers who wish to claim them. Already today, several private entities offer CRUs [74]. They stem from different carbon-removal approaches in different countries with different underlying quality standards and show broad price ranges. Examples are EUR 20/CRU for bio-based construction materials in France to EUR 535/CRU for biochar in Sweden [75]. In November 2022, the European Commission proposed an EU carbon-removal certification framework (CRCF) to establish common rules for the monitoring, verification, and reporting of negative emissions for the voluntary carbon removal market [76]. This EU initiative is still ongoing. However, this standardization process within the geographical boundaries of one of the biggest carbon trading schemes worldwide shows the awareness of the political bodies for the urgent need to create a secure and credible playing field for the commercialization of CRUs. Summing up, negative emissions are already today a marketable product, and, in the future, ongoing standardization processes will increase the visibility, reliability, and, thus, the market volume for negative emissions in Europe and worldwide.

As outlined in Section 4.3, process option 1 results in an NEP of 1.65 kg CO_2 per kg of CH_4 produced, while process option 2 shows an NEP of 4.4 kg CO_2 for the same amount of biomass input. The NEP represents the maximum amount of negative emissions to be produced and qualified for CRUs in each option. Process option 1 generates 1.0 kg of bio-LNG, while process option 2 generates 0.5 kg H_2 for the same amount of biomass input, as outlined in Section 3. The following price ranges, also described above, give the following price averages for the products: For H_2, the price range of 0.93–3.72 EUR/kg H_2 results in an average price of 2.325 EUR/kg H_2. For LNG, the price range of 0.68–1.69 EUR/kg LNG results in an average price of 1.185 EUR/kg LNG. For CRU, the price range of 20–535 EUR/CRU results in an average price of 277.5 EUR/CRU. For process option 1, this means that the products (LNG and CO_2) can generate an income of 459.06 EUR/kg of CH_4 produced. For process option 2, the products (H_2 and CO_2) can generate an income of 1222.16 EUR for the same amount of biomass input. In this simplified exemplary calculation, process option 2 would generate more income. However, cost consideration is necessary for final economic comparison and CRU pricing is still not fixed or legislated. The calculation shows, however, that depending on the market value of the different products, yields determine the superiority in terms of income of the process options and gives first indications and orientation values.

5. Limitations

This paper focuses on comparing the biomethane vs. biohydrogen with CCS options in terms of their energy efficiency, economic aspects, and negative emission potential. Other environmental impacts are not considered. However, both approaches' impacts on the environment must be analyzed for a holistic assessment. Impacts on social sustainability are neglected in this paper.

The energy efficiency for the steam reforming of biogas was calculated under the assumption that an additional 25 kWh of thermal energy is required for the process. This includes, on the one hand, the reformation energy but also, for example, the energy required to heat the gases or to evaporate the liquid water. Depending on the ambient parameters or energetic optimizations, the value for the required thermal energy can be higher or lower, resulting in a change in energy efficiency. This assumption is based on experience values and should be validated. This also applies to all other assumptions, such as the efficiency of the LNG or fuel-cell propulsion and the compression/cooling of the gases in Use Case B or the average biogas composition.

Considering the economic comparison and the wide price ranges, as well as the different cost structures of both process options, requires a deeper economic analysis, taking into consideration more influencing factors such as investment and operational costs, location, and the time of operational initiation of the plant.

6. Summary and Conclusions

Climate change constitutes one of the most pressing challenges of our times. Innovative technologies are needed that can reduce GHG emissions in all sectors. Action is especially necessary in the energy sector, which is currently responsible for the largest amount of emissions. A transition to cleaner energy sources like renewable energies and carbon-free energy carriers like H_2 is thus urgently needed. Additionally, to limit human-induced global warming to less than 2 °C compared to pre-industrial levels, NETs or CDR technologies are indispensable.

In this paper, biomethane production from biogas with CCS (process option 1) was compared to biohydrogen production via the SMR of biogas with CCS (process option 2), i.e., a HyBECCS approach. The analysis considers technical, economic, and environmental aspects of the two options. The aim was to provide insights into the trade-offs to be considered.

Considering energy efficiency, the production of biohydrogen in process option 2 results in an energy loss of approximately 37% in terms of the absolute LHV of the products per kg of biomass or biogas input. Looking at usable driving energy for heavy-duty transport applications, using H_2 produced in process option 2 still results in a comparable loss of approx. 4.2% in terms of usable driving energy for the heavy-duty transport sector. However, this is within the range of several uncertainties due to the assumptions made, e.g., assumed powertrain efficiencies, LNG liquefaction (10–20% energy loss), and different driving behaviors. In conclusion, the useful energy generation for heavy-duty transport can be expected to be in a similar order of magnitude for both process options.

To determine the negative emission potential, the theoretical maximum amount of storable biogenic CO_2 (NEP) was calculated for both process options. In comparison, process option 1 results in an NEP of 1.65 kg CO_2 per kg of CH_4 produced, while the HyBECCS approach (process option 2) shows an NEP of 4.4 kg CO_2 for the same amount of biomass input. This corresponds to about 2.7 times the amount of storable biogenic CO_2. Depending on the quality of the biogas process step (CH_4 content in the biogas), even more biogenic CO_2 can be captured and stored with the HyBECCS approach compared to process option 1. The NEP of process option 2 increases to up to 5 times the amount of process option 1 for a CH_4 content in biogas of 70 vol%. For a CH_4 content of biogas of 55 vol%, the NEP for process option 2 is still 2.2 times higher than that of process option 1.

The costs required for the two process options can vary significantly depending on the specific technology and scale of the reforming plant considered. Biogas SMR requires additional equipment leading to higher investment costs. Further to this, the current market prices for CH_4 are generally lower than for H_2. However, the long-term price forecasts for H_2 indicate a potential for lower prices due to cost reductions through technological advances and economies of scale. Negative emissions are a marketable product already. In the future, ongoing standardization processes will increase their visibility, reliability, and, thus, market potentials in Europe and worldwide. This market potential correlates with the NEP and is thus about 2.7 times higher for process option 2.

In conclusion, producing biohydrogen via the SMR of biogas offers the possibility to capture between 2.2 and 5 times more of the carbon bound in biomass compared to biomethane production. Captured biogenic CO_2 has the potential to create negative emissions that can be marketed as a byproduct besides the resulting energy carrier. However, the production of biohydrogen from biomethane results in an energy loss of approximately 37% in terms of the LHV of the product gases, but this loss can likely be partially compensated by efficient driving technologies such as FCEVs.

7. Outlook

Negative emissions will gain relevance in the coming decades, further highlighting the benefits of HyBECCS approaches such as process option 2 in this paper. Overall, they have the potential to make a significant contribution to lowering GHG emissions and establishing CO_2 sinks, thereby making the energy sector more sustainable. A deep economic analysis, considering several influencing factors such as investment and operational costs, product price forecasts, scale, location, and the time of a plant's operational initiation, must be carried out for a thorough comparison of the presented process options. Furthermore, the ecological impact of both process options has to be analyzed in a holistic assessment, including the GHG emissions caused throughout the entire lifecycle of each product couple. Therefore, developing an approach to determine the positive and negative impacts on the climate to identify the approach with the highest climate-change mitigation potential is required. This includes the development of an approach to evaluate different CCS and CCU options concerning their respective GHG mitigation potential. To allow for comparisons with other HyBECCS and NETs, the central Key Performance Indicators (KPIs) of leveled costs of carbon-negative H_2 (LCCNH) and leveled costs of negative emissions (LCNE) must be calculated for both process options [30]. Comparing the KPIs is essential for cost efficiency in NET and HyBECCS development and deployment.

Market integration of HyBECCS plants depends on establishing infrastructure for transporting both H_2 and CO_2. The different options and their future perspectives must be analyzed considering their influence on the feasibility and economics of HyBECCS approaches. Furthermore, the feasibility of specific HyBECCS plants depends on the market for both products. Thus, analyzing the present and future market potential of H_2 and CO_2 in selected geographical areas is needed.

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Appendix C: Paper C

Contributions to the work

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Data Curation	✓	✓	✓		
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Writing (Review and Editing)				✓	✓
Visualization	✓	✓	✓		
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RESEARCH REPORT

Carbon-negative hydrogen production: Fundamentals for a techno-economic and environmental assessment of HyBECCS approaches

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Abstract

In order to achieve greenhouse gas neutrality, hydrogen generated from renewable sources will play an important role. Additionally, as underlined in the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), new technologies to remove greenhouse gases from the atmosphere are required on a large scale. A novel concept for hydrogen production with net negative emissions referred to as HyBECCS (Hydrogen Bioenergy with Carbon Capture and Storage) combines these two purposes in one technological approach. The HyBECCS concept combines biohydrogen production from biomass with the capture and storage of biogenic carbon dioxide. Various technology combinations of HyBECCS processes are possible, whose ecological effects and economic viability need to be analyzed in order to provide a basis for comparison and decision-making. This paper presents fundamentals for the techno-economic and environmental evaluation of HyBECCS approaches. Transferable frameworks on system boundaries as well as emission, cost, and revenue streams are defined and specifics for the application of existing assessment methods are elaborated. In addition, peculiarities concerning the HyBECCS approach with respect to political regulatory measures and interrelationships between economics and ecology are outlined. Based on these considerations, two key performance indicators (KPIs) are established, referred to as levelized cost of carbon-negative hydrogen (LCCNH) and of negative emissions (LCNE). Both KPIs allow deciding whether a specific HyBECCS project is economically viable and allows its comparison with different hydrogen, energy provision, or negative emission technologies (NETs).

KEYWORDS

HyBECCS, carbon capture and storage, CCS, carbon capture and utilization, CCU, hydrogen, bioenergy, BECCS, DACCS, PCC, biohydrogen, carbon-negative hydrogen, green hydrogen, negative emission technologies, NET, carbon dioxide removal, CDR, bioenergy, waste to energy, waste to hydrogen, biogenic hydrogen, biogenic carbon dioxide, climate protection, greenhouse gas mitigation, GHG mitigation, climate change mitigation, renewable hydrogen, green technologies, carbon removal certificates, carbon removal certification, CRC

1 | INTRODUCTION

On a global level, only with the combination of greenhouse gas (GHG) reductions and the fast deployment of negative emission technologies (NETs), humanity has a chance to limit global warming to 2°C or even 1.5°C, as strikingly alerted by the Intergovernmental Panel on Climate Change (IPCC) in its latest report (Masson-Delmotte, et al., 2021). The IPCC clearly states that a successful limitation of global warming to 1.5°C builds upon two pillars. One is the fast and deep reduction of anthropogenic GHG emissions from fossil fuel combustion and the destruction of natural carbon storages such as forests and wetlands, referred to as GHG mitigation or reduction. The second pillar is the active removal of carbon dioxide (CO_2) from the atmosphere through NETs (IPCC). Only with the combination of these two approaches, humanity can possibly stay on an emission pathway toward 1.5°C. This pathway reaches net-zero GHG emissions around 2050 and enters into a net-negative GHG emission zone afterward (Masson-Delmotte, et al., 2021; IPCC). All scenarios calculate with gross negative GHG emissions, implying the implementation of large-scale NETs (Honegger & Reiner, 2018a, p. 307; Poralla et al., 2021, p. 19; Rogelj et al., 2015; UNEP, 2017, p. 59; UNFCCC). Based on this global target, over 100 countries, together emitting over 50% of global GHG, have set themselves the goal of GHG neutrality or negativity to be achieved at different points in time before 2060 (Poralla et al., 2021, p. 26).

Most nations, as well as international associations, consider technological innovations as key factors to avoid GHG emissions in order to achieve their respective climate goals. In this context, hydrogen (H_2) production from renewable resources as well as the generation of negative emissions by means of bioenergy with carbon capture and storage (BECCS) are frequently listed as key technologies for this transition (Full, Trauner, et al., 2021; FCH JU, 2019; IPCC; Miehe et al., 2019; Wietschel et al., 2021). One innovative approach that combines hydrogen production with BECCS is the production of biohydrogen from biomass with capture and storage of the co-produced biogenic carbon dioxide, abbreviated to HyBECCS (Hydrogen Bioenergy with Carbon Capture and Storage) (Full, Merseberg, et al., 2021; Full, Trauner, et al., 2021). A selection from multiple technology combination options is the next step in the development of the HyBECCS approach. These options have to be comparable and evaluable in terms of ecological and economic aspects. Therefore, the research objective of this paper is to introduce fundamentals for a techno-economic and ecological assessment of HyBECCS approaches or individual HyBECCS projects based on standardized methods and indicators. It shall provide a basis for the optimization toward a more sustainable HyBECCS process design by maximizing the positive effects on the climate and economic returns. This might serve as a reference for private investors, as well as political decision makers, to evaluate HyBECCS approaches and enable targeted public subsidies and private investments. The assessment fundamentals are elaborated as summarized in Figure 1.

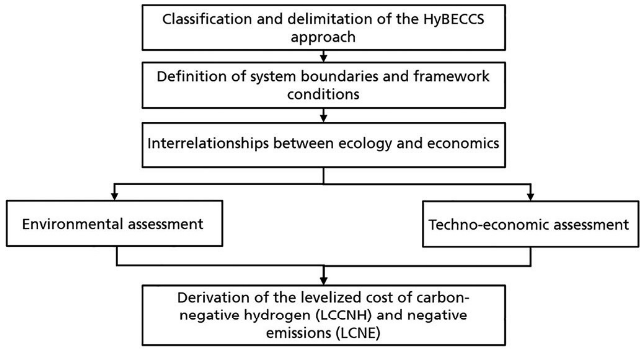

FIGURE 1 Schematic overview of the contents of the paper

First of all, a classification and delimitation of HyBECCS are essential to describe the approach in the context of negative emission technologies. Furthermore, the classification serves to ensure a consistent use of the term "HyBECCS" in further research, thus ensuring its ecological integrity. Uniform system boundaries and framework conditions are elaborated to provide a basis for standardized economic and environmental evaluation of different HyBECCS projects. Within the regulatory status quo of negative emission technologies, existing literature on BECCS and direct air carbon capture and storage (DACCS) is reviewed to identify and highlight the urgent next steps for NET implementation such as HyBECCS. Additionally, the need to develop and implement internalization mechanisms for negative emission technologies is examined. Once these steps are completed, the fundamentals for conducting an environmental and techno-economic assessment of a HyBECCS project are outlined. Based on the environmental and techno-economic assessment, two key performance indicators (KPI) are derived, namely the levelized cost of carbon-negative hydrogen (LCCNH) and the levelized cost of negative emissions (LCNE). These KPIs allow for a comparison of HyBECCS projects with different hydrogen or energy provision technologies and NETs.

2 | BASICS

2.1 | Classification and Delimitation of the HyBECCS Approach

As elaborated by Full et al. 2021, the generation of biogenic CO_2 as a by-product in most biomass to hydrogen

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production processes is the basis for the HyBECCS approach. This applies to both thermochemical and biotechnological technologies of biohydrogen production (Full, Merseburg, et al., 2021; Full, Trauner, et al., 2021). A simplified illustration of the approach is shown in Figure 2: On the left side, atmospheric CO_2 and water are stored via photosynthesis in biomass. In the biomass conversion plant, the biomass is converted mainly into hydrogen and biogenic CO_2. Hydrogen can be used, for example, in fuel cells to generate electricity or heat. With O_2 as educt and water as a product of the reaction, mass balance equilibrium is established for oxygen and water. Biogenic CO_2 can be stored or used in the long term, leading to negative emissions (Full, Merseburg, et al., 2021; Full, Trauner, et al., 2021). The biomass conversion plant and the carbon storage together constitute the HyBECCS project.

According to the work of Full et al. 2021, the HyBECCS approach can be split into four basic process steps: 1. substrate biomass pretreatment, 2. production of biohydrogen and biogenic CO_2, 3. separation of the product gases CO_2 and H_2, and 4. their processing for use of hydrogen and long-term storage or use of biogenic CO_2. For each of the four steps, there are different technology options to choose. The main technological advantage of the HyBECCS approach is the energy-efficient capture of biogenic CO_2 as a point source (Full, Merseburg, et al., 2021). It, furthermore, provides a double effect on climate mitigation through the provision of the emission-free energy carrier hydrogen and its potential as a CO_2 sink. The comparative advantage of HyBECCS over many other bioenergy production approaches, such as the production of hydrocarbon-based biofuels like biogas or biomethane, is that the energy carrier distributed to the end users is CO_2-free and the CO_2 emissions already occur at the plant, where they can be centrally captured (Full, Merseburg, et al., 2021). Another advantage of HyBECCS over the BECCS approach of combined heat and power (CHP) plants burning biomass is the higher flexibility and usability of hydrogen compared to electricity and heat. Hydrogen can be stored over long periods of time, transported over long distances without

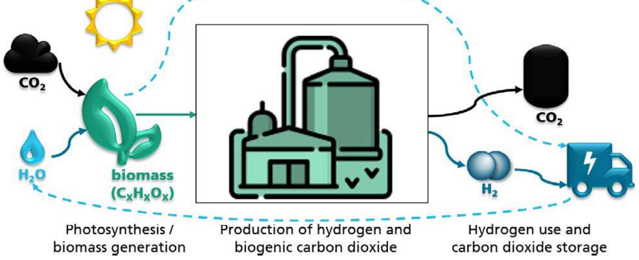

FIGURE 2 Simplified illustration of the HyBECCS approach (arrow = mass flow, dashed arrow = mass balance equilibrium)

significant losses, and has multiple applications beyond the generation of electricity and heat (Wietschel et al., 2021) (S. 20ff). Examples are its use as auxiliary in many industrial applications and as basic material, e.g., in the urea and fertilizer production (IEA) (S. 32); (Hydrogen Council). Based on these advantages, HyBECCS is considered to be a promising and highly effective climate protection technology that is expected to play a major role in future energy systems by making a significant contribution to meeting the world's rapidly growing demand for new renewable energy sources, such as biohydrogen, and negative emissions at the same time (Coalition for Negative Emissions; FCH JU, 2019; IPCC; Wietschel et al., 2021). The approach can also be seen as part of the biological transformation process, aiming to build the economy upon sustainable, nature-based processes instead of fossil resource depletion (Full et al., 2019; Full, Baumgarten, et al., 2021; Miehe et al., 2018, 2019, 2020).

HyBECCS can be placed in the context of existing technology clusters and definitions some of which are not yet clearly distinguished. Experts criticize the continued lack of clarity, for example, on the exact definition of NETs, carbon dioxide removal (CDR), and carbon capture and storage (CCS) (Poralla et al., 2021; Tanzer & Ramírez, 2019). To establish a consistent use of terms in the interest of the ecological integrity of HyBECCS, the following clarifications are stated. Carbon capture and storage (CCS) embraces all anthropogenic activities to capture and store carbon dioxide in the—yet to be defined—long term (IPCC). CO_2 to be stored in CCS approaches can be of any type: fossil, atmospheric or biogenic. It is, however, of utmost importance to keep in mind that CCS of fossil carbon dioxide emissions is not a NET technology and can never generate net-negative emissions. Fossil CO_2 and other GHG are emitted when burning fossil fuels or when their derivatives decompose after use. Even in the yet utopic case of a 100% carbon dioxide capture rate, the process always remains GHG positive, or carbon-neutral when not considering process emissions and other GHG than CO_2. Fossil CCS can, in the best case, only reduce the total GHG footprint of the overall process, qualifying thus merely as a so-called GHG mitigation activity or GHG reduction activity (Poralla et al., 2021). In contrast, carbon dioxide removal (CDR) and NET refer to anthropogenic activities that remove CO_2 from the atmosphere and thus lower its overall atmospheric concentration. Hence, only the CCS of atmospheric or biogenic CO_2 can qualify as CDR or NET. NETs and CDR can be grouped into nature-based approaches such as afforestation or reforestation, wetland restoration, enhanced weathering, soil carbon sequestration and accelerated mineralization, on the one hand, and technological or hybrid approaches such as DACCS and BECCS, on the other hand (Poralla et al., 2021, p. 18). Biohydrogen production technologies that enable the storage of biogenic carbon in solid form, such as biomethane pyrolysis, can also be considered as HyBECCS concepts. However, the focus of consideration in this paper is on the capture and storage of gaseous CO_2 from biohydrogen processes. According to the definitions above, all considered concepts (CCS, NET, CDR) can apply to the HyBECCS concept. It is able to remove carbon dioxide from the atmosphere and can, therefore, be considered as CDR via CCS of biogenic CO_2. This implicit condition is specified in more detail in 3.2. In addition to storage options, the biogenic carbon dioxide can also be combined with carbon utilization (CU). Carbon utilization comprises all approaches where carbon dioxide is used as feedstock or auxiliary (IPCC). In case the utilized carbon dioxide is stored over a very long period for such use, the respective CU approach can be considered as carbon storage (CS). However, the definition of how long CO_2 has to be stored in order to count as "stored" with a positive effect on global climate is still pending for CS, in general, and for long-term CU, in special. The term "CS" within "HyBECCS" comprises the long-term carbon storage as well as the long-term extraction of CO_2 from the atmosphere via carbon utilization. The following Table 1 summarizes the characteristics of the technologies and technology clusters under consideration.

Also for hydrogen, clarification is needed due to inconsistencies and imprecisions in literature. Hydrogen is often categorized in colors. In the "theory of colors" of hydrogen, grey hydrogen is extracted from fossil resources, thus releasing fossil GHG emissions and accelerating global warming. Blue hydrogen is grey hydrogen combined with CCS. Fossil CO_2 emissions from hydrogen production by steam reforming of natural gas are captured and stored in this process. Even though blue hydrogen is partly considered as low-carbon or even carbon-neutral (Bundesministerium für Bildung und Forschung - BMBF; Minli et al., 2021; Noussan et al., 2021; Yan et al., 2020), recent lifecycle assessments show that it causes as little as 9%–12% less GHG than grey hydrogen, especially due to high fugitive methane emissions (Howarth & Jacobson, 2021). Turquoise hydrogen, derived from the pyrolysis of methane and producing solid carbon, can theoretically be GHG neutral when the used electricity is entirely renewable (Newborough & Cooley, 2020). Green hydrogen is either only defined as hydrogen from water electrolysis using electricity generated with renewable energy or additionally includes biomass-based hydrogen production methods, the product being called biogenic hydrogen (Newborough & Cooley, 2020) or biohydrogen (Full, Merseburg, et al., 2021). Hydrogen from electrolysis and biohydrogen is mostly not GHG-neutral due to process GHG emissions, but can mostly be considered as low-carbon hydrogen. Despite on-going initiatives, there is no established uniform threshold of GHG intensity for hydrogen to qualify as "green" or "low-carbon" (certifhy; Hinicio; Newborough & Cooley, 2020). Therefore, hydrogen is categorized in this paper as GHG-neutral, -positive, or -negative according to its GHG balance. The prefix "GHG-" can also be replaced by "carbon-" in this context, resulting in the terms carbon-neutral, -positive, or -negative, which are, respectively, used as synonymous alternatives.

2.2 | System Boundaries and Framework Conditions

To evaluate the economic efficiency and the environmental performance of HyBECCS approaches, a uniform framework is required. Figure 3 represents the system boundaries for techno-economic and environmental assessment of HyBECCS approaches. The system boundary of HyBECCS projects (B3) is divided into two system elements, each of which can be considered separately with its own system boundary: The generation of hydrogen and biogenic CO_2 from biomass is referred to as the system element HyBECC and as system boundary B1. The storage of carbon dioxide or its long-term utilization is referred to as system element CS/CU and as system boundary B2.

In addition to the actual step of hydrogen and carbon dioxide derivation from biomass substrates, the HyBECC

TABLE 1 Summarized classification of the considered technologies and technology clusters and their respective characteristics. (Own elaboration based on AACE International (2020), Couper (2003), Kunysz (2020), Matthes et al. (2020), Towler and Sinnott (2013), Weber (2016), Zimmermann et al. (2020))

Type of CO_2	CCS	CDR/NET	GHG balance	Technology options
Fossil	✓	×	Positive	
Biogenic from non-renewable biomass (e.g. slow-growing biomass)	✓	×	Positive	
Biogenic from renewable biomass (e.g. fast-growing biomass)	✓	✓	Potentially negative	BECCS, HyBECCS
Atmospheric	✓	✓	Potentially negative	DACCS

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system boundary B1 also includes the pretreatment steps of the biomass input (I) as well as gas processing of the resulting hydrogen and the captured CO_2. The CS/CU system boundary B2 includes the transport of captured CO_2 to the storage or utilization site, the storage itself and its maintenance (CS) as well as the processing of the CO_2 for utilization (CU). Both subsystem boundaries B1 and B2 can be considered individually or combined to evaluate the HyBECCS system (B3). Related costs (C), revenues (R), and emissions (E) are assigned to the two subsystem boundaries B1 and B2 and summed up in the HyBECCS system boundary B3. In general, the emission flows E1, E2, E2b, and E3 can be of different types (e.g., noise, pollutants, and greenhouse gases) and the system abstraction above can be used for the analysis of emission flows of any kind. For the present analysis, however, all emission streams only represent the respective greenhouse gas emissions. Their characteristics and interrelationships are described in more detail in the following.

The system element HyBECC (B1) causes GHG emissions (E1), for example, indirectly through the biomass generation, procurement, pretreatment, and process energy demand. Various types of costs (C1) are incurred, such as capital and operating expenditures. Revenues of the HyBECC system element are generated by the sales of hydrogen (R1a) and of biogenic carbon dioxide (R1b), summed up in R1. In addition to the production of hydrogen and biogenic CO_2, fermentation digestates or residues (D) are produced as by-products. Depending on the composition of these residues, either further revenues can be generated by selling them, e.g., as fertilizer, or costs that can incur for their disposal. Therefore, they can either be included in the costs C1 or the revenues R1. The same applies for the purchase of the biomass input (I), which can either generate costs or an income, the latter in case of waste or residues for which disposal fees incur (Thrän & Pfeiffer, 2013). It should be noted that using residual and waste biomass for biohydrogen production, the long-term storage of the carbon bound in the digestates can lead to further negative emissions. This is the case if, for example, the residual is used as agricultural fertilizer and a substantial amount of the carbon in the digestate remains in the soil (Antonini et al., 2020). This effect would be taken into account within B1, where it would be included negatively in the total of E1.

System boundary B2 covers the CS/CU system element. The emissions in subsystem B2 contain the process emissions of the CS/CU process (E2b) and the amount of biogenic CO_2 permanently stored or used, being the gross negative GHG emissions (E2a). Since the amount of biogenic CO_2 permanently stored or used has been removed from the atmosphere during the biomass growth via photosynthesis, negative emissions can be generated (Kemper, 2015). E2a enters the emissions balance as a negative value and is fundamental for HyBECCS approaches to achieve an overall negative GHG balance. It must be noted that the physical amount of negative GHG emissions (E2a) actually stored is not necessarily equal to the amount of biogenic CO_2, which is transferred from balance boundary B1 to B2. This difference is due to potential leakages (L) in the system B2 which can occur during the transport to the storage site or the storage itself. Revenues (R2) accrue when being recompensated through incentives for generating negative emissions. It is important to keep in mind that, in the case of CS, the subsystem B2 does not generate any other income than the compensation for negative emissions. The costs (E2) are composed of the capital and the operational expenditures including the purchase price for biogenic CO_2 produced within B1 (C2b) as well as all other costs for the carbon storage or utilization process (C2a). The material flow of biogenic CO_2 leaving the HyBECC system boundary B1 corresponds to the material flow of biogenic CO_2 entering the CS/CU system boundary B2 as feedstock for negative emission generation. From the perspective of system boundary B1, the biogenic CO_2 generates a revenue flow (R1b) from its sale, whereas, for B2, the same biogenic CO_2 material flow generates costs (C2b) for its purchase. For CU approaches, revenues depend on the respective product. Summarized, the total costs of the HyBECCS approach (C3) incurred within the system boundary B3 can then be calculated according to Equation 1.

$$C3 = C1 + C2 = C1 + C2a + C2b \tag{1}$$

The total profit P3 achieved through HyBECCS can be calculated according to Equation 2. It is summed up from the revenues generated by the sales of hydrogen R1a, of the biogenic carbon dioxide R1b, and of the negative emissions or long-term carbon dioxide utilization R2, which together give the overall revenues for biohydrogen production and negative emissions R3, minus the total costs C3. In the case of separate operation of the system elements HyBECC and CS/CU, the respective profit can also be calculated within the subordinate system boundary B1 and B2. The profit for the production of hydrogen and biogenic CO_2 (P1) is then considered independently of the profit from the storage or long-term use of the biogenic CO_2 (P2).

$$\begin{aligned} \mathrm{P3} &= \mathrm{P1} + \mathrm{P2} = \mathrm{R1} - \mathrm{C1} + \mathrm{R2} - \mathrm{C2} \\ &= \mathrm{R1a} + \mathrm{R1b} - \mathrm{C1} + \mathrm{R2} - \mathrm{C2a} - \mathrm{C2b} = \mathrm{R3} - \mathrm{C3} \end{aligned} \tag{2}$$

To assess the environmental impact of HyBECCS, all emissions of the system boundary B3 have to be considered. As explained above, this paper focuses on the

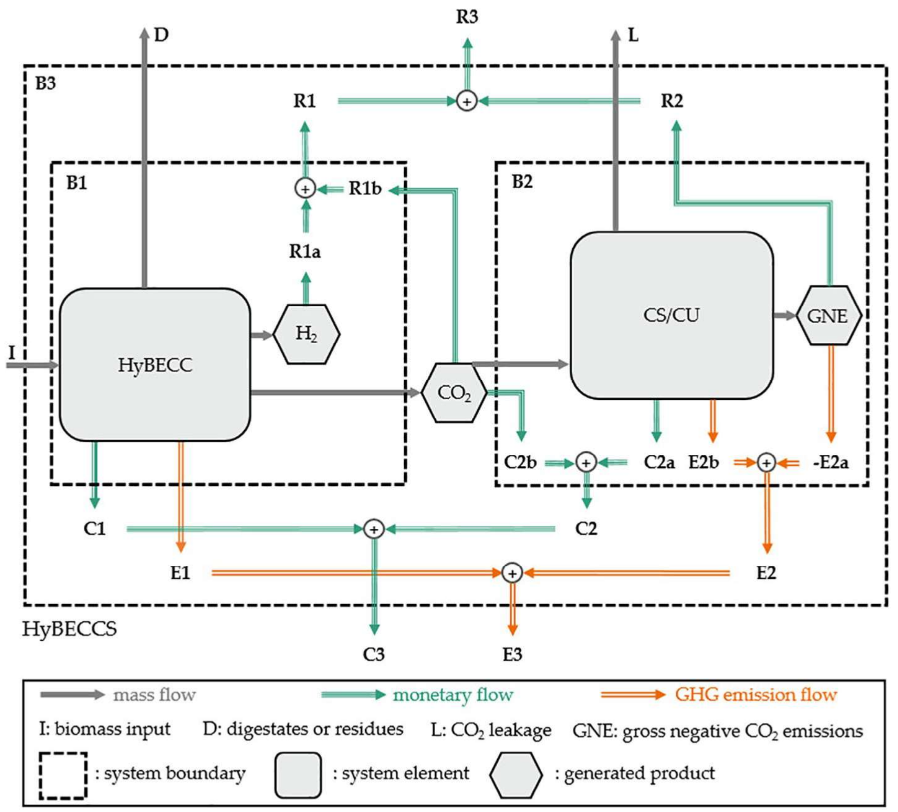

FIGURE 3 System boundaries (B) for HyBECCS approaches with mass flows for biomass input (I), hydrogen (H2), carbon dioxide (CO2), stored carbon dioxide referred to as gross negative emissions (GNE), residues or digestate from biohydrogen production (D) and carbon dioxide leakages (L), monetary flows divided into costs (C), revenues (R), and emission flows (E)

TABLE 2 Framework conditions (FC) for HyBECCS approaches and projects

N°	Framework condition (FC)	Consequence
FC1	$E3 < 0$	HyBECCS project = Negative Emission Technology (NET) project and Biohydrogen = Carbon-Negative Hydrogen (CNH) and permission to issue carbon removal certificates (CRC)
FC2	$P3 > 0$	HyBECCS project is economically viable

impact on the global climate of HyBECCS approaches. For this purpose, only positive and negative (stored) GHG emissions are to be balanced. The sum of all GHG emissions within B3 can be considered as its greenhouse gas footprint, which can be calculated according to Equation 3.

$$E3 = E1 + E2 = E1 - E2a + E2b \quad (3)$$

In case, the greenhouse gas footprint of a specific HyBECCS project (E3) is negative, it actually generates net negative GHG emissions and thus qualifies as a NET project. The co-generated hydrogen can then be considered carbon-negative hydrogen (CNH).

The definitions and framework conditions (FC) summarized in Table 2 are established as described above and apply to all HyBECCS projects:

This means that only HyBECCS projects that fulfill the first framework condition (FC1) above ($E3 < 0$) are NET and CDR and its produced biohydrogen is allowed to be qualified as CNH. Furthermore, only in case the total profit is positive ($P3 > 0$), the HyBECCS project is economically viable as the second framework condition (FC2) states.

2.3 | Regulatory Status Quo of NETs

All emission pathways to limit global warming to 2°C or even 1.5°C calculate with gross-negative GHG emissions, and thus CDR, from 2030 on (Honegger & Reiner, 2018a; Poralla et al., 2021; Rogelj et al., 2015; UNEP, 2017). The CDR amount needed to reach global climate goals is estimated to be 5–20 $GtCO_2$ per year, summing up to 444–1000 $GtCO_2$ until 2100 (Boysen; Honegger & Reiner, 2018b; Poralla et al., 2021). With each lost year that CDR is not implemented on a large scale, the challenge of sufficient adoption of these technologies increases (Poralla et al., 2021, p. 19). However, the scientific evidence and urgency of NET implementation are not reflected in reality: Globally, government policies and private sector initiatives supporting NETs are very sparse to date (Jeffery et al., 2020, p. 9f). The few governmental or private ambitions focus on biological CDR approaches such as afforestation and reforestation. NETs like DACCS and BECCS are supported by single countries such as Sweden, some public funds, and very few private entities. Poralla et al. (2021) provide a good overview on the supportive instruments existing worldwide. Emerging voluntary markets for CDR credits also primarily focus on biological storages (Jeffery et al., 2020, p. 9f; Poralla et al., 2021, p. 31). Incentives to mobilize technological approaches linked with permanent underground storage, such as BECCS and DACCS, are widely missing. As the contribution to GHG mitigation, an external benefit of NETs, does not generate revenues by itself and thus does not translate into an economic advantage for the operator, the externalities of GHG mitigation and emission must be internalized (Mankiw, 2001, p. 172). One option is the internalization of the external costs caused by GHG emissions by carbon pricing mechanisms. However, the internalization approach with result-based crediting of the actual negative emissions achieved is only one option of financial NET support and primarily adequate for mature NETs (Poralla et al., 2021, p. 23). Even though the technology readiness level of BECCS is relatively high with 6–9 for bioenergy processes and 4–7 for CCS, there are only single large-scale BECCS plants in operation (Poralla et al., 2021, p. 17). At the current stage of BECCS implementation, technology selection, learning curves, scale-up, and cost reduction promise significant efficiency gains. For the current development stage of NETs, subsidies for research, design, development, and demonstration (RDD&D) are thus more appropriate and urgently needed (Honegger, 2020). Besides direct subsidies, further instruments to speed up the NET implementation range from tax credits, concessional loans, grants to feed-in tariffs, all instruments successfully applied for the deployment of renewable energies around the world (Poralla et al., 2021, p. 23). Furthermore, existing barriers that hinder the implementation of CDR, such as the regulatory uncertainty on the export of CO_2 for geological storage, or on the geological storage itself, have to be abolished (Poralla et al., 2021, p. 31). There will be no NET activities without external incentives due to the special economics of these approaches. This is especially true—and unfortunate from a climate protection perspective—for HyBECCS as it has multiple benefits for the global climate, not only actively removing CO_2 from the atmosphere, but at the same time mitigating fossil GHG emissions by generating biohydrogen, potentially pushing fossil alternatives from the market. The special economics of HyBECCS and how to solve the dependency between the political framework, its economics, and climatic impact, will be discussed in the following subsection.

2.4 | Interrelationships between Ecology and Economics

The economic and ecological, especially climatic benefits of HyBECCS approaches can be best explained by looking at the two main products of HyBECCS: biohydrogen and negative emissions. On the one hand, the generation of hydrogen from biomass provides the valuable energy carrier hydrogen at a low GHG footprint and is carbon neutral when only considering the biomass conversion. The reason for this is that the CO_2 emitted during the biomass conversion equals the amount of CO_2 removed from the atmosphere during the growth of the biomass (Singh & Rathore, 2017). GHG emissions of HyBECCS processes are thus limited to process emissions from the hydrogen production process (incl. biomass generation) (E1) and CCS (E2b). Compared to fossil energy carriers, the use of biohydrogen avoids fossil GHG emissions from fossil fuel generation and its combustion or the decomposition of its derivatives after utilization. This contribution to GHG mitigation is the first external benefit of HyBECCS, as depicted as white box in Figure 4. It does not generate revenues by itself and thus does not translate into an economic advantage for the operator. Without external intervention, the GHG reduction would not entail any financial added value. Ideally following the so-called "polluter pays principle," the external costs caused by GHG emissions are internalized. Common approaches are cap-and-trade systems such as the EU-ETS, where GHG-emitting installations have to purchase emission allowances, or carbon taxes, potentially complemented by baseline-and-credit mechanisms such as the Clean Development Mechanism (CDM) (European Commission). If applied sufficiently, this translates into a comparative price advantage for biohydrogen in case it causes less GHG emissions and thus has lower GHG internalization costs to bear than fossil alternatives, as depicted as grey boxes in Figure 4. It is important to mention that the GHG emissions of all technologies, even if considered as low- or zero-emission technologies, should be included in such GHG internalization mechanisms to allow the comparison of the social costs of HyBECCS products with alternatives for energy or hydrogen provision. The negative CO_2 emissions depicted as green box in Figure 4 constitute the second external benefit of HyBECCS. The generation of negative emissions is linked with costs for CO_2 capture, transportation, and storage (cf. Equation 1). CCS cost estimations in the

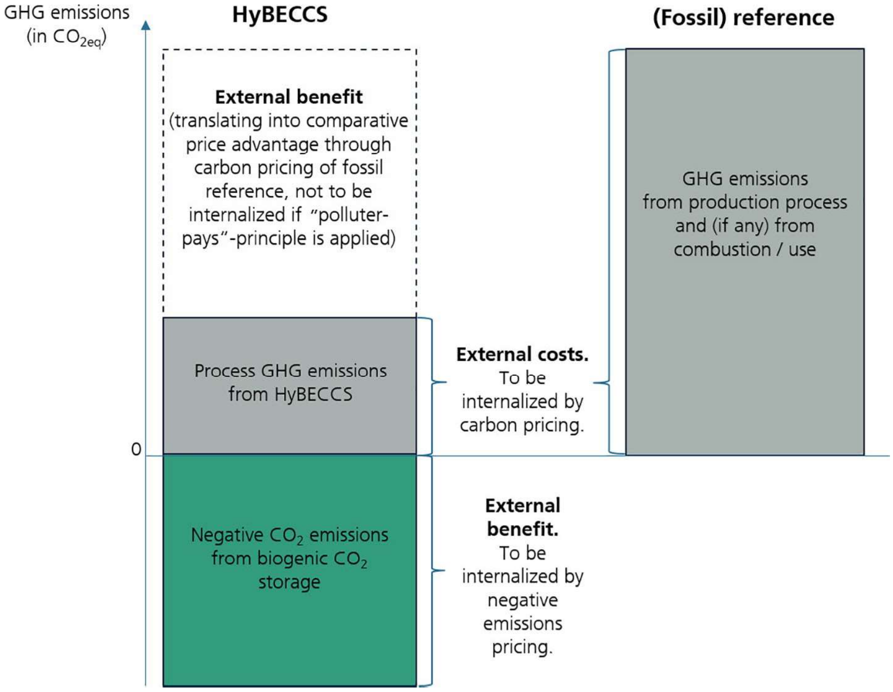

FIGURE 4 External benefits of HyBECCS compared to a (fossil) reference. green bar = negative emissions; grey bar = process emissions; dashed white bar = difference of process emissions resulting in external benefit (Not to scale)

literature vary broadly and depend, beyond others, on the CO_2 concentration at source, plant scale, transportation mode, the distance to the storage site, and the type of storage (Agora Energiewende und Wuppertal Institut, 2019; Poralla et al., 2021; Trippe, 2013). These costs are—from the operator's perspective—not (over)compensated by any income. The external benefit of the negative emissions for global climate must thus be internalized to make them happen.

High concentration and purity of the CO_2 to be captured using HyBECCS approaches compared to direct air capture (DAC) or post-combustion capture (PCC) as well as the emission-free use of hydrogen resulting in a higher possible CO_2 capture rate compared to hydrocarbon-based biofuels generated with other BECCS technologies are further advantages of the HyBECCS approach. They reduce the total energy demand and increase the CO_2 yield (Full, Merseburg, et al., 2021, p. 15; Singh & Rathore, 2017). However, these advantages translate into lower production costs—and comparative advantages of HyBECCS over other NETs. They thus do not have to be internalized. The production of hydrogen as a marketable product likewise constitutes a direct economic advantage of HyBECCS over other NETs, who often lack any revenue other than from negative emissions. This reduces the external financial need of HyBECCS approaches or increases the possible profit margin, making it a highly valuable model for both efficient GHG mitigation and removal in the pursuit of the 1.5°C goal. The example of HyBECCS and its externalities—a typical case of market failure in political economics (Mankiw, 2001, p. 172)—proves the urgency of developing and implementing internalization mechanisms for negative emissions and of sharpening existing instruments for GHG reduction.

3 | FUNDAMENTALS AND GUIDELINES FOR ENVIRONMENTAL ASSESSMENT

Over the last decades, the increasing awareness of the negative impact of human activities on the environment and the regulatory adoption of environmental awareness gave birth to many ecological guidelines and standards. They range from macro-level approaches such as national GHG inventories over meso-level analysis like environmental assessments to micro-level assessments addressing products or services (DIN e.V. DIN EN ISO 14040, 2021, p. 8; Frischknecht, p. 17; Hauschild et al., 2018; Kaltschmitt & Schebek, 2015; Klöpffer & Grahl, 2009). HyBECCS projects can have multiple impacts on the environment, such as acidification and eutrophication or the depletion of the ozone layer and abiotic resources. They depend on the feedstock used, the distances and mode of transportation of biomass and products as well as the chosen conversion technology (Fajardy et al., 2019). All those impacts have to be evaluated in an environmental assessment (EA). The EA has to follow the local legislation or, if not existent or insufficient, best international practice, always aiming to minimize negative impacts. However, the key of HyBECCS in climate protection lies in its ability to deliver biohydrogen and negative emissions. Any HyBECCS approach or project can only contribute as NET in case it actually has a negative GHG balance, which means that it actually removes more CO_2 from the atmosphere than it emits GHG. In such a case, the co-generated hydrogen can be considered as CNH as per framework condition FC1 above. The focus herein is to develop a guideline to assess the ability of a HyBECCS project to deliver negative emissions and to produce CNH. Even though all environmental impacts are equally important, they are not included in the further assessment, as established evaluation methods already exist. The following fundamentals for environmental assessment of HyBECCS are limited to considerations on climate change mitigation. A distinction is made between technology level (3.1.) assessing the technology choice as a first step and project level (3.2.) evaluating the actual GHG balance of the specific HyBECCS project.

3.1 | Eligibility on a Technology Level

There are two conditions that need to be fulfilled on a technology level for a HyBECCS project in order to be able to deliver net negative emissions: The theoretical ability for CO_2 removal and the theoretical permanence of the CO_2 storage. The theoretical ability for CO_2 removal is given for all types of BECCS approaches, as the CO_2 in the product gas is removed from the atmosphere during biomass growth. Accordingly, this has also to be verified for HyBECCS technology options. Controversy exists over biomass substrates that are not clearly assigned. For example, very slow-growing biomass, such as peat, does not qualify as renewable (Kaltschmitt & Schebek, 2015, p. 246). Consequently, for HyBECCS or BECCS approaches in general, a positive list of eligible technologies and raw material has to be elaborated and adapted to the state of the art and technology over time. Only in case technology and raw material from that list are applied, the HyBECCS project has the theoretical ability to generate negative emissions. The second condition for a HyBECCS approach in order to deliver negative emissions is that the captured CO_2 is permanently removed from the atmosphere. Different storage options are characterized by different time horizons of storage as well as different risk profiles concerning reversibility and leakage. Considering the current state of the art, HyBECCS approaches can be combined with three different storage options: (1) mineral carbonation, also known as mineralization or enhanced weathering, (2) geological underground storage, for instance in depleted oil/gas reservoirs or saline aquifers, and (3) in long-term CCU application, such as in the built environment in low-carbon concrete (Azapagic et al., 2018, p. 21; IPCC, p. 39). Mineralized carbon is safely stored in the long term, whereas geological underground storage is estimated to be safe for over 1000 years when best practice is applied (IPCC, 2005b; Möllersten et al., 2020; Poralla et al., 2021, p. 21). The third storage option for biogenic CO_2 from HyBECCS, long-term CCU applications, has a higher risk of reversals, insecurity concerning the time horizon of storage, and further challenges such as monitoring the permanence due to the dispersed places of use (Otto et al., 2017). Moreover, there is no clear definition of how long CO_2 has to be safely stored in order to count as negative emission with an effective impact on global climate. For the CO_2 storage technologies, a positive list of eligible approaches has to be elaborated and updated over time to reflect the state of the art. Only in case technology from that list is applied, the HyBECCS project has the theoretical ability to generate negative emissions. In case a HyBECCS approach or project fulfills both conditions on the technology eligibility, it has the theoretical ability to generate negative emissions and CNH, which means that it has the theoretical ability to fulfill the framework condition FC1 above.

3.2 | Eligibility and Assessment on a Project Level

Even though a HyBECCS approach has the theoretical ability on the technological level to deliver net negative emissions according to 3.1., this does not mean that every HyBECCS project applying such a technological approach is able to do so, which means that not every HyBECCS project is able to fulfill framework condition FC1 above. The actual GHG footprint highly depends, for instance, on the raw material production, the efficiency of the bioenergy conversion, and the distance to the CO_2 storage site. For each project, the expected climatic performance thus has to be assessed ex-ante before its implementation and monitored ex-post during its operation. The relevant category to evaluate the contribution of HyBECCS to a global negative emission budget are the GHG emissions, internationally convened to be quantified in CO_2 equivalents (CO_2eq) and with regard to the global warming potential over 100 years (GWP_{100}) (DIN e.V. DIN EN ISO 14044), p. 31; IPCC, 2015c; p. 87; Lozanovski, 2013, p. 60). A proven practice to quantify the GHG emissions of projects and services is a life cycle assessment (LCA) in line with the regulations of the international standards ISO 14040 and 14044 (DIN e.V. DIN EN ISO 14040: 2021; Klöpffer & Grahl, 2009; Kaltschmitt & Schebek, 2015; DIN e.V. DIN EN ISO 14044: Lozanovski, 2013). The application of these LCA standards guarantees the scientific veracity of the assessment and is the basis for the comparability of the results with competing approaches. Furthermore, the holistic perspective of an LCA is especially suitable for new approaches like HyBECCS. In addition to GHG emissions, potential sustainability issues other than the contribution to global warming can be revealed during the inventory phase of the LCA. Specifics for the determination of the GHG footprint of a HyBECCS project are elaborated in the following.

First, as the LCA allows climatic assessments relative to a specific product or service, a so-called functional unit has to be defined. To answer the question whether a HyBECCS project generates negative emissions, the functional unit shall be one ton of CO_2 permanently stored. For the climatic appraisal of the HyBECCS approach, negative emissions are thus considered to be the main product of the process. Hydrogen is considered as co-product. For different valuation approaches like the economic and the holistic assessment, however, other perspectives can be chosen. Equation 3 above can thus be converted as follows, now expressing the GHG emission factor (EF) of the negative emissions, in tCO_2eq per tCO_2 stored.

$$EF = \frac{E1 + E2b}{|E2a|} \tag{4}$$

In case the emission factor is smaller than one ($EF < 1$), the HyBECCS project generates net negative emissions and the eligibility to qualify as NET is proven; the framework condition FC1 above is fulfilled. The hydrogen produced can thus be referred to as CNH. In case of an emission factor bigger than one ($EF > 1$), more process GHG emissions are generated than CO_2 is permanently stored, the project generates net positive emissions and contributes to global warming. The comparison of the emission factors of different HyBECCS approaches or NETs, in general, allows conclusions on the efficiency of the different approaches. The GHG emissions of HyBECCS to be considered are the following, according to Figure 3 above: The process GHG emissions emitted during the HyBECC process of producing hydrogen and biogenic CO_2 (E1), the process GHG emissions emitted for the storage (CS) or long-term use (CU) of the biogenic CO_2 (E2b) and the amount of CO_2 stored in the long term, being the negative CO_2 emissions (E2a). The GHG footprint of the HyBECCS project can be calculated according to Equation 3 and allows the determination of the emission factor EF. It shows whether—in the case of ex-ante estimations—the project is expected to generate net negative emissions and—in case of measurements during operation—whether it actually generates net negative emissions. In case the total emissions (E3) are negative, which means that EF is smaller than one, the HyBECCS project actually generates net negative emissions and the generated hydrogen can thus be considered as CNH, as defined in the framework condition FC1 above. The specifics to determine E1, E2a, and E2b are discussed in detail in the following. The calculation of the process GHG emissions E1 and E2b shall, in general, follow the rules of the ISO 14040 and 14044 standards. However, the following specifications and choices given by the ISO framework should be followed in order to safeguard the ecological integrity of HyBECCS approaches. For the sake of comparability and fairness, the same rules must be applied to competing approaches. The process GHG emissions of HyBECC (E1) are generated during all steps necessary to provide hydrogen and biogenic carbon dioxide. The provision of the biomass used, which can have an important share in the total GHG emissions, must be considered (IE, p. 26). This is especially important for international traded biomass in order to avoid GHG accounting leakages in global supply chains. All direct emissions for machines, transportation, etc., and indirect emissions generated, for example, during the production of fuels or fertilizers, the generation of purchased electricity, or due to land-use changes shall be included (Hauschild et al., 2018, p. 494). However, double accounting of GHG has to be avoided. No direct and indirect GHG emissions are allocated on waste and residues. They "leave" the upstream product system without being burdened with any GHG footprint (DIN e.V. DIN EN ISO 14044, p. 26; Thrän & Pfeiffer, 2013, p. 87). This means that for bioenergy approaches using waste or residues as raw material for the energy conversion, no GHG emissions must be taken into account for the provision of such biomass except for its transportation to the plant and its processing. This rule honors the ecological advantages of approaches growing or obtaining raw material in an efficient and ecological way, whereas dedicated, land- or resource-intensive cultivation of biomass is disadvantaged. A recent study shows that optimization of the hydrogen production process can lead to negative emissions even without CCS: In case the digestates from the hydrogen production are used as fertilizer and a major part of its carbon content is stored in the soil, the GHG balance of the hydrogen production over its entire life cycle can be negative (Antonini et al., 2020). Consequently, when CCS is additionally applied, the GHG negativity of this optimized HyBECCS approach and its contribution to climate change mitigation can increase.

The process emissions E1 should furthermore ideally include the making, construction, and deconstruction of the infrastructure needed for the biohydrogen generation process in order to realistically calculate the total GHG emissions. For the main process, the biomass conversion to hydrogen, all relevant material and energy streams have to be taken into account. For the present impact category, the global warming potential, minor inputs, and outputs can be cut-off to a maximum of 5%, the impact of such cut-off however being scrutinized in a sensitivity analysis (Lozanovski, 2013, p. 56). For hydrogen, all steps of further processing and transportation until its intended end use should be included in the LCA. Long transportation routes to the site of usage might spoil the ecological advantages of hydrogen. The inclusion of all transportation emissions thus favors decentralized projects using local biomass over large-scale projects located far from any site of consumption. This might alleviate the disadvantages of missing economies of scale of decentralized plants. The required conditions (e.g., pureness and pressure) of the produced hydrogen depend on the envisaged use. It also affects the energy need, thus the GHG footprint and needs to be defined beforehand. The same applies for the required characteristics of the biogenic CO_2, to be defined as so-called reference flow in the LCA (Klöpffer & Grahl, 2009, p. 37). One major advantage of hydrogen is that it oxidizes to water; its use is thus CO_2-emission-free. Fossil fuels, on the contrary, emit GHG when burned. A "cradle-to-grave" approach of the LCA is thus advisable for a realistic comparison of fossil and hydrogen-based applications in order to reward this benefit. The HyBECC system element simultaneously delivers hydrogen and biogenic CO_2. Potentially, further co-products like digestates usable as fertilizer or other usable components in the product gas can be generated. An allocation of the total GHG emission over the different products would be possible (DIN e.V. DIN EN ISO 14044, p. 26; Lozanovski, 2013, p. 43). However, the complete accounting of all GHG is essential for the present assessment and thus no allocation is undertaken in order to avoid an accounting leakage through co-products not covered by GHG internalization mechanisms. Concerning the biogenic carbon dioxide, only its generation, capture, compression and, if needed, conditioning for transportation (IPCC, p. 5) are to be included in the LCA of the HyBECC system boundary B1. Assumptions for the project lifetime can be taken from proven comparable technologies. Dividing the total GHG emissions (E1) resulting from the HyBECC system element by the product quantity, results in the GHG intensity of such product, for example, in $tCO_2eq/kWh\ H_2$. The comparison of the results from several HyBECC approaches allows a prioritization according to the climatic efficiency of biomass conversion.

The further lifecycle of the biogenic CO_2 is covered by the system boundary B2. For process, GHG emissions of CS/CU (E2b), multiple factors like the CO_2 transportation mode, distance and storage or long-term utilization technology (Honegger & Reiner, 2018b, p. 308; Poralla et al., 2021, p. 21) influence the GHG footprint of CS/CU and have thus to be considered. The calculation of the GHG emissions emitted for the storage of the biogenic carbon dioxide shall, in general, follow the same rules elaborated above for the HyBECC process within the framework of the ISO 14040 and 14044. The system boundary encompasses all processes needed for the transportation of the CO_2 from its site of generation to the storage site, the storage itself, for example, the injection into the underground, as well as all provisions necessary to assure the permanence of the storage. Further compression might be needed at the storage site in case the pressure of the arriving CO_2 is not sufficient for the storage (IPCC, p. 11). All direct and indirect process GHG emissions are to be included in the LCA. In the case of biogenic CO_2, losses of this product through equipment leaks or accidental releases are GHG-neutral and only result in a loss of negative emissions. Contrary to fugitive emissions of fossil CO_2 (IPCC, p. 7), they do not have to be included in the LCA. They should, however, be avoided. The first result of the LCA of boundary B2 is the total GHG emission accruing for the transportation and storage of the biogenic carbon dioxide. The second result is, when dividing the total GHG by the product amount, the GHG intensity of the product, in $tCO_2eq/\ tCO_2stored$. The comparison of different CS/CU approaches allows selecting efficient technologies to minimize their impact on global warming.

Negative emissions (E2a) are the total amount of biogenic CO_2 stored in the long term. The stored CO_2 amount has to be measured continuously by proven measurement equipment at the injection or storage site (IPCC, p. 11). CO_2 leakage from transportation and compression is already taken into account at this point, as they occur before measurement. Other types of leakages, such as CO_2 migration and blowouts, have to be avoided by a diligent selection of technology and site as well as the use of adequate equipment, materials, and techniques (IPCC). However, as they cannot be excluded to happen, risk deductions depending on the technology applied are likely to be necessary for a realistic estimation of negative emissions over the long term. Such deductions may be applied as default values depending on the specifics of the CS plant and need to be elaborated and introduced on a global level. Pre-operational estimations of the negative emissions are possible by stoichiometric approaches and experimental results on the product gas composition, giving the amount of biogenic CO_2. After the deduction of transportation and storage losses, as well as risk deductions for leakages at the storage site, the amount of CO_2 actually stored in the long term can be estimated.

After the determination of E1, E2a, and E2b, the emission factor EF of the specific HyBECCS project under evaluation can be calculated according to Equation 4 above. In case the emission factor is smaller than one, the HyBECCS project generates net-negative GHG emissions and, consequently, carbon-negative hydrogen. This means that the framework condition FC1 above is fulfilled. Such HyBECCS project thus contributes to the deceleration of global warming.

It is important that E1, E2a, and E2b are stated separately in order to allow evaluations on the absolute impact of the HyBECCS approach or project on the environment.

Two projects with the same amount of net-negative emissions could show significant differences in the absolute amount of positive (E1 + E2b) and negative (E2a) emissions. The separate statement is thus especially important to save potentially scarce CO_2 storage capacities (Azapagic et al., 2018) and to safeguard resources. Furthermore, a separate statement is required in case different incentive schemes (or prices) apply to the different types of emissions. Another reason for the separate statement is that the climate goals for emission reduction, on the one hand, and negative emissions, on the other, might change over time, reflecting the progressing defossilization and the increasing need of global net negative emissions. Moreover, different emission caps for each process type (BECC, CCS) might be introduced to enforce the technological progress and would only be verifiable in case of separate statements.

The following Table 3 shows an overview of the most relevant aspects for the calculation of the GHG balance of a HyBECCS project.

4 | FUNDAMENTALS AND GUIDELINES FOR TECHNO-ECONOMIC ASSESSMENT

HyBECCS approaches have to be economically viable in order to bring its products—hydrogen and negative emissions—to the market. Techno-economic assessments of production processes are of great importance in order to examine their profitability, to identify potential barriers for a successful market integration like cost drivers, and give an important basis for technical development. Furthermore, they help to identify business cases and are valuable tools for decision making and monitoring (Zimmermann et al., 2020). Generally, to estimate profitability, the capital and operational expenditures must be determined. At the example of the HyBECCS processes, these must be derived for the biohydrogen production as well as for the capture, transport, and storage or the use of biogenic carbon dioxide, according to Equation 1. Fundamentals for the cost estimation of HyBECCS processes and proposals for the selection of suitable estimation methods are outlined in 4.1. Once both the capital and operating costs of the HyBECC and the CS/CU plant are determined, the total profit P3 of the HyBECCS plant can be calculated by summing up the costs (C3) and revenues (R3), according to Equation 2. In case of higher revenues than costs (R3 > C3), the HyBECCS project is profitable (P3 > 0), which represents the second framework condition (FC2). If the costs outweigh the revenues (C3 > R3), the project should not be implemented from an economic point of view.

In system boundary B1, the main product is biohydrogen, which generates revenues (R1a) as shown in 2.2. The additional revenues from the sale of co-products, here coming from the sales of biogenic CO_2 (R1b), are deducted from the total production costs. Dividing the annualized production costs by the annual product quantity results in the unit production costs, in the case of hydrogen the levelized cost of energy (LCOE) (IE). The LCOE can be related either to mass (e.g., in EUR/kg H_2) or to net calorific value (e.g., in EUR/kWh H_2) (Lozanovski, 2013; Matthes et al., 2020). In case biohydrogen from HyBECCS is only compared to other hydrogen generation systems, mass-based production costs can be chosen. A more general comparison with other types of energy conversion technologies can be envisaged by choosing the energy-based LCOE. In case only the carbon storage system (B2) is considered, where negative emissions are the main product, the unit production costs are expressed in EUR/tCO_2stored. In case the HyBECCS system boundary (B3) is considered, the main product may either be biohydrogen or negative emissions. In such a case, the revenues from the sales of the co-product must be deducted from the total costs when determining the unit production costs of the main product. In case the negative emissions are chosen as the main product, the comparison of the HyBECCS approach with other NETs is possible. The outcome is the unit production costs of the main product in EUR per unit of the main product, for example, the LCOE of biohydrogen. In the following, the unit production costs *before* the internalization of external costs and benefits are defined as "internal LCOE" of the product. The GHG internalization costs are stated separately from the internal LCOE. This differentiation applies independently from whether the external costs and benefits are partly or entirely internalized, which is partly the case in some countries and/or sectors with established carbon pricing mechanisms. The separate statement of the GHG internalization costs shall raise the transparency and comparability of different alternatives in terms of their climatic impact. The internal LCOE for hydrogen with biogenic CO_2 as co-product (system boundary B1) is defined, for example, in EUR/kWh H_2, according to Equation 5.

$$internal\ LCOE\,(B1) = \frac{C1 - R1b}{annual\ H2\ production} \tag{5}$$

The internal levelized costs of stored carbon (LCSC) for the system boundary B2 can be defined as follows, in EUR/tCO_2stored.

$$internal\ \ LCSC\,(B2) = \frac{C2}{E2a} \tag{6}$$

TABLE 3 Overview of relevant aspects for the calculation of GHG balance of HyBECCS projects

E1: GHG emissions from HyBECC (Hydrogen Bioenergy & Carbon Capture)
Life Cycle Assessment according to ISO 14040/14044
Impact category: Global warming potential over 100 years (GWP_{100})
Functional unit: one ton of CO_2 permanently stored
"Cradle-to-grave"-approach, including GHG emissions from: • Biomass cultivation/provision • All direct emissions (transportation, etc.) • All indirect emissions (incl. land use changes, infrastructure, deconstruction)
No allocation (side effect: co-product biohydrogen is "zero-emission")
No GHG allocation on waste and residues → "zero-emission" biomass input
Double accounting of GHG has to be avoided
Cut-off of material & energy flows at maximum of 5% → effect to be checked in sensitivity analysis
+ Potential sustainability issues of new HyBECCS approaches can be revealed during LCA inventory phase
E2b: GHG emissions from CS (Carbon Transport & Storage)
Life Cycle Assessment according to ISO 14040/14044
Impact category: Global warming potential over 100 years (GWP_{100})
Functional unit: one ton of CO_2 permanently stored
"Cradle-to-grave"-approach, including GHG emissions from: • CO_2 transportation from HyBECC plant to the storage site • Storage (for example, injection into the underground) • O&M (Operation and Maintenance) (all provisions necessary to assure the permanence of the storage)
E2a: Negative Emissions
Unit: tons of CO_2 permanently stored
Ex-ante estimations through stoichiometric approaches & experimental results on the product gas composition
Measurements during operation must be: • continuously • with proven measurement equipment • at the injection or storage site − Lack of uniform standards for measurement, reporting and verification (MRV)
Risk deductions (for leakage, accidental release) to be applied − Lack of uniform definition of default values for risks
− Scientific & regulatory uncertainty on necessary duration of storage, responsibilities, liabilities, etc.
! Separate statement of absolute amount of E1, E2a and E2b necessary.
! Uniform LCA system boundaries for comparative assessments

The internal levelized costs of negative emissions (LCNE) for the HyBECCS system boundary B3 can be defined according to the following equation, in EUR/tCO_2stored.

$$internal\ LCNE\,(B3) = \frac{C3 - R1}{E2a} \tag{7}$$

The internal LCOE for carbon-negative hydrogen (system boundary B3) is defined as follows, where no revenues from the co-product, the negative emissions, are included. This is because they come from the internalization of the external benefit from negative emissions, not considered in the internal cost calculation (expressed, for example, in EUR/kWh H_2).

$$internal\ LCOE = \frac{C3}{annual\ H2\ production} \tag{8}$$

However, an important aspect for the economic viability of HyBECCS concepts is monetary incentives for GHG reduction as well as for storing biogenic CO_2. After presenting the most relevant aspects for the capital and operational cost estimation in 4.1., the internalization of those external benefits will be discussed in 4.2, resulting in the derivation of two key performance indicators (KPIs) for the evaluation of HyBECCS projects: The levelized cost of carbon-negative hydrogen (LCCNH) and negative emissions (LCNE). The chapter closes by presenting an exemplary basic model for HyBECCS regulatory systems in net-zero or net-negative emission economies.

4.1 | Capital and Operational Cost Estimation

Suitable estimating approaches for capital costs of HyBECCS projects like capacity, factor, module, and detail methods are to be chosen in terms of estimation accuracy and effort and must be selected depending on the project planning degree of the HyBECCS project, the data availability, and the objective of the estimation (Weber, 2016). In order to select an adequate method for estimating capital cost for HyBECCS approaches, the current degree of the project definition and some key indicators or information about the cost of the equipment must be known (Kunysz, 2020). The degree of the project definition depends solely on the available information about the project. Certain project states are associated with a certain degree of the project definition. In preliminary, approval and detailed planning it ranges from 10% to 15%, 25% to 35%, and 85% to 95%, respectively (Weber, 2016). Figure 5 illustrates a schematic guide to select one of the mentioned methods described below.

Capacity methods usually are applied for projects with planning degrees below 2% (Kunysz, 2020) for giving order-of-magnitude estimates or to carry out process comparisons. The capital expenditures can be estimated using key indicators such as investment costs and capacity of similar existing plants or through gross annual sales and capital turnover ratio. If the technical sizing has not yet been carried out, but key indicators are known, the capacity methods are suitable (Kunysz, 2020; Towler & Sinnott, 2013). Factorial methods are based on rough technical sizing of the plant and an estimate of the major equipment´s purchase cost. They usually are applied at project definition degrees up to about 30% (Weber, 2016). Depending on the applied factorial method, purchase equipment costs are estimated by multiplication with specific factors, for instance, location or material peculiarities (Towler & Sinnott, 2013). Due to its higher project planning degree, factorial methods often deliver higher estimation accuracies than capacity methods, which is why they commonly are used for more detailed estimations like feasibility studies, concept assessments, or preliminary budget approvals (AACE International, 2020). Cost estimations according to the module methods require a functional classification of the plant into modules and are typically deployed for budget approvals. Each module is designed based on a P&I diagram by cost-relevant equipment data, such as material, process temperatures, or pressures. Therefore, higher project planning degrees than 2%, as well as information about module costs are required (Weber, 2016). Due to the modularity of HyBECCS technologies, the module method is especially suitable. If the project definition lies in between 2 and 30%, either factorial or module methods are applicable (AACE International, 2020). Module methods are more commonly used at higher project definition degrees. Otherwise, in the case of known equipment cost factors, such as Lang- or Hand-factors, the factorial methods can be applied (Couper, 2003; Kunysz, 2020). The detailed estimation methods are based on binding offers or offers from completed similar projects and are applied for cost control or budget compilation. They require the highest project planning degrees and provide the most accurate estimation of these four methods (Kunysz, 2020). If the project definition is above 30% (AACE International, 2020) and binding offers or offers of already completed, similar projects are available, detailed methods are commonly used (Kunysz, 2020; Towler & Sinnott, 2013). If there are no offers, but it is possible to form functional units and information about modular costs is available, the module method can be applied. If equipment cost factors are known, the factorial methods are suitable. Access to reliable data for completely new developed technologies is often not available. As recent data on actual prices for similar process equipment is a highly reliable source, economic data from existing plants can be used as a basis for the techno-economic assessment (Towler & Sinnott, 2013). Therefore, as HyBECCS is a combination of biohydrogen production and CCS/CCU, data from existing BECCS- or CCS-plants and biohydrogen processes can be used for HyBECCS plant cost estimations.

Operational expenditures can be divided into variable and fixed production costs. Variable costs are proportional to plant output, meaning for HyBECCS, increased hydrogen and carbon dioxide production or a greater amount of carbon dioxide stored is generally associated with increasing variable costs. Typical variable costs for HyBECCS plants comprise costs for raw materials like biomass, auxiliaries such as process water or electricity, consumables, waste disposal for biomass residues as well as the costs for hydrogen and carbon dioxide processing and its transport to the CS/CU plant site. Variable costs can usually be decreased by operating the plant more efficiently, for instance by increasing the biomass to hydrogen conversion rate or energy efficiency. Estimating the raw material or consumable costs of a new plant requires an estimate of the amounts of raw materials or consumables needed as well as corresponding prices. The prices can either be forecasted using existing pricing methods or determined from current market prices. Estimating the utility costs of the HyBECCS system requires mass and energy balances as well as a preliminary design of the heat recovery system. Costs for waste

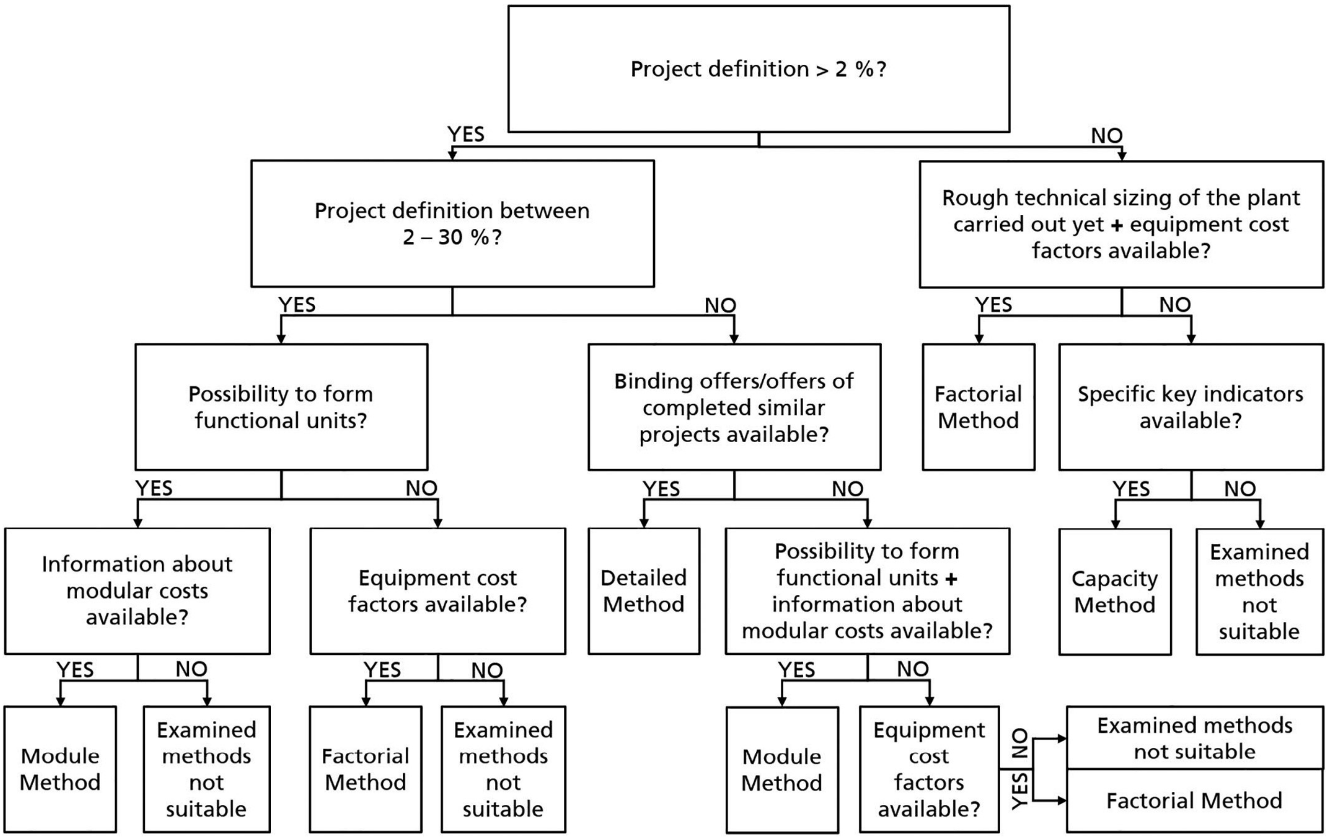

FIGURE 5 Guideline for the selection of a capital cost estimation method (Own elaboration based on AACE International (2020), Couper (2003), Kunysz (2020), Peters et al. (2003), Towler and Sinnott (2013), Weber (2016), Zimmermann et al. (2020))

disposal in HyBECC (B1) may occur, for instance, from biomass residues or wastewater that cannot be recycled or sold as a by-product. As HyBECCS plants can be configurated on a variety due to their modularity regarding the biomass pretreatment, hydrogen production pathway, product gas separation, and its processing as well as in terms of the carbon storage option or carbon utilization case, specific raw materials, consumables, auxiliaries, and additional waste treatments can be required. Fixed costs incur irrespective of the plant output, meaning that a decrease in production does not lead to a reduction in fixed costs. Fixed costs for HyBECCS generally include operating labor, supervision, maintenance, property taxes and insurance, general plant overhead, sales and marketing costs as well as license fees and capital charges. Labor costs, property taxes, and insurance or capital charges depend on the location of a plant (Towler & Sinnott, 2013). Due to the high variety of possible HyBECCS configurations and the dependence of some fixed costs on the plant location, operational expenditures need to be estimated for each HyBECCS plant individually. Guidelines and general reference values for estimating variable and fixed costs are outlined, for example, in Towler and Sinnott, (2013) (p. 373ff) or Peters et al. (2003) (pp. 259ff).

4.2 | Internalization of External Costs

The economics of HyBECCS approaches are characterized by a very high dependency on the regulatory framework it is embedded in and, in the ideal case, its ecological benefits. In order to evaluate HyBECCS concepts with regard to their economic viability, these aspects must be considered. In 4.2.1., two single-value KPI are developed taking into account monetary incentive schemes for environmental benefits. These KPIs allow the comparison of different HyBECCS approaches or projects, but also the comparison with other NETs like BECCS approaches or even conventional, potentially fossil-based alternatives. The target KPIs presented merge the outcome of the economic analysis with the outcome of the climatic assessment (cf. 3.). It represents the production costs of a product, including the internalization costs and benefits of the external effects on the global climate. For CNH, it can be considered as the levelized cost of carbon-negative hydrogen (LCCNH), and, for negative emissions, as the levelized cost of negative emissions (LCNE). Uniform incentive schemes for external cost savings through greenhouse gas reduction as well as the creation of negative emission have to be established in order to reach and maintain greenhouse gas neutrality. A basic model for such a regulatory, result-based system building on carbon removal certificates (CRCs), also known as negative emission certificates (NECs), is shown in 4.2.2.

4.2.1 | Determination of the Levelized Cost of Carbon-Negative Hydrogen (LCCNH) and Negative Emissions (LCNE)

One result of the techno-economic assessment, to be carried out in accordance with the provisions elaborated in 4.1., are the total internal production costs of the main product. To understand the economic interrelationships of the HyBECCS approach in a more holistic view, the internalization of the external costs and benefits of the HyBECCS project must be considered. As elaborated in 2.4., external costs are caused by the process GHG emissions of the HyBECC system element (E1) and the CS/CU system element (E2b). The total amount of E1 and E2b is an outcome of the LCA (cf. 3.2.). For the internalization, the external costs of the GHG emissions have to be monetarized. An option is the offsetting of process GHG emissions with emission reduction certificates from renewable energy projects. Such offsetting renders all HyBECCS products GHG neutral. An alternative to be discussed is the offset of unavoidable process GHG emission against CO_2 permanently stored. After this first internalization step, the biohydrogen can thus be considered carbon-neutral hydrogen. The offsetting means that only the net-negative emissions, meaning those negative emissions that exceed the process emissions of the HyBECCS process, are fully rewarded on the market. The internalization costs have to be added to the total production costs. When the annualized internalization costs are divided by the annual product quantity, they can be added to the internal LCOE. In case the internal LCOE and internalization costs per unit are stated separately, different approaches can be compared in terms of their relative GHG footprint. For such a comparison, the same carbon price has to be applied to all alternatives.

Additionally, the external, GHG-related benefit of the HyBECCS project, which is according to 3.4., the negative emissions, need to be internalized. The determination of the total amount of biogenic carbon dioxide that is permanently stored, referred to as gross negative emissions (E2a), is an outcome of the LCA (cf. 4.2.). In case the project generates net-negative emissions (EF < 1) as per framework condition FC1, the project qualifies to receive a revenue stream (R2) based on a uniform negative emission unit price for each ton of gross negative emissions. The price to be received per unit of gross negative emissions has to be the same for all alternative NETs in order to render the different approaches comparable. In reality, however, different prices may be negotiated in direct carbon removal certificates (CRCs) purchase contracts. A possible approach for incentives based on CRCs is described in 4.2.2. As the process GHG emissions have been internalized, only the net-negativity is fully rewarded through additional income. In case the hydrogen to be sold can prove that the co-produced biogenic CO_2 is actually used for long-term storage or use and the project generates net-negative emissions (EF < 1), the biohydrogen, already carbon-neutral after the first internalization step, can be considered as CNH. For the internalization of the external profit of the negative emissions, the revenue from the sales of the co-product, the negative emissions, is to be deducted from the total production costs. As a quality feature for mere marketing purposes, either the “net negative intensity” (in tCO_2stored/kWh H_2) could be indicated. Alternatively, only the share of hydrogen equal to the total amount of net negative emissions can be declared as CNH, whereas the remainder is to be declared carbon-neutral hydrogen. The production costs of one unit of carbon-negative hydrogen produced, including (i) the internalization costs for all process GHG emissions as well as (ii) the revenue for the negative emissions, for example in EUR/kWh H_2, is referred to as levelized cost of carbon-negative hydrogen (LCCNH). It has to be underlined that only in case the biogenic CO_2 is actually used for long-term storage or use and the project generates net-negative emissions (EF < 1), the product is CNH and the KPI can be called LCCNH, as defined in the framework condition FC1 above. This means that the designation as LCCNH already includes the validation of the hydrogen being carbon-negative. In all other cases, the resulting KPI would merely represent and be called the external, GHG-related LCOE of hydrogen. The target KPI for NET comparison is the levelized cost of negative emissions (LCNE), expressed in EUR/tCO_2stored. Also, LCNE can only be used in case the biogenic CO_2 is actually used for long-term storage or use and the project generates net-negative emissions (EF < 1). For a better understanding, the stepwise internalization procedure is exemplarily shown for the HyBECCS system (B3) in the following and expressed as Equation 9.

First, the internal LCOE of produced biohydrogen, in EUR/kWh H_2, is determined from the total production costs. If the project generates net-negative emissions, as per framework condition FC1, all process GHG emissions (E1 and E2b) are monetized via carbon pricing, leading to an increase in the LCOE. Afterward, the revenues from the sales of gross negative emissions (R2) are deducted, leading to a decrease in the LCOE. The sum of the internalization costs is divided by the annual H_2 production amount (in kWh H_2). The result is the LCCNH (in EUR/kWh H_2), which can be easily compared to the LCCNH of other specific HyBECCS projects or the LCOE of any other energy carrier such as fossil fuels.

$$LCCNH = Internal\ \ LCOE + \frac{E1\ internalization\ \ costs + E2\ binternalization\ \ costs - R2}{annual\ \ H2\ \ production} \quad (9)$$

Figure 6 illustrates the functionality of one of the developed KPI. The LCCNH from an exemplary HyBECCS process is compared to the LCOEs of several other energy carriers. Due to missing data from real HyBECCS plants, the LCCNH is only an assumption for illustration purposes and not based on real values. The values of the alternatives are based on actual data from Howarth and Jacobson, (2021), IPCC and Couper, (2003). The blue bars represent the respective internal LCOE (before GHG internalization). The red bars represent the internalized costs for the specific GHG emissions depending on the assumed carbon price. The GHG internalization costs are shown separately in this example (in red), independently from whether the GHG emissions are partly already internalized through carbon pricing mechanisms for some alternatives and in some countries (World Bank, 2021) and would thus be part of the internal costs. For HyBECCS, the green bars represent the LCOE reduction due to the application of CCS. This means that, in this example, the capture and storage of the biogenic CO_2 generate more income from sales of carbon removal certificates than costs (including GHG internalization costs for CCS process emissions). In this example, the costs can be reduced from a total of 0,20 EURO/kWh to a final LCCNH of 0,13 EURO/kWh (dotted line) at an assumed carbon price of 300 EUR/tCO_2eq. The LCCNH as the final KPI shows the competitiveness of biohydrogen from HyBECCS in comparison to alternatives. Here, the LCCNH of biohydrogen from an exemplary HyBECCS plant is compared to the LCOE of hydrogen from other sources as well as to the wholesale prices of fossil energy carriers (IRENA, 2019; Matthes et al., 2020, p. 29).

Figure 7 compares the levelized costs of negative emissions (LCNE) from HyBECCS with the LCNE of other negative emission technologies. Due to missing data from real HyBECCS plants, the LCNE for HyBECCS is only an assumption for illustration purposes and not based on real values. The values of the alternatives are based on actual data from Poralla et al. (2021) and Möllersten et al. (2020). For HyBECCS, the purple bar represents the internal LCNE before GHG internalization. The red bars represent the internalization costs for the specific GHG emissions depending on the assumed carbon price. For HyBECCS, the green bar represents the cost reduction due to the generation and sale of hydrogen. This means that, in this example, the total unit costs can be reduced from a total of 360 EUR/tCO2stored to a final LCNE of 110 EUR/tCO2stored (dotted line) at a carbon price of 300 EUR/tCO_2eq. The LCNE as the final KPI shows the competitiveness of negative emissions from HyBECCS in comparison to alternative NETs. Here, the LCNE of negative emissions from an exemplary HyBECCS plant is compared to the costs of BECCS and DACCS. For both alternatives, the striped bars represent cost ranges gathered from studies (Möllersten et al., 2020; Poralla et al., 2021). As long as no GHG internalization for process emissions is undertaken for DACCS and BECCS, those cost ranges represent the internal LCNE.

4.2.2 | Exemplary Basic Model for HyBECCS Regulatory Systems in Net-zero or Net-negative Emission Economies

As the CS/CU subsystem of HyBECCS, in most cases, does not generate any other marketable product than the

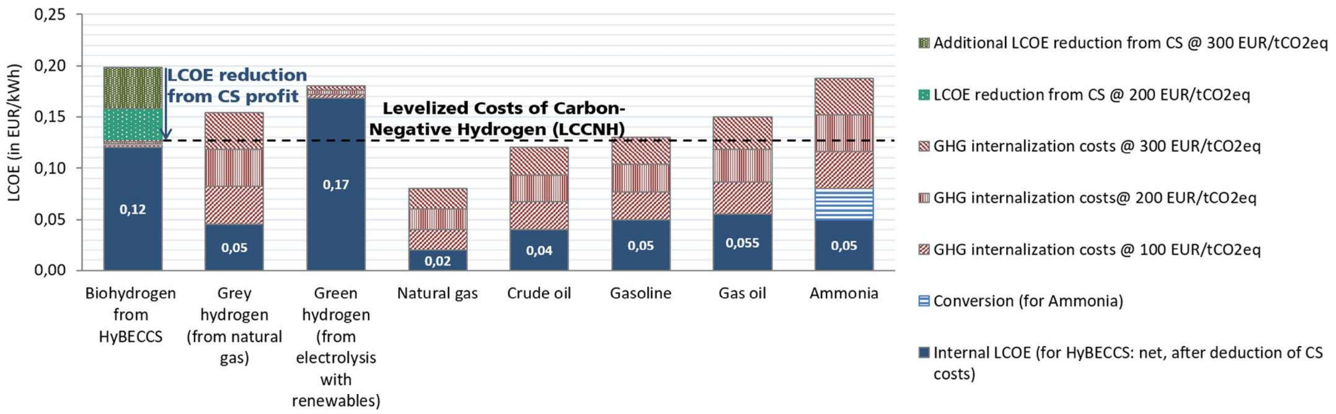

FIGURE 6 Exemplary comparison of the Levelized Costs of Carbon-Negative Hydrogen (LCCNH) of biohydrogen from HyBECCS with hydrogen from other sources and wholesale prices of fossil energy carriers. Assumptions: Net calorific value for hydrogen. Specific GHG emission for ammonia corresponds to those of grey hydrogen. Ammonia is calculated as H2 equivalents. (Own elaboration based on Fischedick and Adolf (2017), Hinicio, Matthes et al. (2020))

negative emissions, but generate costs for the carbon storage, the CS/CU subsystem would not be implemented without external incentives to (over)compensate such CO_2 capture and storage costs. In order to achieve a global economy with first net-zero and then net-negative GHG emissions, according to the emission pathways of the IPCC (Masson-Delmotte, et al., 2021), uniform incentive schemes have to be established. Various approaches have been developed and rules for such certification systems have been set forth (Honegger & Reiner, 2018a; Tanzer & Ramírez, 2019). The variety of incentives schemes can be divided into result-based and non-result-based approaches. In the early implementation phase of HyBECCS, non-result-based incentives schemes are appropriate and urgently needed. Examples are subsidies for research, design, development, and demonstration (RDD&D), tax credits, concessional loans, and grants (Poralla et al., 2021, p. 23). At a later stage with HyBECCS and other NETs being broadly operational, a result-based approach, based on carbon removal certificates (CRCs), can be established to strive for cost efficiency (Rickels et al.). The European Commission aims to develop such a regulatory framework for the certification of carbon removals in 2022 (European Commission). A basic model for such a regulatory, result-based system building on CRCs from HyBECCS could work as described in the following. It shall give an example of how negative emissions from HyBECCS plants can be economically rewarded in order to convert HyBECCS into a working business case. This basic model respects the general rules elaborated and broadly accepted in scientific discussion on carbon removal certification (Honegger, 2020; Tanzer & Ramírez, 2019).

In HyBECCS plants, CRCs can be generated when verified negative emissions are produced, for example, through measurement at CS sites that store certified and GHG-neutral (after internalization) biogenic CO_2. The precondition for the issuance of CRCs is that net-negative emissions are generated as per framework condition FC1 ($E3 < 0$). CRCs can be issued on a quantity basis per ton of biogenic CO_2 permanently stored. These certificates can be sold on a free market to offset emissions of certain, predefined types. Figure 8 below depicts the mechanism at the example of HyBECCS. As shown in the figure, the process emissions of the HyBECCS process chain (E1 and E2b) could be compensated through CRC purchase and offsetting. For an operator with internal access to negative emissions, e.g. when considering the whole HyBECCS process (B3) or only the CS boundary (B2), the offset could be done with the cancellation of CRCs in the amount of process emissions. At the same time, a revenue stream is generated by the sale of CRCs issued for the negative emissions (E2a) and sold on the CRC market. This would create a self-regulating market mechanism ensuring, in a first step, net-zero emissions, in case all process emissions are obliged to be offset against negative emissions. Risk deductions for uncertainties on the permanence of CO_2 storage would have to be considered within such an offsetting mechanism.

Regulatory intervention is also possible and enables the targeted pursuit of predefined emission paths: By removing

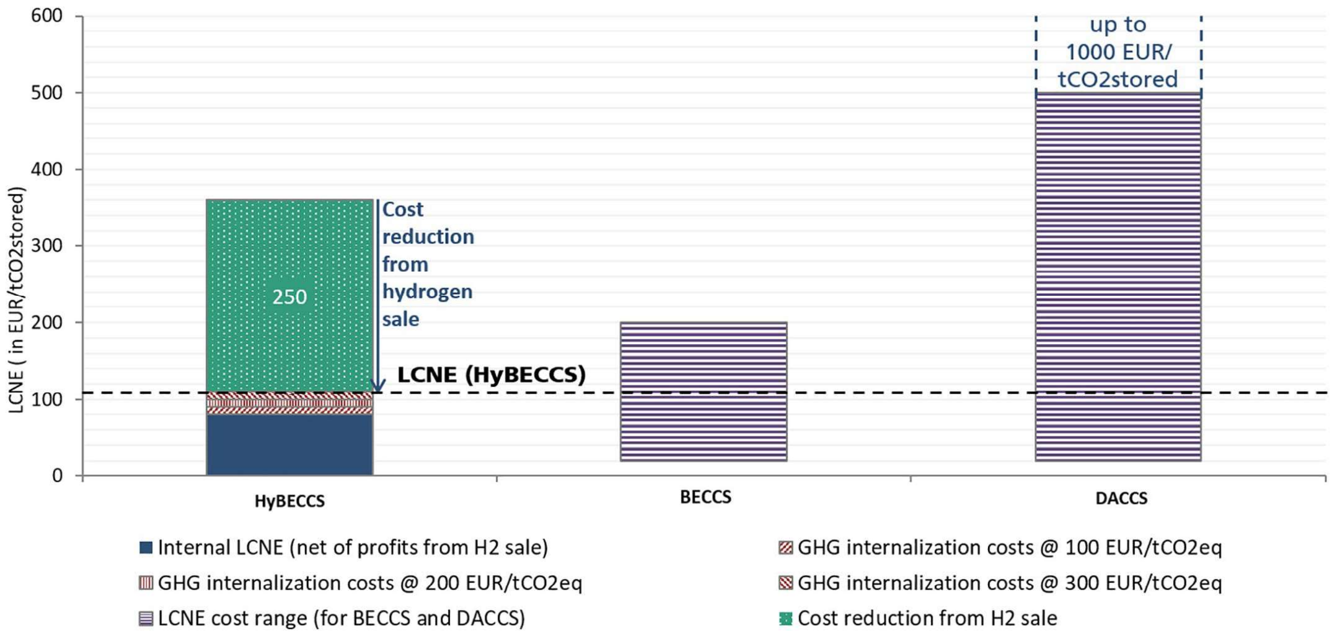

FIGURE 7 Exemplary comparison of the Levelized Costs of Negative Emissions (LCNE) of negative emissions from HyBECCS with other NETs. (Own elaboration based on Möllersten et al. (2020), Poralla et al. (2021))

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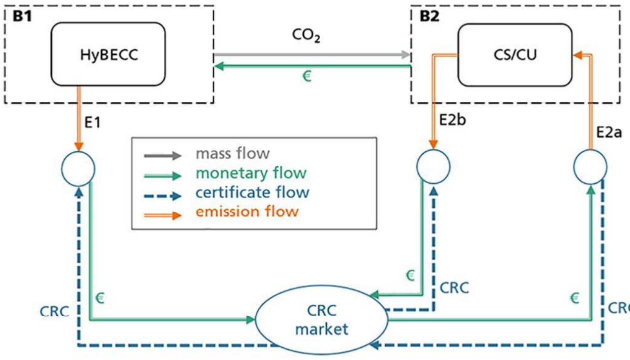

FIGURE 8 Basic model for regulatory systems based on carbon removal certificates (CRCs) at the example of HyBECCS processes (Abbreviations cf. Figure 3)

certificates from the market, negative emission paths can also be ensured. Potential buyers of CRCs are thus government or private institutions aiming to build up a negative emission budget through the reduction of CRCs. The second group who could be obliged to purchase CRCs are emitters of unavoidable emissions. It is, however, important that the unavoidability of GHG emissions is regularly questioned in the light of technological progress. It must be avoided that the CRC offsetting hinders or decelerates innovation for GHG mitigation. Furthermore, the priority of avoiding GHG emissions should be secured by excluding the offsetting of avoidable (fossil) emissions with CRCs, as it would prolong the lifetime of fossil utilities. Moreover, the offsetting of CRCs with fossil GHG emissions would have the same GHG balance as the CCS of fossil carbon dioxide: Both are, at a maximum, GHG-neutral, but would occupy potentially scarce CO_2 storage capacities (Azapagic et al., 2018). Such GHG-neutral or -positive uses of storage capacities would increase the costs of NETs: Storage sites would be scarce, potentially less accessible, and thus more expensive to access when the economically best locations are already used for the storage of avoidable, GHG-neutral, or -positive CO_2. This would limit the total potential of HyBECCS and NETs in general. CRC offsetting with avoidable GHG emission thus has to be ruled out, such as CCS of avoidable fossil CO_2, both ideally by the avoidance of such avoidable CO_2 emissions in the first place. In the proposed offsetting mechanism for HyBECCS, potentially avoidable GHG emissions (of the HyBECCS process) are offset against CRCs. It should be discussed if such offsetting is allowed, in the interest of the NET implementation, whether the GHG emission internalization should happen via offsetting of process emissions against emission reduction certificates from renewable energy projects, or if a ratio for emission reduction certificates and CRCs should be introduced for NETs (Geden, 2021). The approach presented above gives an example of how an incentive scheme for the generation of negative emissions might look like aiming to present a basis for discussion of how to solve the externalities of NETs in a positive way.

5 | DISCUSSION AND LIMITATIONS

It must be clearly stated that there is no claim to the completeness of the described methods for a final techno-economic and ecological evaluation of HyBECCS projects. However, the evaluation basics and specifics are provided in order to enable a uniform evaluation of these approaches. Using those basics and discussing the elaborated KPIs LCCNH or LCNE, a review of the TEA and EA results should be carried out in order to check the completeness, reliability, and consistency of the model, assumptions, data quality, and outputs. Therefore, an uncertainty and sensitivity analysis should be conducted to identify the most influential input indicators. (Zimmermann et al., 2020). Based on the technical evaluation and the uncertainty and sensitivity analyses, targeted technical optimization can be carried out to improve efficiency in terms of energy consumption and biomass conversion as well as the economics and ecological aspects of the HyBECCS plant (Zimmermann et al., 2020). The LCCNH (and LCNE) can only serve as a benchmark to price scenarios and projections for external costs and benefits of HyBECCS processes into cost calculations as long as they are not internalized and reflected as actual internal costs in the calculations.

Further, for the environmental assessment specifics elaborated, a special focus is on the impact category of global warming potential. This is due to the main objective of the considered HyBECCS technologies for climate protection. However, many important impact categories remain unconsidered. These include, for example, acidification and eutrophication potential or photochemical oxidant formation as well as ozone layer and abiotic depletion according to ISO 14040/44. As HyBECCS represents a BECCS technology, this novel approach is subject to the sustainability criteria of BECCS technologies. Therefore, it should secure food supply, avoid land degradation and land use conflicts, conserve water resources, as well as preserve biodiversity in order to be socially and ethically tenable (Fajardy et al., 2019). The implementation of HyBECCS projects also depends on social acceptance and social compatibility (Gough et al., 2018), since social values are crucial in decision-making (Wainger et al., 2010) and technological development (Buck, 2016). Hence, HyBECCS projects must take place in a socio-ethical context, which is why those impacts need to be assessed in order to determine the full implementation potential of HyBECCS projects (Gough et al., 2018). Therefore, a social life cycle analysis (S-LCA) should be carried out. Furthermore, the deployment of each HyBECCS plant should be aligned with the Sustainable Development Goals (Fajardy et al., 2019). In addition, any other category that influences a social-ethical friendly environment, such as health and safety conditions, local work and employment conditions, fair competition, respect of indigenous rights, infrastructure development, etc. must be investigated within the S-LCA (Benoît Norris et al., 2013). These aspects were not considered in the present work. Thus, guidelines for an S-LCA for HyBECCS approaches need to be elaborated.

6 | SUMMARY AND OUTLOOK

In this paper, fundamentals for the holistic evaluation of HyBECCS process combinations in terms of techno-economic and climatic performance are presented for the first time. Since there is no HyBECCS plant so far, this work provides the theoretical basis for comparing future HyBECCS plants. For this purpose, first, a classification and delimitation of the HyBECCS approach are elaborated. Respectively, the concepts CCS, NET, and CDR apply to the HyBECCS approach as it removes biogenic carbon dioxide from the atmosphere. However, further requirements must be met: Only if the GHG footprint of a specific HyBECCS project is negative, it actually generates net negative GHG emissions and thus qualifies as NET and the generated hydrogen is carbon-negative hydrogen (CNH). System boundaries to be applied and emission streams to be considered are described in order to provide a comparable frame of reference. Thereby, the HyBECCS approach is divided into two system elements, each with an associated subsystem boundary: First, the biohydrogen production with CO_2 co-production and capturing (HyBECC) and, second, the storage or long-term use of biogenic CO_2 (CS/CU). In addition to the emission flows, monetary flows of the system boundaries are defined as a basis for a better understanding of the economic relationships. A special focus was put on the description of interrelationships between climatic and economic aspects by elaborating the double climate protection effect through GHG emission reduction and removal and their resulting possibilities to receive incentives.

In the main part, this basis was used to explain how the economic viability as well as ecological effects, specifically on the climate, can be determined. On the ecological side, firstly, the conditions for positive climate impacts of the HyBECCS technology are discussed. This is done within an eligibility check related to the selection of the basic technology as well as project-specific life cycle impacts. The eligibility check on technology level ensures that the approach considered is suitable for the production of CNH. The theoretical ability for CO_2 removal and the theoretical permanence of the CO_2 storage is evaluated by matching the substrate biomass and the selected CO_2 storage technology via positive lists. These lists should be drawn up and continuously maintained by authorities. Second, if this step is successful, a life cycle assessment is carried out for the specific project proposal and the suitability for generating net negative emissions is verified via the greenhouse gas balance. Special features for the greenhouse gas balancing that apply to the HyBECCS subsystems are elaborated and described. As a key figure for the climatic impact, the emission factor EF was established and defined as the most important indicator for the classification of the HyBECCS approach as NET and the designation of the produced hydrogen as CNH. Eligibility on project level to qualify as NET is proven if the calculated emission factor EF is less than 1. The EF can be estimated ex-ante based on the project planning, but has to be verified ex-post through on-site measurements during the operation of the HyBECCS plant(s).

On the economic side, particularities for the determination of profitability were explained. Special focus was placed on determining internal capital and operating costs, initially without taking into account external effects and incentive systems. The selection of appropriate methods for estimating capital cost with respect to the current degree of the project definition and data availability is elaborated within this part. Afterward, peculiarities concerning the HyBECCS approach with respect to political regulatory measures and interrelationships between economics and ecology are outlined. Based on this, two key performance indicators (KPIs) are determined: The levelized costs of carbon-negative hydrogen (LCCNH) and negative emission (LCNE). Both KPIs allow deciding whether a specific HyBECCS project is economically viable when compared to the LCOE of competing technologies for the provision of negative emissions, hydrogen, or energy, in general. It furthermore allows the comparison of HyBECCS projects with different hydrogen or energy provision technologies and NETs. This is especially important to ensure that the biological transformation process of modern economies is efficient, minimizing the depletion of scarce resources such as energy, non-waste biomass, land, potentially CO_2 storage sites, and, ultimately, money. The guidelines for the KPI determination furthermore give first indications of how to optimize the GHG balance of a HyBECCS project. For instance, the design of the HyBECCS project as a "waste to hydrogen" plant, using waste or residuals as biomass feedstock, may significantly reduce the process emissions, allowing for a higher output of net negative emissions footprint (DIN e.V. DIN EN ISO 14044: Umweltmanagement - Ökobilanz - Anforderungen und

Anleitungen (ISO 14044:2006 + Amd 1:2017 + Amd. 2:2020); IE; Thrän & Pfeiffer, 2013). These holistic target KPIs can be calculated based on the total production costs and GHG balance. Both the negative emissions and the co-generated biohydrogen contribute to limiting global warming. However, only the internalization of these external benefits and the external costs of GHG emissions can turn innovative technologies such as HyBECCS into viable business cases. This particularity is reflected by the LCCNH. The LCCNH should represent the value to be optimized in order to achieve higher sustainability. However, this KPI depends strongly on political framework conditions, which must be taken into account.

In order to reach the GHG reduction targets set by governments worldwide, existing carbon pricing schemes have to be expanded and sharpened, as well as incentive schemes for negative emissions need to be disseminated. As shown in this paper, both of them affect the economic viability of HyBECCS. It is important to underline that the complete internalization of all GHG emissions and negative emissions – as proposed here – is important to give a realistic picture of the real costs of energy provision and climate protection. The still missing or incomplete internalization of external costs of conventional technologies hinders the implementation of novel, climate-friendly approaches such as HyBECCS, giving the presented assessment approaches a speculative component. Only realistic carbon price levels will have the needed steering effect on the individual decision process of operators and investors to direct investment into eco-friendly and efficient options like HyBECCS (OECD, 2021). The implementation of regulations to account for all GHG emissions of all processes should thus be the aim on a global level and the basis for future negative emission incentive schemes. This paper increased the understanding of these regulation´s impact on the economics of HyBECCS systems, and evaluability, as well as comparability, have been initiated via suggestions for basic frameworks and metrics. The work can be understood as an initial standard that enables meaningful comparison of HyBECCS systems. However, it needs to be confirmed by implementing the assessment approaches on real plants.

Furthermore, the innovative concept of HyBECCS with its novel product carbon-negative hydrogen calls for a more detailed categorization of hydrogen. On-going initiatives work on the establishment of a uniform threshold of GHG intensity for hydrogen to qualify as "green" or "low-carbon" (certifhy; Hinicio; Newborough & Cooley, 2020). However, as the GHG footprint of "green" hydrogen from different sources and projects varies significantly, the "theory of colors" always falls short of introducing real transparency. Imposing a product declaration stating the specific GHG intensity of hydrogen (e.g., in kg-CO_2eq/kgH_2) would allow such transparency. Besides the economic steering effect of the monetary internalization schemes introduced in this paper, such transparency could give an important impulse for the dissemination of CNH. Moreover, in order to safeguard the economic integrity of HyBECCS, efforts need to be directed toward the integration of scientific evidence on the risks of specific CO_2 storage technologies into a regulatory framework. The same applies to the definition of a minimum time horizon of storage for carbon utilization applications. Further needs for regulations will appear during the future development of the HyBECCS concept. Thorough monitoring, reporting, and verification (MRV) standards need to be elaborated and generally adopted so that market mechanisms, such as a CRC market exemplary described above, can lead the world on emission pathways toward the 1.5°C target.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Writing, J.F., S.Z., and M.G.; supervision, R.M. and A.S. All authors have read and agreed to the published version of the manuscript.

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Appendix D: Paper D

Contributions to the work

Title: Carbon-Negative Hydrogen Production (HyBECCS) from Organic Waste Materials in Germany: How to Estimate Bioenergy and Greenhouse Gas Mitigation Potential

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Methodology	✓	✓		
Formal analysis	✓	✓		
Investigation	✓	✓		
Data Curation	✓	✓		
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Writing (Review and Editing)			✓	✓
Visualization	✓	✓		
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Article

Carbon-Negative Hydrogen Production (HyBECCS) from Organic Waste Materials in Germany: How to Estimate Bioenergy and Greenhouse Gas Mitigation Potential

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Abstract: Hydrogen derived from biomass feedstock (biohydrogen) can play a significant role in Germany's hydrogen economy. However, the bioenergy potential and environmental benefits of biohydrogen production are still largely unknown. Additionally, there are no uniform evaluation methods present for these emerging technologies. Therefore, this paper presents a methodological approach for the evaluation of bioenergy potentials and the attainable environmental impacts of these processes in terms of their carbon footprints. A procedure for determining bioenergy potentials is presented, which provides information on the amount of usable energy after conversion when applied. Therefore, it elaborates a four-step methodical conduct, dealing with available waste materials, uncertainties of early-stage processes, and calculation aspects. The bioenergy to be generated can result in carbon emission savings by substituting fossil energy carriers as well as in negative emissions by applying biohydrogen production with carbon capture and storage (HyBECCS). Hence, a procedure for determining the negative emissions potential is also presented. Moreover, the developed approach can also serve as a guideline for decision makers in research, industry, and politics and might also serve as a basis for further investigations such as implementation strategies or quantification of the benefits of biohydrogen production from organic waste material in Germany.

Keywords: HyBECCS; biohydrogen; bioenergy potential; hydrogen; waste-to-hydrogen

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1. Introduction

The findings in the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) show that the 1.5 °C target is likely already being reached in the timeframe from 2021–2040, with each 1000 $GtCO_2$ estimated to increase the global surface temperature from 0.27 °C to 0.63 °C and approximately 900 to 2300 $GtCO_2$ remaining of the carbon budget to limit warming by 2 °C. A rapid and profound reduction in anthropogenic greenhouse gas emissions from fossil fuel combustion and, in addition, active removal of carbon dioxide from the atmosphere through negative emission technologies (NETs) are inevitably required in the immediate future [1].

In this regard, hydrogen is globally considered to be a key energy carrier of the future to be used as a substitute for fossil energy sources. Germany and many other countries have adopted a hydrogen strategy to bring it into widespread application. Hydrogen can not only be used for fuel or energy storage but is also a key substance of ammonia production or for refineries. In the future, it will be capable of decarbonizing decisive industries, such as steel or cement [2] (p. 2). What distinguishes hydrogen from conventional fuels is that the only combustion product—besides energy—is water. Further, hydrogen gas releases an astonishing amount of 142.35 kJ per g when reacting with oxygen. Natural gas, in comparison, releases energy of between 35 and 45 kJ per g during combustion [3]

(p. 42). Hydrogen can be produced sustainably using renewable electrical energy for water electrolysis or from biomass through several processes, with the product being called biohydrogen. Utilizing waste materials for biohydrogen production offers several benefits, as it increases the economic and ecological potential, avoids competitive land use, and represents another step towards a circular economy. According to Full et al. the ecological benefits for climate change mitigation can be further increased by capturing the produced biogenic CO_2 during the process and thereby achieving biohydrogen production as a carbon-negative process [4]. This means a net effect of CO_2 being removed from—rather than emitted to—the atmosphere during energy generation. This NET approach of carbon-negative hydrogen production by capturing biogenic CO_2 during biohydrogen processes is referred to as hydrogen bioenergy with carbon capture and storage (HyBECCS) [4].

There are many different ways to produce renewable energy. Bioenergy is one option that is of great importance, as biomass accounted for about 54% of the total share of renewable energy in Germany's primary energy consumption in 2017 [5]. A common way of producing bioenergy is the production of biomethane [6]. Biohydrogen production with additional carbon capture and storage or long-term use (HyBECCS) presents an alternative to biogas and -methane production and allows the generation of a carbon-negative product with growing demand [4,7]. The development of HyBECCS processes can additionally contribute to the global climate goals by creating negative emissions. Such methods of carbon dioxide removal (CDR) are key measures in the pathways to achieve climate targets [1]. Moreover, in order to decarbonize the energy sector more quickly and sustainably, non-utilized resources such as residual and waste materials should also be harnessed. These resources should be used primarily for NETs, such as the HyBECCS technology, as they are scarce. However, in order to accelerate the development and rollout of such promising technologies, it must be made clear to potential investors that they are economically viable [8]. An analysis of how much bioenergy from waste materials is available and suitable for biohydrogen production provides a basis for making such a statement. Research dealing with the estimation of bioenergy potential already exists [9–16]. However, none of the work deals with bioenergy potentials for biohydrogen production. Hence, there are no uniform evaluation methods for biohydrogen production. Therefore, the overall objective of this paper is summarized by the central question:

'How can the feasible bioenergy potential of several biohydrogen production processes from organic residuals and waste materials in Germany be evaluated and how much reduction in greenhouse gas emissions can be attained as a result?'

Initially, the classification and legal framework of biomass and organic waste materials are analyzed in general. The suggested methodical conduct is presented by the means of an exemplary biotechnological biohydrogen process. These specifications lay the foundation for identifying available material flows suitable to be converted into biohydrogen. After ascertaining and quantifying the amount of utilizable substances, the bioenergy potential can be estimated. Subsequently, this potential can be adopted into a possible amount of non-emitted and captured GHGs using HyBECCS approaches.

In this paper, for the first time, a recommendation for estimating bioenergy potentials specifically tailored for biohydrogen production in the German energy and waste system is developed. Furthermore, it should help to establish a generally accepted method to determine bioenergy potentials in order to make their quantification more accessible and uniform, which will additionally contribute to the development of new emerging technologies and their market rollout.

2. Basics

This section lays the foundation for this work by providing essential information regarding the different topics touched upon in this work.

2.1. Organic Waste Classification in Germany

This section outlines the legal framework for renewable energy as well as biomass utilization and disposal in Germany. Moreover, common treatment processes for biomass are presented, briefly touching upon their (dis)advantages and products. Lastly, two significant challenges concerning biomass are outlined, which are also highly relevant to this work.

The general regulation concerning renewable energies is the Renewable Energy Act (orig. Erneuerbare-Energien-Gesetz, EEG), which serves the purpose of enabling sustainable development of energy supply, reducing the economic costs by including long-term external effects, saving fossil resources, and supporting the development of technologies which generate electricity from renewable sources [§1, EEG]. A key development in the 2021 amendment of the law is that carbon neutrality of German electricity by 2050 and a 65% share of renewable energy by 2030 are made statutory [17]. The application of the EEG regarding the biomass definition, utilization technologies, and environmental requirements is established in the Biomass Ordinance (orig. Biomasseverordnung, BiomasseV). At the same time, the Circular Economy Act (orig. Kreislaufwirtschaftsgesetz, KrWG) aims to support a circular economy in order to save natural resources and to protect people and the environment during waste generation and management [§1, KrWG]. More specifically, the treatment, utilization, and disposal of organic waste material are widely regulated in the Organic Waste Ordinance (orig. Bioabfallverordnung, BioAbfV). Material of animal origin falls within the scope of the Animal By-Products Disposal Ordinance (orig. Tierische Nebenprodukte-Beseitigungsverordnung, TierNebV), which sets additional requirements on how such material is handled and disposed of, due to its potential hazard for the health of humans and animals. Data collection, processing, and publication are regulated by the Environmental Statistics Act (orig. Umweltstatistikgesetz, UStatG), which delivers a foundation for (environmental) policy decision making and fulfills the reporting obligation to European and other institutions [18]. German waste statistics are published annually by the German Federal Statistical Office (orig. Statistisches Bundesamt) on its GENESIS-online database, which is open access and provides a list of all waste types and their respective annual amounts. The different types of waste and their respective hazardousness are defined in the German Waste Classification Ordinance (orig. Abfallverzeichnisverordnung, AVV), which transposed the European Waste List into German national law. This work draws upon the definition of biomass from the BiomasseV. It defines biomass as energy sources consisting of phytomass and zoomass, including secondary products, by-products, residues, and wastes of which the energy content originates from phytomass and zoomass [(1),§2, BiomasseV]. In accordance with the KrWG, waste means any substance or object which the holder discards or intends or is required to discard [(1),§3, KrWG]. By-products are a substance or object resulting from a production process, the primary aim of which is not the production of that substance or object. They are different from waste if they meet the following criteria:

1. Further use of the substance or object is certain;
2. The substance or object can be used directly without any further processing other than normal industrial practice;
3. The substance or object is produced as an integral part of a production process;
4. Further use is lawful, i.e., the substance or object fulfills all relevant product, environmental, and health protection requirements for the specific use and will not lead to overall adverse environmental or human health impacts [(1),§4, KrWG].

The term residue is not defined specifically but used in various works and legal documents. As a consequence, the term cannot be clearly distinguished from waste or by-products. In this work, all biomass material, which is not produced as a primary product, falls within the definition of residues. That includes by-products and waste [19] (p. 21). In general, the sectors of agriculture, forestry, fisheries, food production, animal feed production, and municipalities are mainly accountable for organic residues and wastes in Germany [20] (p. 39). All varieties of material such as wastes from livestock farming, fish and animal processing, crop harvesting, fruit and vegetable agriculture and processing to organic household waste, green waste, sewage sludge, and secondary wastes need to be evaluated regarding their potential usability for biohydrogen production. Therefore, this work classifies the present biomass flows as listed in Annex 6 of Brosowski et al. [21], as their work provides estimations of potential material flows from the German Biomass Research Centre, DBFZ.

Organic wastes can be used via several pathways, depending on the origin and composition of the material. First, organic material can be used directly, such as animal excrements as fertilizer, bark as mulch, or food industry residues as animal feed. Harvest residues are often left on the field as well [22] (p. 81). Second, various composting processes are established, which treat the material in order to be consecutively applied to (agricultural) land. Advantages are that the stabilized organic substances in compost contribute to the formation of humus, which sustains the productivity of land and increases the water storing capacity of the surface soil [23] (pp. 11, 12). Third, energetic use can be realized by fermenting organic material under anaerobic conditions, incinerating material of suitable composition, or using gasification as a means of treatment. Anaerobic fermentation is mainly used for animal excrements, but also for household biowaste or industry residues to a certain extent [24] (p. 38). Sewage sludge is also treated anaerobically on the site of large water treatment plants, whereas the majority of smaller ones have no such treatment option [25] (p. 18). The desired product of anaerobic digestion is biogas, which can be used directly in a combined heat and power plant or treated further to obtain biomethane, which can be fed into the gas grid, for instance. Biohydrogen production from biomass is also a promising utilization pathway in the future. Incineration or gasification is possible for material with low water content that is not usable for fermentation. As a consequence, mainly wood, wood-like residues, or straw are used as input material for those processes [25] (pp. 10-13). Lastly, biodiesel production is a widely applied technology to utilize oils and fats via transesterification [25] (p. 17).

At present, a lot of organic waste material is not used efficiently. It should be noted that material use of biomass, which also includes use as animal feed, is generally seen as higher value than energetic use [22] (p. 20), cf. Figure 1. What is considered inefficient is material use of substrates, which could be used energetically prior to material use. Examples are biowaste or animal excrements, which could be utilized energetically first and subsequently be composted and/or applied to land. This multiple-use principle is suggested to be a more efficient way to utilize organic wastes [22,26] and is also part of the Circular Economy Act [§8, KrWG]. Currently, just 40% of organic household waste, 12% of manure, and 2% of dung are utilized energetically [24,27], even though it would not impede the subsequent material use. In the following, only material flows which do not compete with established, high-value utilization routes such as animal feed, for instance, will be considered. In addition, the material is only analyzed for biohydrogen production, if it is not directly competing with food production or other human use. Overall, this work is based on the principles that food production is prioritized over energy crop cultivation in all cases and focuses on the utilization of true waste products, avoiding material which can be treated through a utilization path of higher value, cf. Figure 1. In consequence, certain biomass flows, theoretically utilizable for biohydrogen production, will be discarded, as higher-value utilization is assumed. However, biomass flows with an established material utilization pathway in which their potential is not harnessed will also be considered available for this process. Animal excrements are an example of that. Further, usable municipal wastes and certain industrial residues can be considered available for biohydrogen production.

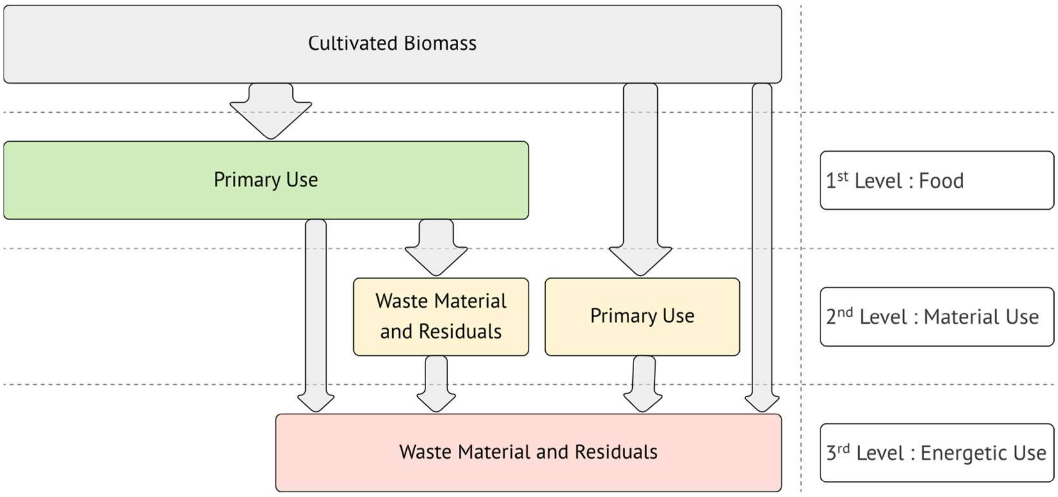

Figure 1. Hierarchy of use for biomass [22].

Another challenge is that, as of 2020, 39% of mixed municipal solid waste (MMSW) is still of native organic origin [28]. This fact is problematic for several reasons. First, the EU set the goal to recycle 60% of municipal wastes by 2030, which urges Germany to act [28] (p. 26). Redirecting organic material from mixed fractions to biowaste could be a crucial opportunity to do so, as 97% of separately collected material from the organic waste bin is already being recycled [29] (p. 30). Secondly, organic waste, with its relatively high water content and hence lower caloric value, is not a desired input material for thermal treatment, which is the major route of disposal for mixed municipal waste [29] (p. 30). Even though organic waste is not causing problems in incineration, the desired high-quality utilization of biomass for biogas or, in this case, biohydrogen with multiple uses, is again preferred and demanded by the Circular Economy Act [24] (p. 92).The separate collection of recyclables and organic waste is already mandatory, but the necessary collection systems are not yet implemented consistently [28] (p. 27).

2.2. Biohydrogen Production and the HyBECCS Approach

Hydrogen produced from renewable energy or biomass is called green hydrogen as it is CO_2 neutral [30]. Furthermore, hydrogen derived from biomass feedstock is called biohydrogen. Processes for producing such green biohydrogen comprise electrochemical, thermochemical, and biotechnological production routes. Microbial electrolysis represents the electrochemical pathway. Thermochemical biohydrogen production processes comprise pyrolysis and gasification, whereas biotechnological process options are biophotolysis, photo-fermentation, dark fermentation, and dark photosynthesis. The following summary is limited to a number of relevant technologies according to the material source. Each technology is briefly described in 2.2.1. Further, in 2.2.2., the HyBECCS approach is presented, which is, at present, the only known way to produce hydrogen with a negative carbon footprint [4].

2.2.1. Biohydrogen Technologies

Thermochemical biohydrogen production processes include, for example, pyrolysis and gasification. Pyrolysis is gasification under the absence of oxygen at temperatures between 500 and 900 °C and pressures between 0.1 and 0.5 MPa. As a result, no dioxins or carbon oxides are formed, given that the input material is dry and no air or oxygen is present. The products are synthesis gas and carbon residues, such as liquid oils and solid charcoal [31] (p. 14), see reaction (1.1) in Table 1. Advantages of the process are the wide variety of possible input materials, a simple underlying process, compact plants, a clean carbon by-product (fuel oil or char), and reduced CO or CO_2 emissions compared to gasification [32] (p. 5). That is, the hydrogen produced from biomass conversion can be classified as green, due to the carbon-neutral nature of all biomass. In other words, the resulting GHGs during the processes were already removed from the atmosphere in the first place. Biomass is seen as the most feasible candidate to substitute fossil fuels in the near future [32] (p. 5) and thermochemical processes, especially gasification, are already mature. However, biomass conversion faces logistics issues since it requires enormous amounts of input material in large-scale plants. Another problem is tar fouling the plant and the produced gas, which impedes wider market implementation. Possible solutions for the logistics issue are efficient plant downscaling and the smart distribution of conversion plants [32] (p. 5), paving the way for thermochemical processes as the only non-biological means of hydrogen production from biomass [31] (p. 13).

Table 1. Overview of chemical reactions for H_2 production from biomass [32–34].

Number	Process	Reaction
(1.1)	Biomass pyrolysis	$C_nH_m \rightarrow n\ C + 0.5\ m\ H_2$
(1.2)	Glucose formation	$6\ H_2O + 6\ CO_2 \rightarrow C_6H_{12}O_6 + 6\ O_2$
(1.3)	Enzymatic hydrogen generation	$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2 + 12\ H_2$
(1.4)	Microbial electrolysis (acetate)	$CH_3COO^- + 4\ H_2O \rightarrow 2\ HCO_3^- + H^+ + 4\ H_2$
(1.5)	Photo-fermentation (acetic acid)	$CH_3COOH + 2\ H_2O \rightarrow 4\ H_2 + 2\ CO_2$
(1.6)	Acidogenesis (butyric acid)	$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2\ CO_2 + 2\ H_2$

One of the biotechnological process options is biophotolysis. In this process, light-sensitive microorganisms in illuminated reactors perform photosynthesis first to convert water and CO_2 to glucose and oxygen (1.2) before photo-activated enzymes split the sugar and release hydrogen gas (1.3). Microalgae are promising organisms for this process, as they can be cultured and allow better hydrogen capture. In general, the process happens under standard conditions in a water environment and does not require cost-intensive input material, although the sufficient illumination of the substrate is an arising upscaling issue [34] (p. 11101). Moreover, the hydrogenase is inhibited by O_2, which presents an additional obstacle in the process [33] (p. 8).

Another process, microbial electrolysis, is based on the ability of certain microorganisms, called exoelectrogenic microbes, to produce electric current by oxidizing organic matters. To generate hydrogen, a small external power supply drives electrons—produced from organic matter in the anode chamber—through a wire to the cathode. The applied current is typically 0.2 V, which is very low compared to 1.6–1.8 V for water electrolysis [33] (p. 11). Together with protons, which permeate through the proton exchange membrane, the electrons form hydrogen gas in the cathode chamber. An exemplary reaction for acetate as an organic compound (1.4) is shown in Table 1. This system is called a microbial electrolysis cell, which presents high hydrogen yields and efficiencies. However, the performance depends on the microbes used and the exchange efficiency of the membrane, as well as on the electrical conductivity and chemical stability of anode and cathode. Additional tasks are the reduction in internal resistance and material cost, as well as the increase in biomass concentration in the anode chamber [33] (p. 11, 12).

Photo-fermentative purple and green bacteria are able to preferably convert organic acids, but also carbohydrates or industrial effluents, to H_2 and CO_2, utilizing energy from light in anaerobic environments [33,35]. An exemplary reaction of this photo-fermentation process is executed by purple non-sulfur bacteria, as shown for acetic acid (1.5) in Table 1. The process is highly sensitive to the presence of oxygen or ammonia and depends on light intensity, carbon source, and type of microorganism [35] (p. 575). The utilization of solar energy and organic wastes promises cheap operation. However, as hydrogen production rates and efficiencies for light conversion are low, while reactor costs are high and illumination problems immense, the process is rather impractical [33] (p. 9).

Compared to photo-fermentation and bio-photolysis, the so-called dark fermentation provides the huge advantage of not being dependent on light as well as featuring simple reactor design and operation [33] (p. 10). The main idea in dark fermentation is to inhibit the hydrogen-consuming methanogenesis, which is the last step of an anaerobic biogas process, and harvest the hydrogen. The environment can be mesophilic, thermophilic, or hyperthermophilic, depending on the microbial strain to be used for production [36] (pp. 24, 25). The acidogenic phase particularly degrades carbohydrates, fats, and proteins to volatile fatty acids (VFAs), alcohols, amino acids, H_2, and CO_2. For example, pyruvate—an intermediate in the metabolization of glucose—is converted to volatile fatty acids, e.g., acetic, butyric, propionic, and malic acid, and hydrogen [31] (p. 9). As an example, the reaction of glucose to butyric acid (1.6) is shown in Table 1. Due to the similarity to the classical biogas process, dark fermentation is seen as a feasible way to produce hydrogen from organic wastes. However, low hydrogen yields and substrate degradation need to be optimized. To achieve that, process operation is still a matter of development, with the suppression of methanogens being crucial to the final hydrogen yield [32] (p. 11).

The so-called dark photosynthesis process is defined by the possibility of accomplishing photosynthetic growth patterns for Rhodospirillum rubrum, a Gram-negative, non-sulfur purple bacterium and a facultative anaerobe, with a special culture medium under dark conditions. This growth medium, called M2SF, is capable of enabling mass cultivation under semi-aerobic dark conditions. Such behavior is usually limited to anaerobic, photo-heterotrophic growth [37,38]. The result of this new means of growth—mimicking light signals to the photosynthetic genes in a dark environment—is that the versatile metabolism of R. rubrum can be utilized in the absence of light, which makes it perfectly scalable.

2.2.2. The HyBECCS Approach

According to the sixth assessment report of the IPCC, emissions pathways that limit global average warming to 1.5 °C or 2 °C by 2100 require the use of carbon dioxide removal (CDR) approaches in combination with emissions reductions to pursue a pathway with net negative CO_2 emissions from 2050 on. Hence, affordable as well as environmentally and socially responsible CDR options on a large scale well before 2050 are an important element for climate mitigation and play a central role in limiting global warming to 1.5 °C or 2 °C [1]. Negative emission technologies (NETs), of which bioenergy carbon capture and storage (BECCS) as well as ocean fertilization, mineral carbonation, afforestation, and direct air capture (DAC) are part, are important by means of reducing anthropogenic net emissions in the near future [39] (pp. 1124, 1125). An emerging subclass of BECCS technologies is the concept of hydrogen bioenergy coupled with carbon capture and storage (CCS) technology [4]. These process combinations, referred to as HyBECCS, are described briefly below.

Most of the biohydrogen technologies are able to split biomass substrates into H_2 and CO_2, which is beneficial for an effective carbon capturing process, as this mixture can be separated. The hydrogen fraction can be used to substitute fossil energy carriers in industry or transport in order to decarbonize these sectors. The carbon dioxide can be put to long-term use or in storage, leading to a carbon sink since it was previously removed from the atmosphere through plant biomass growth in relatively short periods of time. Carbon dioxide storage possibilities include enhanced oil or gas recovery, storage in saline formations, depleted oil and gas fields, and others [39] (Figure 1). An alternative to storage is usage, where CO_2 is stored for a certain period of time in applications such as fuels, construction materials, chemicals, and plastics [39]. All process combinations referred to as HyBECCS can be split into four basic process steps: biomass pretreatment, biohydrogen production, product gas separation, and its processing. For each of the four steps, there are variable options to be selected and combined into an overall process.

The main technological advantages of HyBECCS over competing NETs are, on the one hand, the energy-efficient capture of CO_2 with high purity and concentration compared to DAC approaches. On the other hand, it offers high carbon dioxide removal potential compared to BECCS technologies based on hydrocarbon energy carriers, which emit CO_2 during their decentralized use. Based on these advantages, HyBECCS is considered to be a promising and highly effective BECCS approach that is expected to play a major role in future energy systems by making a significant contribution to meeting the world's rapidly growing demand for green hydrogen and negative emissions [4]. The HyBECCS approach can also be seen as part of the biological transformation process, which aims to achieve a sustainable economy that is no longer dependent on the depletion of fossil fuels by linking classical production with bio- and information technologies, leading to a new and disruptive innovation space [40,41].

2.3. Terminology and System Boundaries

In the past, the term 'potential' was not clearly defined in various studies, decreasing comparability and complicating interpretation. System boundaries define the resulting potentials and need to be chosen to reduce the effort of elaboration, but they still have to support the purpose of a piece of work, so it is strictly necessary to define them precisely. As a result, the terminology and systematic approach for this sort of estimation of potential have been standardized to some extent. In this work, the definitions according to Thrän et al. are used and summarized in the following [19]. The different types of potentials are outlined and their differences, e.g., level of observation and system boundaries, are highlighted and placed in the present context.

Biomass potentials can be differentiated according to the level of consideration [19]. Land potential, feedstock potential, fuel potential, and bioenergy potential can be distinguished. An overview of these levels and the resulting potential terms can be seen in Figure 2. The land potential describes the area available for energy crop cultivation, which is not relevant to this work, as it deals with organic waste material, and the feedstock potential is not calculated from the underlying land potential but represents the amount of applicable material for biohydrogen production. From that point, the fuel potential can be obtained from the hydrogen yield per unit of substrate and the respective lower heating value of H_2. Lastly, the bioenergy potential can be derived by considering the relevant conversion efficiency of hydrogen to heat and/or electric energy and the energy input for pretreatment and process operation.

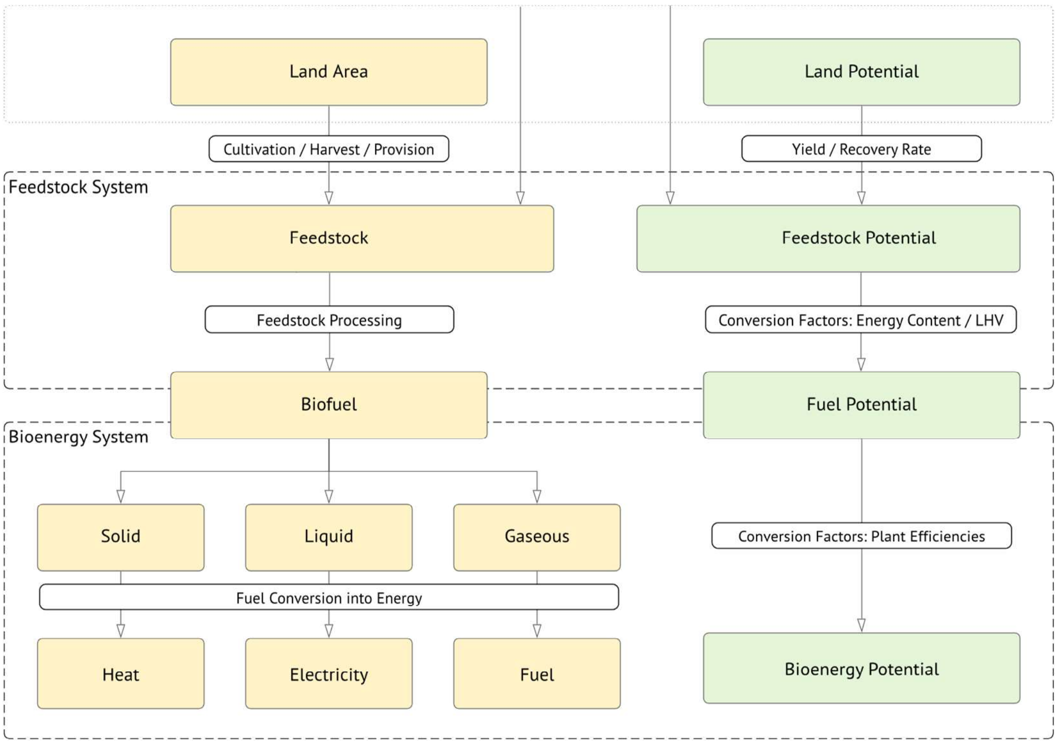

Figure 2. Levels of utilization pathway and corresponding potential terms [19].

Each potential requires specific system boundaries and framework conditions, necessitating further explanations. The biomass potentials obtained in a piece of work depend on a variety of different factors, such as the biomass material considered, the geographic level, the temporal reference, the type of data collection, and the methodology of conduction. In addition, different perceptions of competitive usage, sustainability aspects, or nature conservation issues often cause confusion [19] (p. 40).

These aforementioned potentials need to be defined more precisely, as to whether they reflect a theoretical, technical, or other potential. First, a theoretical potential describes the overall energy amount for a specific region in a specified period of time. It resembles the maximum amount of energy supply contained in the considered biomass, as it is based on the physical utilization boundaries alone. The practical relevance is minor, because the theoretical potential provides no statement of the actually usable amount of energy [19] (p. 42).

Second, the technical potential considers certain restrictions, and hence gives a more realistic result of utilizable biomass in a specific region and time. Considered restrictions are of technical (e.g., recovery rates and conversion losses), legal, environmental (e.g., environmental protection regulations, cross-compliance regulation), and social (e.g., food production, material utilization) concern. The technical potential is widely used in studies, as it is less affected by temporal fluctuations than the economic potential, for instance [19] (p. 42).

The economic potential reflects a part of the technical potential, which can be utilized considering further restrictions related to the economic framework. Adding even more restrictions allows for distinguishing additional potential terms. If increased importance is laid on ecological and environmental factors, one is speaking of sustainable biomass potential. Going one step further in the implementation direction, realizable potential can be obtained by further considering sociopolitical and practical restrictions [19] (p. 43).

That is, a scientific piece of work needs to explicitly lay out its use and interpretation of the mentioned terms. Moreover, the boundary conditions such as region, timescale, considered biomass, process operation, material handling, output, and methodical conduct need to be mentioned. An overview of the relevant potential terms is given in Figure 3. The following restrictions are suggested to be included when deriving a technical potential by Thrän et al. [19] (p. 44):

- Societal variables (as general agreement whether certain feedstock should receive a generally preferred form of utilization).
- Technical variables (cultivation, harvest, recovery, and conversion technology).
- Demand for food and material utilization.
- Ecological/environmental variables (legal requirements to ensure a sustainable resource base).

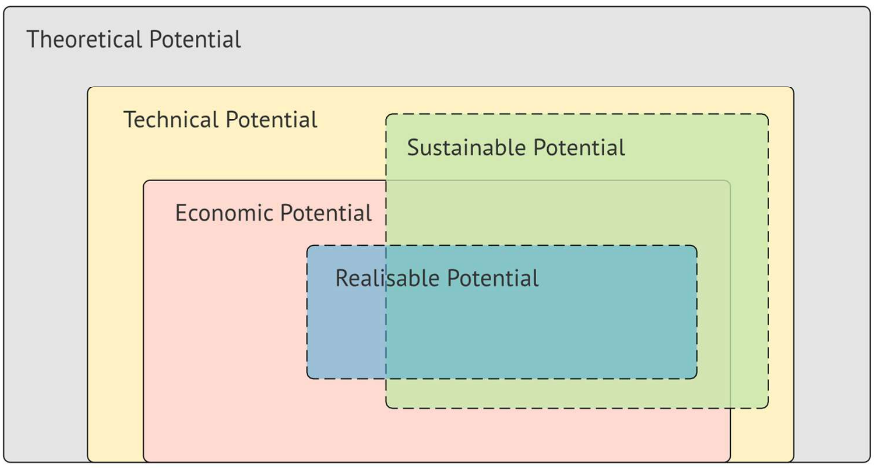

Figure 3. Types of potential according to system boundaries [19].

As this work aims to present a methodological approach to derive technical potential for biohydrogen production, these factors are included as far as possible. Some aspects, however, have to be simplified or neglected. Relevant factors, which exceed the scope of this work, are of demographic background, such as population trend, of socio-economic background, such as consumption habits and environmental consciousness, or of policy-making, regulatory, or organizational background, such as improved circular economy, reduced food waste, or stricter EHS standards [22] (p. 84). Other specific topics relevant to this process have not been included, such as substrate logistics, and storage or process residue handling. The restrictions applied to theoretical amounts of waste materials are, together with chosen simplifications and unincluded aspects, laid out in Section 3.

3. Methodological Approach

The following presents a systematic four-step methodological approach to obtain bioenergy potential and negative emission potential of biohydrogen production. Each step is elaborated in the following subsections, as shown in Figure 4. In the first step, a procedure to select relevant biomass categories for hydrogen production is elaborated, which is divided into six sub-steps. Second, suggestions are made for assumptions and framework conditions regarding biomass pretreatment, process energy demand, and logistical specifics. In the third step, in order to derive a calculation equation for the determination of the bioenergy potential for biohydrogen production, relevant indicators such as the lower heating value (LHV) or the fuel potential (FP) are introduced. This was done in accordance with standard practice and in compliance with certain criteria intended to ensure comparability and transparency. Finally, the estimation of the negative emission potential of biohydrogen processes is discussed regarding their contributions to climate mitigation. Furthermore, a calculation to estimate the saved amount of CO_2 emissions as well as for the substitutable amount of (fossil) energy carriers is presented.

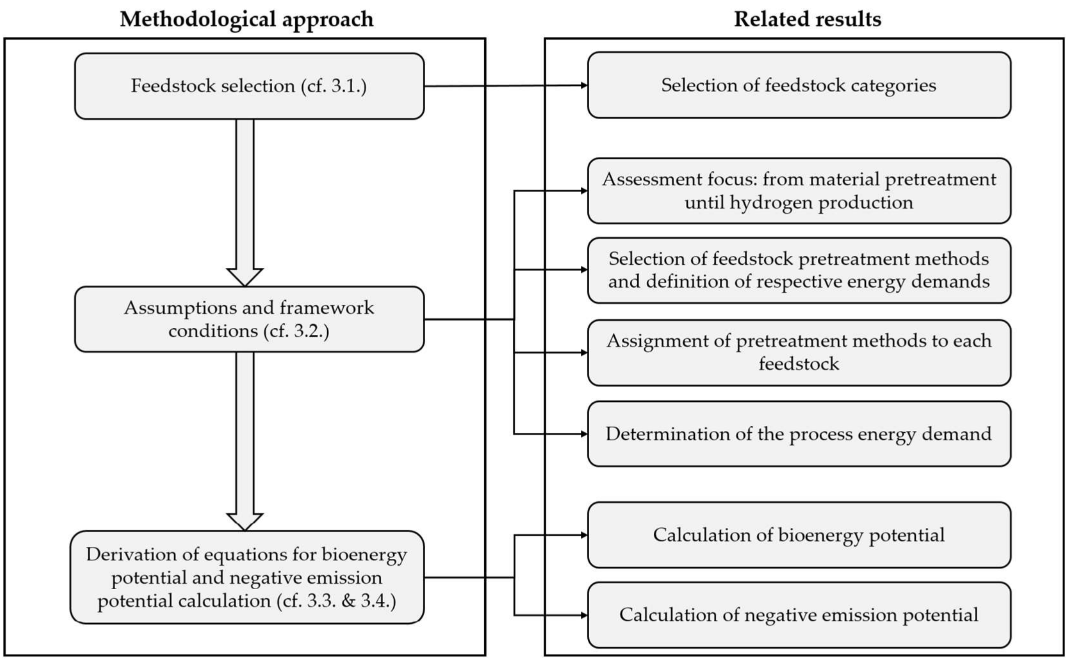

Figure 4. Overview of the presented methodological approach for bioenergy potential estimation and ecological assessment (**left**) and the respective results (**right**).

3.1. Feedstock Selection

The first and most important step is to identify and quantify biomass flows utilizable for biohydrogen production. These resource streams are the basis, as the hydrogen yield and all further results directly depend on the amount of utilizable substrate. Brosowski et al. defined 93 different biomass categories (BCs), which are drawn upon as a foundation for substrate selection in this work. In this section, the different BCs are evaluated regarding their applicability to the considered biohydrogen process, taking into account the prerequisites of the process and the biomass utilization hierarchy. All of the categories can be seen in Annex 6 of Brosowski et al. [21]. The selection process, which is conducted according to the following steps exemplified for biotechnological, fermentative biohydrogen production, can be illustrated in a decision tree as seen in Figure 5:

- Step 1 Data validity, utilization pathways, and classification issues: According to Brosowski et al., data and information are inconsistent for 16 biomass categories (BCs) and no technical potential is presented for eight categories. Those classes are sorted out in this step. Moreover, many food industry wastes, such as coffee or tobacco residues, must be disposed of according to special regulations. Other biomass flows, such as residues from convenience food production, are highly heterogeneous and assumed not to contain large amounts of relevant contents [42] (Chapter 2). Thus, it is not possible to make reasonable assumptions about the composition and such material flows should not be considered for utilization. In this case, 32/93 BCs can be discarded in this step.
- Step 2 Lignocellulosic biomass: Biomass categories containing wood or wood-like waste, straw, stalk, or other green waste are currently not suitable for some biotechnological processes, as they need to be readily biodegradable by microorganisms. Wood essentially consists of cellulose, hemicellulose, and lignin, which are poorly biodegradable without extensive pretreatment. Hence, they are rather unsuitable for fermentative processes [20] (p. 53); 28/93 BCs match this criterion and should be sorted out.
- Step 3 Wastes of animal origin: Such wastes should not be considered for alternative use because of the potentially contagious material and an established industry for efficient utilization of animal origin wastes. Gaida et al. describe the utilization of this biomass as already optimized. For instance, animal skin is processed to leather, and protein-rich residues are processed into tankage or fertilizer. Other potential pathways are biodiesel production and utilization as substances in the oleochemical industry [42] (pp. 22, 24). However, if a special suitability can be derived for specific biohydrogen process options, a comparison with the respective reference processes might be of interest. If not, 2/93 BCs match this criterion and should be sorted out.
- Step 4 Oils and fats: In a comprehensive evaluation of utilization pathways for this category, Fehrenbach et al. found that biodiesel production might be superior to other means of utilization [22] (pp. 112, 179). A comparison of the biohydrogen process under consideration with this form of use is therefore to be initiated. If the comparison is decided in favor of biodiesel production, another 2/93 BCs are sorted out in this step.
- Step 5 Waste material untypical for fermentation: Some waste types can be considered as biomass, but are not readily biodegradable, such as textiles or packaging material. These must also be subjected to a special test to determine their suitability for biohydrogen production. If this test is negative, 2/93 BCs match this criterion and have to be sorted out.
- Step 6 Animal feed or low sugar content: According to Section 2.1., material use of biomass should be preferred over energetic use in the case of animal feed, for instance. Hence, plenty of different process residues from the food industry cannot be seen as waste and are consequently not considered in this estimation of potential. Usage competition can arise if such materials are utilized energetically. Residues from the sugar industry would be perfectly suitable for fermentative biohydrogen processes, due to their sugar content. However, this material is widely used as animal feed, in the yeast industry, or in distilleries. The work of Gaida et al. indicates high-value material use for most food industry residues at present [42] (Section 2). However,

dairy industry residues, which mostly consist of whey [42] (p. 40), are excluded from this step. The amount currently fed to pigs is found to be better used for human consumption, which mainly consists of the contained whey protein [43] (p. 271). The contained lactose, which is a substrate for homolactic fermentation, remains in the permeate after protein extraction, hence it can be considered. Other biomass categories, such as residues from alcohol production, must first be checked as to whether they contain significant amounts of utilizable substances for biohydrogen production. Finally, 17/93 BCs could be excluded in this step.

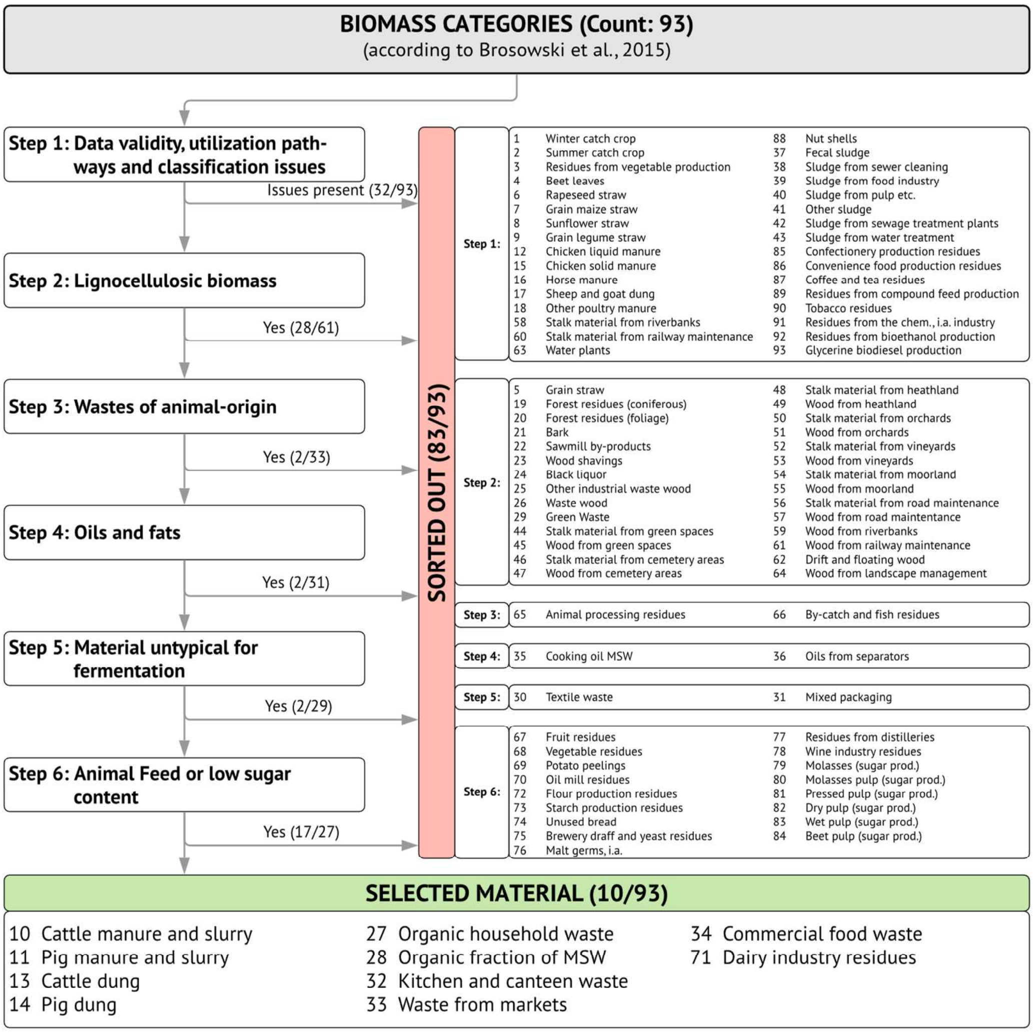

Figure 5. Decision tree to select suitable biomass categories for an exemplary biotechnological biohydrogen process.

In summary, the majority of waste types can be sorted out for this exemplary biotechnological biohydrogen production, as illustrated in Figure 5. Technical feedstock potentials with maximum and minimum values are available in Brosowski et al. [21] for the respective material flows. Since those estimations of potential are of different sources, going as far back as 2000, certain values can be updated where possible. For instance, technical figures of potential are in some cases directly related to official waste statistics, or new values for 2015 can be accessed in the online database of the DBFZ. In the next sections, the waste flows are developed into a technical bioenergy potential by making assumptions according to Sections 3.2 and 3.3.

3.2. Definition of Assumptions and Framework Conditions

This section briefly presents proposed assumptions required by certain steps in the process of developing energy potentials.

3.2.1. Substrate Pretreatment

To increase process efficiency and hydrogen output, it is necessary to prevent disruptions and clogging and ensure sufficient homogenization for stable process operation. Additionally, the pretreatment of substrate is essential in biochemical conversion processes [44] (p. 34). The considered pretreatment methods for this exemplary process are grinding, hygienization, and thermochemical hydrolysis. Homolactic fermentation and anaerobic storage are more of a recommended storage option, rather than a pretreatment measure in that sense. Filtration or other more elaborate pretreatments (e.g., fructose extraction) could be required. All of the mentioned processes are shortly described and reasoned in the following. After that, each type of waste is assigned a probably suitable pretreatment method or combination of methods to ensure ideal process operation. This allocation is carried out based on subjective estimations. Certain pretreatments are especially common in biogas processes but are assumed necessary or advantageous for biohydrogen production, especially for biotechnological process routes. The derived energy demands are related to tons of fresh mass (FM).

Grinding (G): Grinding is a common pretreatment of substrates in biogas processes for several reasons. It increases the surface area, which supports sufficient and fast microbial degradation. In addition, it reduces the risk of issues such as clogging, reduced pumping ability, and agitator stagnation [44] (p. 35). Water or liquids, such as dairy industry residues, can be added during grinding to transform the substrate into the right condition. For the energy demand of grinding, a shredder (P = 37 kW with a throughput of 15 t/h) was adduced as an example. This results in an electric energy demand of W_{el} = 2.46 kWh/t ≙ 8.9 MJ/t.

Hygienization (H): As the selected material flows can include smaller amounts of material from animal origin, e.g., municipal waste, hygienization could be necessary. If no material from category 1 or 2 (except animal feces, which are subject to exceptions) is assumed to be in the selected material, pasteurization at 70 °C for 60 min (Cat. 3: ground to <12 mm) is a sufficient treatment, according to Regulation (EC) No 1774/2002 Annex VI, Chapter II, C. In this work, pasteurization is considered sufficient to ensure hygienic input substrate. Besides that, pasteurization might trigger certain hydrolysis processes in the material and consequently increase process output. An advanced sterilization method would be pressure sterilization (133 °C, 3 bar for at least 20 min), which could be used if pasteurization does not achieve satisfactory bacterial reduction. The energy demand for pasteurization can be considered as follows:

- electric: W_{el} = 2.5 kWh/t ≙ 9 MJ/t (W_{el} = 2.1–2:3 kWh/m^3 [45] (p. 105); assumed substrate density 1000 kg/m^3);
- thermal: W_{th} = 12 kWh/t ≙ 43.2 MJ/t (W_{th} = 11.6–11.9 kWh/m^3 [45] (p. 105).

Thermochemical hydrolysis (TCH): Vavouraki, Angelis, and Kornaros showed that a lot of glucose can be mobilized in kitchen wastes through thermochemical hydrolysis (TCH) by relatively simple hydrochloric acid pretreatment. As all material needs to be hygienized, especially for biotechnological biohydrogen production, this process can be used for additional sugar mobilization. Tests showed that glucose content can be increased by almost 600% by treating kitchen wastes at 100 °C with 1.12% added hydrochloric acid for a period of 108 min [46] (p. 744). It is assumed that the thermal energy demand is higher by 50% than for hygienization while the electrical one remains equal. It should be noted that hydrolyzed material requires subsequent neutralization to not harm the culture. The energy demand for TCH can be considered as follows:

- electric: W_{el} = 2.5 kWh/t ≙ 9 MJ/t (W_{el} = 2.1–2.3 kWh/m^3 [45] (p. 105); assumed substrate density 1000 kg/m^3);
- thermal: W_{th} = 18 kWh/t ≙ 64.8 MJ/t.

The controlled anaerobic storage (AS) of animal excrements enables an initial hydrolysis process, in which VFAs are produced [47] (p. 160). In consequence, anaerobically stored slurry and manure present a significantly higher content of VFAs, which are considered utilizable for certain biohydrogen processes. The temperatures observed in [47] ranged between close to 0 and almost 25 °C, therefore no thermal energy input is assumed. The electrical energy input is neglected.

Enhanced homolactic fermentation (HLF) is another suitable pretreatment step for wastes from the dairy industry. In this step, lactic acid is produced, which is utilizable for some biohydrogen processes. Dairy products, especially whey, are suitable raw materials as they already contain lactic acid-producing bacteria and important nutrients such as lactose [48] (p. 2). As the process temperatures range between 5 and 45 °C, no energy input must be considered for this pretreatment. Further details, such as reactor type, retention times, or potential additives, are not further discussed in this work.

All pretreatment methods, including the respective energy demands, are listed in Table 2. In addition, a suitable pretreatment or a combination of pretreatments is assigned to each type of biomass, which can be seen in Table 3.

Table 2. Overview of energy demands for pretreatment methods.

Method		Energy Demand	
Symbol	**Name**	**W_{el} in MJ/t**	**W_{th} in MJ/t**
(G)	Grinding	8.9	0 *
(H)	Hygienization	9	43.2
(TCH)	Thermochemical hydrolysis	9	64.8
(AS)	Anaerobic storage	0 *	0 *
(HLF)	Homolactic fermentation	0 *	0 *

* No energy input allocated or negligible as described in Section 3.2.1.

Table 3. Overview of selected pretreatment for each type of waste.

Biomass Category	Pretreatment				
	(G)	**(H)**	**(TCH)**	**(AS)**	**(HLF)**
Cattle manure and slurry		x		x	
Pig manure and slurry		x		x	
Cattle dung	x	x		x	
Pig dung	x	x		x	
Organic household waste	x		x		
Kitchen and canteen waste	x		x		
Waste from markets	x		x		
Dairy industry residues		x			x
Organic fraction of MSW	x		x		
Commercial food waste	x		x		

3.2.2. Process Energy Demand

As the process requires similar technical equipment and reactor design compared to a biogas process (e.g., agitators, pumps), the overall process energy demand for biotechnological biohydrogen processes can be estimated by average figures for biogas production from the Agency for Renewable Resources (orig. Fachagentur Nachwachsende Rohstoffe e. V., FNR). Energy-demanding features for biohydrogen-specific subprocesses have to be estimated separately or can be neglected in some cases. The FNR publishes key figures from several sources and its own calculations on its webpage, where the estimated figures represent percentages of the plant´s total energy output. Pasteurization and thermochemical hydrolysis already preheat the material, therefore the actual thermal energy demand (heating) of the bioreactors can be neglected in this case. Preheated substrate from pasteurization is assumed to maintain process temperatures between 25 and 30 °C. The process energy demand is estimated to be 7.6% electric (f_{el}) [49] and, due to the aforementioned reasons, 0% instead of 28% thermal (f_{th}) of the overall energy generation capacity.

3.2.3. Logistics, Substrate Storage, and Handling of Residues

A comprehensive assessment of technical energy potentials is a multi-faceted challenge, which also requires examination of the material throughout its life cycle. For biohydrogen processes, real sustainability also includes avoiding long transport routes, efficient use of existing infrastructure, and material sources, among other aspects. This paper does not cover such aspects, due to their complex nature, regional variation, and the lack of traceability for waste materials on a large-scale basis. Such elaborate factors are found to be difficult to generalize due to the wide variety of possible hydrogen production options, and hence are to be assessed on a case-by-case basis. In the scope of this work, the process impact is evaluated from material pretreatment until hydrogen generation. The residues of the process can contain additional potential, which could further enhance the efficiency of the overall utilization. In any case, the material needs to be disposed of or treated by other means consecutively.

3.2.4. Produce Gas Separation

Depending on the biohydrogen production process, the initial produce or synthesis gas may be composed of various compounds. For biotechnological biohydrogen production, occurring produce gas compounds include CO_2 and H_2 and may contain N_2, water vapor, or trace compounds such as NH_3, CO, and H_2S, for instance [50,51]. As fuel cell technology demands high hydrogen purities (99.99%), effective separation is a key process in biohydrogen production [51] (p. 1277). Common separation systems include scrubbing, pressure swing adsorption, and cryogenic separation, all of which are energy intensive, and membrane technologies show great potential, but many are still in development [31,51]. Membrane technologies allow for simple separation at lower energy requirements, hence further development of these technologies is essential for biohydrogen production as a whole. The detailed consideration of energy inputs during this part of a production process is not part of this work. Nevertheless, this process step and its related energy inputs demand consideration in bioenergy potential estimations and should be included in future research and case studies.

3.3. Calculation of Energy Potential

In this step, the obtained feedstock potential and producible hydrogen can be converted into fuel and bioenergy potentials, respectively. With an established amount of moles H_2 (n_{H_2}), the annual mass of hydrogen gas output (m_{H_2}) can be calculated. The total energy content of an energy carrier is described either by the higher heating value (*HHV*) or the lower heating value (*LHV*), with combustion being the underlying process. The difference between *HHV* and *LHV* is that *HHV* assumes the produced water to be in a liquid state. Combustions usually include fuel of organic origin or, in this case, hydrogen, which reacts with oxygen. The reaction products are CO_2 and H_2O for carbon-containing sources and H_2O for hydrogen. In practice, the heat generation causes water to evaporate, hence the *HHV* can only be achieved if the flue gas energy is also fully harnessed, which is not always possible [48] (p. 23). As a result, the *LHV* is used to determine the utilizable energy content in this work. For hydrogen gas, the *LHV* is 120 MJ per kg [36] (p. 239). The resulting fuel potential (*FP*) can be calculated according to Equation (1).

$$FP = m_{H_2} \cdot LHV_{H_2} \tag{1}$$

The overall energy conversion efficiency of modern fuel cells can be as high as 90%, with 45–60% electrical. Hydrogen-only operation of such cells, which currently mostly use natural gas as fuel, can bring several benefits and even higher efficiencies [52] (pp.

374, 377). This work considers an overall conversion efficiency of 90% total (η_{tot}) and 50% electrical efficiency. In addition, the energy demands for substrate pretreatment (W_{PT}) and process operation (W_{PO}), which reduce the overall energy output, are considered in this final step. The respective energy amount of pretreatment is calculated by summing up the electric and thermal energy consumption for each method, see Equation (2). To include the process energy demand, the bioenergy potential can be reduced by the factors of Section 3.2.2 (f_{el} and f_{th}). The resulting bioenergy potential (*BEP*) is the final, utilizable amount of energy after conversion [19] (p. 41), reduced by the amount of energy consumed by pretreatment and process operation, and is calculated according to Equation (3). Additional energy inputs from logistics, storage, residue treatment, or gas separation can be included here for more detailed case studies.

$$W_{PT} = W_G + W_H + W_{TCH} + W_{AS} + W_{HLF} \quad (2)$$

$$BEP = FP \cdot \eta_{tot} \cdot (1 - \text{fel} - \text{fth}) - W_{PT} \quad (3)$$

3.4. Negative Emission Potential Estimation

In the last step, the environmental impact of the biohydrogen process is estimated. Aspects such as the achievable substitution of other energy carriers and the resulting emission reduction, as well as the extent of the possible negative carbon footprint by adding CCS to the process leading to HyBECCS approaches, are to be considered in this assessment step. It should be mentioned that HyBECCS projects can have multiple impacts on the environment, such as acidification and eutrophication or the depletion of the ozone layer and abiotic resources [53]. Even though all environmental impacts are equally important, they are not included in the following estimation, as it is limited to considerations on climate mitigation.

First, the carbon-neutral energy output of the biohydrogen process can be expressed by an equivalent mass of other energy carriers, which could be substituted ($m_{subs,x}$). This step can be realized by dividing the bioenergy potential (*BEP*) by the *LHV* of other energy carriers (LHV_x), see Equation (4). At the same time, the saved amount of CO_2 emissions ($m_{CO_2,x}$) can be calculated by dividing the energy output of the biohydrogen process by respective CO_2 emission factors from other energy carriers (ef_x), see Equation (5).

$$m_{subs,x} = \frac{BEP}{LHV_x} \quad (4)$$

$$m_{CO_2,x} = \frac{BEP}{ef_x} \quad (5)$$

The considered fossil energy carriers to be substituted are natural gas, coke, hard coal, and heavy fuel oil and hydrogen from natural gas steam reforming and water electrolysis powered by the German electricity mix. Further, green hydrogen from renewable electrical power can be considered. The fossil energy sources were chosen for comparison, as they are currently used in potential future application fields for hydrogen (e.g., steel industry, (heavy-duty) traffic, heat generation). The alternative hydrogen generation options highlight the direct benefits of biohydrogen (with and without CCS) as compared to other energy sources. Reference values for LHV_x and ef_x can be seen in Table 4.

Table 4. Reference values for various energy carriers.

Energy Carrier	LHV_x in MJ/kg	ef_x in t_{CO_2}/TJ	References
Natural gas (NG)	47.4 [3]	56	[54] (p. 138)
Coke (C)	27.6	105	[54] (p. 138)
Hard coal (HC)	28.3	93	[54] (p. 138)
Heavy fuel oil (HFO)	39.5	81	[54] (p. 138)
H_2 steam reforming (SR) [1]	120	67	[36] (p. 239) [55] (Table 1)
H_2 electrolysis electricity mix (EM) [2]	120	83	
H_2 electrolysis renewables (REN) [2]	120	0	

[1] η = 84%; 1190 GJ_{NG}/GJ_{H_2}; [2] η = 70%; 1428 GJ_{el}/GJ_{H_2}, EM 2018 has 30% lower emission factor compared to 2012 [56]. Hence, the value from [57] (Table 1) is reduced by the same percentage. [3] LHV_{NG} = 36.0 MJ/Nm^3 and assumed density ρ_{NG} = 0.76 kg/Nm^3 (Nm^3 = norm cubic meter).

HyBECCS was introduced in Section 2.2. as an innovative way to produce carbon-negative hydrogen and is considered as an evaluation step in this work. The methodical conduct to obtain a theoretically storable amount of CO_2 through HyBECCS is defined as follows: The mass of the product gas mixture (m_{gas}) in the respective biohydrogen process and its CO_2 content (x_{CO_2}) must be known or estimated. It should be noted that the real CO_2 production rate often is a matter of uncertainty and depends largely on the composition of the input substrate. Real data are therefore to be preferred for the specific process. The resulting amount of CO_2 produced during the biohydrogen process can be calculated according to Equation (6). This can be seen as the theoretical amount of storable biogenic carbon dioxide leading to the same value of theoretically achievable negative emission potential (NEP) in $CO_{2,eq}$ through the specific HyBECCS approach.

$$NEP = x_{CO_2} \cdot m_{gas} \tag{6}$$

4. Discussion

This section discusses the conducted work. First, the considered material flows are briefly touched upon. Next, limiting factors and assumptions are taken up and evaluated in light of associated uncertainties, restrictions, and alternative points of view.

Initially, a range of biomasses applicable to the process can be determined using the methodological approach presented. The decision to exclude by-products and biomass, which can be used as material resources, is a very important first restriction. Utilizing industrial residues, for instance, which are commonly used as animal feed, could create shortages in the supply for animal feed production. Consequently, this shortage would have to be filled by other resources. In terms of sustainable impact, those resources could possibly be of higher value, such as maize or soy, resulting in a shortage for human consumption so that in the further course these resources would have to be imported from other countries. This is just one example of emerging competition for usage, especially of relevance with industrial residues. In fact, the efficient use of by-products saves a lot of resources and energy as they fulfill demand, which otherwise would have to be satisfied elsewhere, potentially in a more energy-intensive manner. For those reasons, the material considered in this work is chosen to not present competition in material usage. Theoretically, industrial residues, animal-processing wastes, or oils and fats, amongst others, could still be used in biohydrogen production processes. However, the consideration of such material would have to be conducted in greater detail for specific regions or industries, as several sources indicate that nationwide data for industry by-products and other smaller biomass fractions are not available or based on vague assumptions. Hence, the respective data embody broad spreads and limited reliability [20] (p. 17), [22] (p. 103), [42] (p. 108).

An initial and expected finding based on the methodological approach shown in this paper is that pretreatment—especially hygienization—has an extensive impact on the bioenergy potential. The additional step of including other means of treatment, though not being necessary in the same sense as hygienization, can be reasoned by the expected increased degree of mobilization and the resulting enhanced process outputs. Altogether, the reliability of the obtained energy values and substrate properties can be considered as high, as they are taken from scientific papers. Associated risk factors are, on the one hand, the requirement of pressure sterilization in case of insufficient sterilization performance of pasteurization. On the other hand, the necessity to extract utilizable substances from the substrate could be required. Both of these factors could significantly increase pretreatment energy demand. Next, the process energy demand is an essential factor as well. The uncertainties concerning the process energy demand are associated with inaccuracies. Additional energy demand might result from further heat demand for process operation, for instance. Overall, a conservative approach has to be chosen to evaluate the processes.

The derivation of environmental impacts can provide an initial basis for decisions on the sustainability of the processes. Other relevant aspects, however, are substrate logistics and storage, as well as the handling of process residues, which have not been considered in the methodological approach presented. These topics were beyond the scope of this work but might pose certain risks or chances. For example, lengthy substrate transportation or improper storage could decrease the overall net potential of the biohydrogen processes, depending on the hauling distance or the loss of utilizable substances during storage. On the contrary, process residues might contain substances to be metabolized in further energetic treatment or biomass with high-value components. As a result, extraction of such high-value components, further energy generation from the substrate, or just compost producible from it could improve the economic and ecological value of the process.

The methodological approach shows weaknesses regarding process-specific developments. Some of those factors affecting the amount of available waste materials could be increased awareness of food waste, changing consumption habits, and the population trend. Regulatory measures, policy goals, and environmental concerns have been considered to some extent, but not in greater detail. It is considered acceptable to assume a status quo situation for these factors in the short term but has to be adjusted for the evaluation of long-term potentials. This work provides a starting point for evaluating bioenergy and climate mitigation potentials by providing a quickly implementable guide for estimating the bioenergy potential for hydrogen production from biomass and its potential greenhouse gas savings in Germany. However, many technology-specific factors that influence these potentials remain unconsidered. In addition to substrate suitability and conditions like wetness and hydrogen yield, these include, for example, technology maturity, energy efficiency, conversion rates, and plant complexity, in order to obtain a conclusive picture for the assessment. In addition, other environmental impact categories according to DIN EN ISO 14040/44, besides global warming potential, such as acidification and eutrophication potential or photochemical oxidant formation, as well as ozone layer and abiotic depletion, should be considered within holistic assessments.

5. Summary and Prospect

It is common ground that the future energy market requires efficient carbon-neutral or negative solutions in green energy production. Biohydrogen production technologies are expected to be capable of producing large amounts of hydrogen from organic biomass in the near future. Further, co-produced biogenic carbon dioxide can be stored or put to long-term use by applying hydrogen bioenergy with carbon capture and storage (HyBECCS) approaches to generate greenhouse gas sinks. This work aims to provide a guideline for deriving the bioenergy potential of organic waste material and the connected ecological impacts of biohydrogen and HyBECCS processes in Germany.

A four-step methodical conduct, including material selection, assumptions, calculation of energy potential, and environmental impact evaluation, is elaborated to achieve the desired outcome. First, biomass categories are evaluated regarding their applicability to an exemplary biohydrogen process. Therefore, a six-step selection process to exclude material is conducted, resulting in specific biomass categories found to be utilizable and fulfilling the criteria of waste material. Second, a number of assumptions regarding the pretreatment of the substrate and the required process energy demand are made to include the energy input required by the process. Third, the derivation of energy potentials is conducted following common practice and adhering to certain criteria for comparability and transparency. Lastly, the substitutable amount of (fossil) energy carriers and related emission savings, on the one hand, and the negative emissions by applying HyBECCS approaches, on the other hand, are evaluated to obtain a statement about the environmental benefits. The scientific contribution of this article was to develop a methodological approach for a bioenergy potential and a negative emission potential analysis illustrated using a fictitious fermentative hydrogen production process, rather than research based on experimental studies.

In conclusion, rising demand and a functioning hydrogen market are not only expected in Germany, but throughout Europe, which is key to triggering scaling effects and research progress for biohydrogen processes and HyBECCS approaches [2] (p. 5). Therefore, the use of hydrogen as an energy source in the transport sector and decisive industries (steel, cement, and chemical) is desired. These industries play a key role in the development of a German hydrogen market. In addition, the often decentralized produced hydrogen needs to be distributed all over the continent, demanding a modern network of storage and pipelines, suitable for safe H_2 transport. Safety concerns and the applicability of existing infrastructure are to be evaluated and resolved on the part of the German government. Lastly, research on and development of hydrogen production, storage, distribution, and utilization are still in their early stages. This means that technologies are often not advanced enough for market rollout. More applied research and development are needed on biohydrogen processes and HyBECCS approaches as they can contribute to climate mitigation targets to a large extent [5]. Additionally, the new technologies need to be fully analyzable and evaluable during the innovation and upscaling processes in order to be successful on the market and prove their ecological potential. Therefore, the ecological and economic potential including all life cycle costs and emissions should be further investigated and a common framework be created, since the competitive performance is the main short-term indicator of success for biohydrogen processes in Germany. Additionally, the processes need to be compared to the competitive utilization technologies for various biomass flows in order to see whether biohydrogen production can be a better option in terms of energy output, carbon emissions, and life cycle impact. In addition, other impact categories besides global warming potential, such as acidification and eutrophication potential or photochemical oxidant formation, as well as ozone layer and abiotic depletion, should be considered using the LCA method according to DIN EN ISO 14040/44. This work, however, provides a starting point for investigating bioenergy and climate mitigation potentials.

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Appendix E: Paper E

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Carbon-negative hydrogen production (HyBECCS): An exemplary techno-economic and environmental assessment

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HIGHLIGHTS

- A techno-economic and ecological assessment for an exemplary HyBECCS approach is conducted.
- Effects resulting from the greenhouse gas (GHG) balance are considered in the assessment.
- Compared to other negative emission technologies, the approach shows high GHG removal efficiency.
- Compared to other hydrogen production processes, it shows environmental-economic advantages.

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ABSTRACT

An exemplary techno-economic and environmental assessment of carbon-negative hydrogen (H_2) production is carried out in this work. It is based on the so-called “dark photosynthesis” with carbon dioxide (CO_2) capture and geological storage. As a special feature of the assessment, the economic consequences due to the impact on the global climate are taken into account. The results indicate that the example project would be capable of generating negative GHG emissions under the assumptions made. The amount is estimated to be 17.72 $kgCO_2$ to be removed from the atmosphere per kilogram of H_2 produced. The levelized costs of carbon-negative hydrogen are obtained, considering the economic impact of greenhouse gas emissions and removals. They are estimated to be 0.013 $EUR/kWhH_2$. Compared to grey hydrogen from natural gas (0.12 $EUR/kWhH_2$) and green hydrogen from electrolysis using renewable electricity (0.18 $EUR/kWhH_2$), this shows a potential environmental-economic advantage of the considered example. Even without internalization of GHG impacts, an economic advantage of the project (0.12 $EUR/kWhH_2$) over green hydrogen (0.17 $EUR/kWhH_2$) is indicated. Compared to other NETs, the GHG removal efficiency is at the lower end of both BECCS and DACCS approaches.

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1. Introduction

To limit global warming below 2 °C, a combination of two climate change mitigation measures is required. First, a fast and deep reduction of anthropogenic greenhouse gas (GHG) emissions is essential. Within GHG reduction, substituting fossil fuels with sustainably produced bioenergy can play an important role. For 2050, bioenergy with a total of 465 TWh per year is predicted to contribute with 23% to the total energy demand of the Federal Republic of Germany [1]. Thereof, 279 TWh can be obtained from biogenic residual and waste materials [1]. Second, in addition to GHG reductions, a fast deployment of negative emission technologies (NETs) is required to enable removal of carbon dioxide (CO_2) from the atmosphere [2,3]. The permanent storage or long-term use of biogenic carbon dioxide in so-called BECCS (Bioenergy with Carbon Capture and Storage) approaches can lead to a reduction of greenhouse gas concentration in the atmosphere [4,5]. This permanent net removal is labeled negative emissions [6]. BECCS can play a major role in the area of NETs. Therefore, carbon dioxide captured during the process must be of biogenic and renewable origin, i.e. derived from fast-growing renewable biomass, biogenic waste or residues [7,8]. In Europe, the potential for negative emissions through BECCS is estimated to be 200 $MtCO_2$ per year [9]. In Germany, the potential for negative emissions through BECCS is estimated to be about 62 $MtCO_2$ per year [10]. The Federal Climate Change Act stipulates that GHG emissions in Germany must be reduced by 88% compared to 1990 until 2040 and GHG neutrality must be achieved in 2045. This means that from 2040 to 2045, approximately 130 $MtCO_2eq$ of remaining GHG emissions would need to be reduced or offset annually [11]. With a potential of approx. 62 $MtCO_2$ per year, BECCS could contribute almost the half of this amount through the generation of negative emissions [10].

HyBECCS (Hydrogen Bioenergy with Carbon Capture and Storage) is a BECCS approach based on the production of biogenic hydrogen or biohydrogen. The concept combines biohydrogen production from biomass with capture and storage of carbon dioxide, aiming to produce carbon-negative hydrogen (CNH) [12]. An important basis for the HyBECCS approach is the generation of biogenic carbon dioxide as a by-product in most biohydrogen processes. Each HyBECCS implementation project (short: HyBECCS project) consists of four modular basic process steps: 1. biomass selection and pretreatment, 2. biohydrogen production, 3. gas processing, and 4. H_2 utilization and CO_2 storage [13]. The selection of biomass for the process has a major impact on the economic efficiency and environmental impact of the processes. It is advisable to use residual and waste materials [12]. Different technology options can be applied for the four basic process steps. The variety of technology options contributes to the capability of using a wide range of residual and waste materials. A general technological advantage of HyBECCS over other NETs is e.g. the energy-efficient capture of carbon dioxide at a point source compared to Direct Air Capture (DAC) approaches [13]. In addition, the relative carbon dioxide removal potential of HyBECCS is higher compared to other BECCS technologies that produce hydrocarbon-based energy carriers. For example, in biogas or biomethane production with carbon capture and storage (CCS), a stoichiometric fraction of the carbon from the biomass remains in the methane (CH_4) energy carrier. This carbon is usually distributed decentrally in the energy system (e.g., as fuels for transport applications or for building heating) and emitted as carbon dioxide during the biogas or biomethane combustion [13]. In HyBECCS projects, the carbon-free energy carrier biohydrogen is produced and carbon dioxide is already emitted centrally as a point source at the plant, where it is captured energy efficiently and stored. Generally, HyBECCS projects can be designed from the ground up or existing plants, e.g. biogas plants, can be upgraded to HyBECCS plants [14]. The HyBECCS production process with a negative carbon footprint and the ability to substitute fossil energy carriers with biohydrogen result in contributing to both necessary climate change mitigation measures: the reduction of GHG emissions and carbon dioxide removal.

For HyBECCS technologies, techno-economic assessment fundamentals and guidelines have been elaborated by Full et al. (2022) [15]. The abstractions, standardizations, uniform system boundaries and key performance indicators (KPIs) can serve as an important basis for their comparison with other hydrogen production technologies or NETs. In addition to classical techno-economic evaluation approaches, the economic consequences due to the impact on the global climate are taken into account. In this paper, a techno-economic and environmental analysis of an exemplary HyBECCS project is carried out according to these guidelines. The objective of the work is to validate the suitability of the methodology and KPIs developed in Ref. [15].

2. Description of the evaluated example project

The example project assessed in this work is based on the production of biohydrogen via so-called "dark photosynthesis" process. This specific biohydrogen production process has been established by Ghosh and Autenrieth at the University of Stuttgart, Germany [16] and is introduced briefly in the following. The "dark photosynthesis" is a biotechnological process that is based on the purple bacterium *Rhodospirillum rubrum* (*R. rubrum*) to produce biohydrogen from different biomass sources containing fructose or lactate. For example, waste residues from the milk or fruit processing industry can be used. For the evaluation in this paper, fruit waste and residues are assumed as a substrate for the biological process. The material selection meets the criteria for appropriate residual and waste streams as it can be assigned to the category of "commercial food waste" according to Ref. [12]. The uniqueness of the process stems from the ability of the bacteria to induce - in the absence of light - the "photosynthetic" growth regime, during which all components of the photosynthetic membranes (i.e. the photosynthetic units consisting of protein subunits, bacteriochlorophylls and carotenoids), as well as components for electron transfer (i.e. quinones, ferredoxins), and the enzymes for biohydrogen production, are expressed at photosynthetic levels [17]. The "light"-signal during microaerophilic growth in the dark in M2SF medium is the establishment of a negative redox state of the quinone pool in the membranes as a result of the breakdown of fructose via the Embden-Meyerhof-Parnas pathway [18,19]. The independency from light facilitates an easier scale-up to industrial size using basic steel fermentation technology instead of photo-bioreactors. Fig. 1 represents a simplified overview of the "dark photosynthesis" process. The gaseous products of this process are biohydrogen and biogenic carbon dioxide, which constitutes a prerequisite for being extended to a HyBECCS project by capturing and storing the carbon dioxide [13,20].

For carbon storage (CS), the approach of geological underground storage in saline formations is selected for the example project under evaluation. This appears a suitable choice, as the amount of carbon dioxide that is injected into saline formations can be measured, and the storage can be considered permanent. Risks like short storage periods before releasing the carbon dioxide back into the atmosphere, reversals, insecurity concerning the time horizon of storage, and challenges such as monitoring the permanence due to the dispersed places of use, as they are often associated with carbon utilization (CU) approaches, can be kept as low as possible with the selected process [21]. Saline formations that are CS-suitable are porous and permeable salt water-filled rock formations that are sealed by a clay-rich cap rock. Together, the saline formations and the cap rock form an upward closed structure that keeps the carbon dioxide safely in place. Thus preventing it from reentering the atmosphere. Storage periods of over 1000 years are possible and the actual amount of stored carbon dioxide can be monitored by continuous pressure and regular seismic measurements [22]. Several commercial and demonstration plants are already operating successfully and technological maturity is given [23–26].

Fig. 2 illustrates the overall process chain of the HyBECCS example project evaluated within the scope of this work. The production system is divided into the system elements "HyBECC" (Hydrogen Bioenergy with Carbon Capture) with the associated subsystem boundary B1, and "CS" (Carbon Storage) with the associated subsystem boundary B2, according to Ref. [15]. HyBECC includes the production of biohydrogen and the capturing of biogenic carbon dioxide from biomass through "dark photosynthesis". CS includes the transport of carbon dioxide and its geological storage. The cultivation, harvesting, transportation, and processing of fruits are not considered within system boundary B3 as they are part of fruit juice production. Within the system element HyBECC, fruit waste or residues must be grinded and hygienized before being used as a substrate for "dark photosynthesis". The inoculum (*R. rubrum*) and processed substrate are then fed into the bioreactor where biohydrogen and biogenic carbon dioxide are produced under micro-aerobic conditions. After that, the product gas is separated and the relevant product fractions (H_2, CO_2) are purified and compressed by a gas

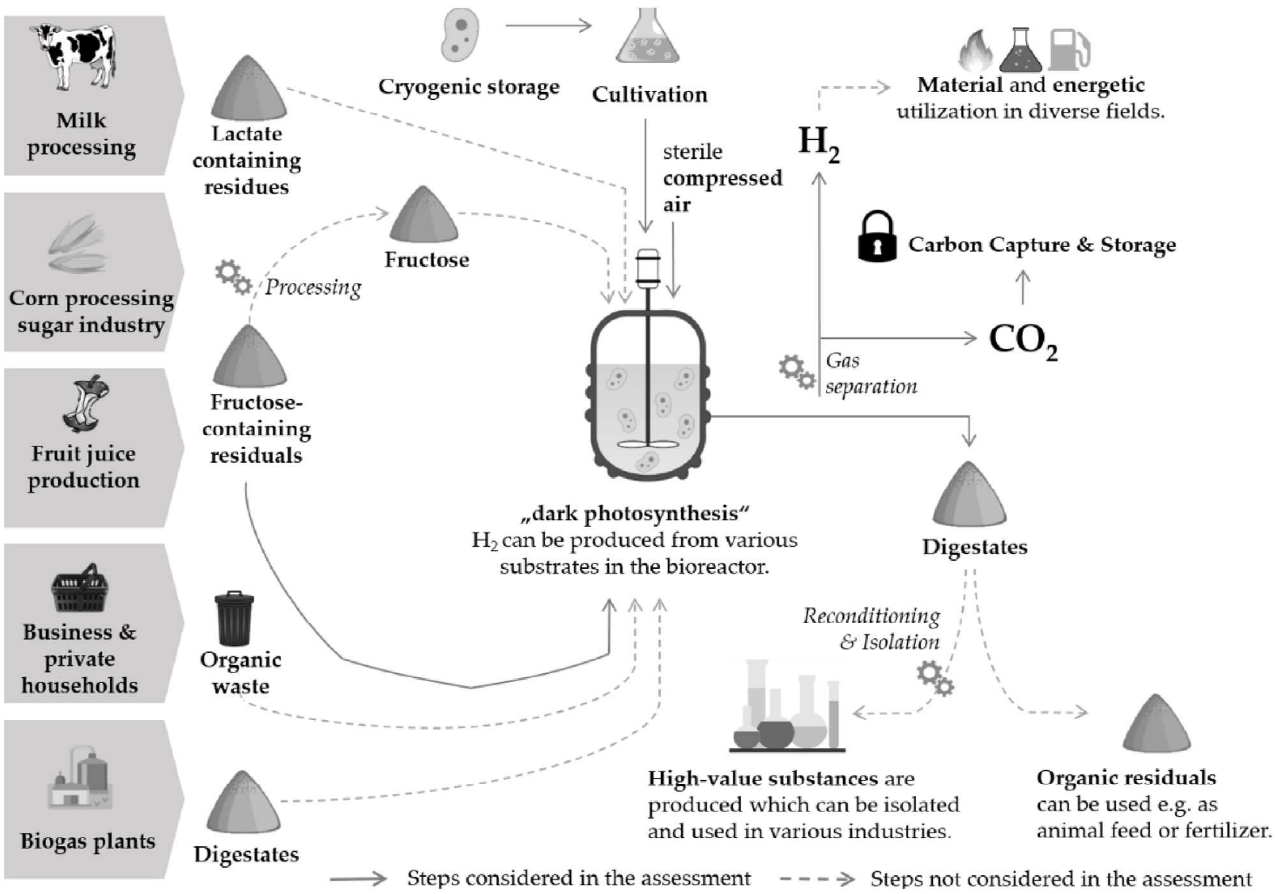

Fig. 1 – General overview of the "dark photosynthesis" process (own representation).

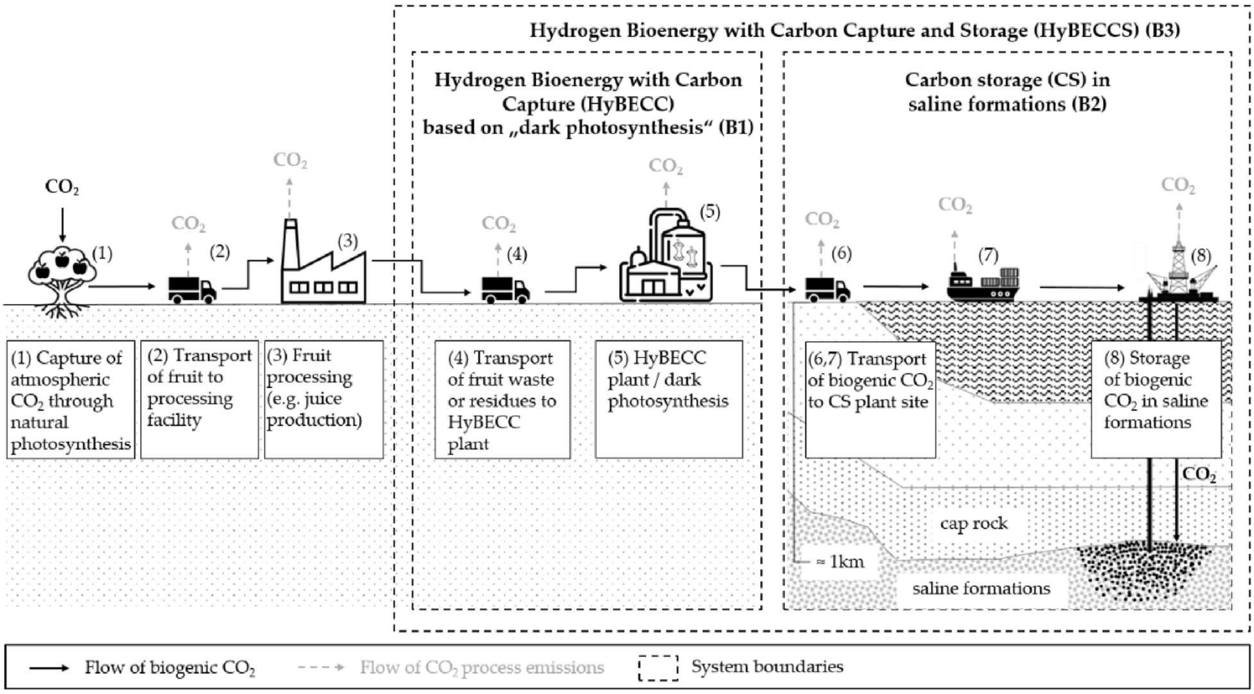

Fig. 2 – Illustration of the exemplary HyBECCS project, divided into the subsystem boundaries B1 (system element HyBECC), B2 (system element CS), and overall system boundary B3. Illustration of CS process based on [22].

processing system. Digestates are processed and separated into liquid and solid components. They can be used as further valuable goods such as fertilizers, which however, is not part of the present assessment. The biogenic carbon dioxide is transported over an assumed average distance of 1500 km to the CS plant, first via trucks to the North Sea 500 km and then by ship another 1000 km to the CS plant site. There, it is injected into saline formations located about 1 km below sea level [22].

3. Assumptions and framework conditions

The example project considered in this paper is a compilation of sub-processes, each of which has been implemented at different locations and different scales, combining to a fictitious HyBECCS project. All assumptions regarding these sub-processes are explained in the following and are summarized in Appendix A, Table A1. Fig. 3 illustrates the plant diagram of biohydrogen and biogenic carbon dioxide production (HyBECC facility) from fruit waste or residues based on the described “dark photosynthesis” process in section 2.

It is assumed to be located close to the fruit processing facility generating the waste or residue used as substrate. Therefore, no costs and GHG emissions are assumed to occur for transporting the substrate to the HyBECC facility. The gross and net working volumes of the bioreactor are assumed to be 7200 m^3 and 6000 m^3, respectively. The net working volume refers to the maximum filling volume of the bioreactor with the substrate. An additional volume of about 20% is considered for the product gas above the substrate, summing up to the gross working volume. The net working volume is filled 80% with substrate and 20% with process water. Based on averages for biogas plants in Germany, annual full load hours for “dark photosynthesis” are assumed to be 8000 h/a, resulting in an annual plant availability of 91% [27]. Also, based on average biogas plants in Germany, the lifetime of the HyBECC facility, showing similar plant configurations as biogas plants, is conservatively assumed to be 20 years [27,28]. Based on unpublished data from experiments, the gross biohydrogen yield and the gross amount of biogenic carbon dioxide are assumed to be approximately 896 and 19,521 tons per year, respectively. These assumptions are based on the usage of waste or residues from fruit juice production with a fructose content of 6% as feedstock and considering the plant availability of 91%. It results in a plant capacity of approximately 3409 kW_{el}.

The gas processing system to separate, purify and compress the product gas includes a low-pressure gas tank, a carbon dioxide compressor, an activated carbon filter, an absorbing type desiccator, a compression refrigerator, and a storage tank. Since “dark photosynthesis” and dark fermentation processes are similar in terms of the produced product gas, it is assumed that the gross biohydrogen yield is reduced by 8% due to losses in the gas processing system [29]. The product gas reaches a purity level of 99% hydrogen, as the practice of dark fermentation processes shows [29,30]. It is assumed to be compressed to 700 bar. Further losses or leakages for hydrogen are not taken into account.

The amount of biogenic carbon dioxide produced within system boundary B1 represents the theoretical maximum potential for the generation of negative emissions, also referred to as negative emission potential (NEP) [12]. Losses and leakages are considered throughout the process chain. During the carbon dioxide capture process using pressure swing adsorption, 10% of losses are assumed due to a limited

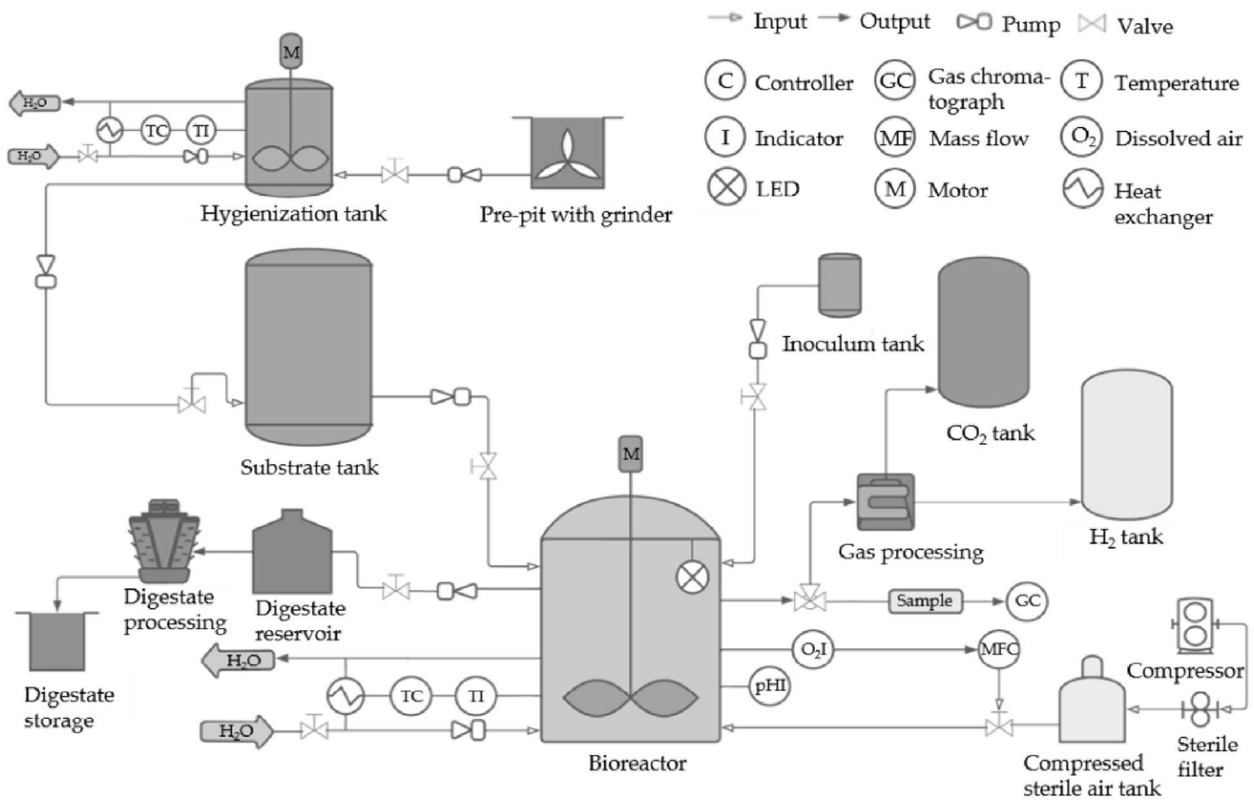

Fig. 3 – Plant diagram of the HyBECC system element (own representation).

capture rate of 90% [31,32]. Transportation by truck and ship is assumed to cause boil-off losses of carbon dioxide from the storage vessel into the atmosphere within a range of 3–4% per 1000 km [22]. Estimated conservatively, this accounts for another 6% of leakage over the assumed distance of 1500 km from the HyBECC facility to the CS plant site. Summing up, a total deduction of 15.4% and is assumed. Thus a NEP of about 16,515 tons of carbon dioxide per year can be assumed.

As no project-specific data on the purchase price for fruit waste or residues and the disposal of its digestates is available, it is assumed that the costs associated with the disposal of digestates are equal to the profit realized from the acceptance of fruit waste or residues, or vice versa. The bulk density of the substrate is assumed to be 0.35 t/m^3 [33]. Based on the reactor volume, plant availability, and feedstock bulk density, 186,667 tons of waste or residues are assumed to be processed annually. The power demand of the HyBECC plant is set to account for 7.25% of the total amount of generated electricity, based on typical values for biogas plants [27]. This covers the electricity needed, including substrate pre-treatment (grinding, pumping, measurement, and control technology) and product gas processing. Electricity is received from the German grid at an average price for the industry of 0.176 EUR/kWh$_{el}$ [34]. Heat is used for substrate hygienization. Its demand is estimated based on the amount of substrate and process water. Heating costs are assumed to be 0.09 EUR/kWh$_{th}$ [35]. District heating supply temperatures are sufficient to heat up the fruit waste or residues to the needed temperature level of approx. 70 °C [36]. Recovering heat from the fruit processing plant lowers the annual heat consumption, assuming that the substrate can be preheated to 50 °C using waste heat. The amount of bacteria used as inoculum as well as the respective purchase and transport costs are neglected, since cultivation of the inoculum is carried out at the HyBECC facility by its operators.

Based on commercial CS plants, the CS plant lifetime of the example project is assumed to be 40 years, in which carbon dioxide can be injected consistently [26]. Capital expenditures of 11.33 EUR/tCO_2stored and operational expenditures of 14.90 EUR/tCO_2stored are assumed for the transport of biogenic carbon dioxide from the HyBECC facility to the CS plant site, its storage and monitoring [26, 28 + 34]. Market prices for hydrogen of 9.50 EUR/kgH_2 and for biogenic carbon dioxide of 19.30 EUR/tCO_2 are assumed [37,38]. Prices for negative emissions and GHG internalization are set at 195 EUR/tCO_2eq [39].

4. Methodology

The methodological approach for techno-economic and environmental assessment applied in this study can be subdivided into eight basic steps, as summarized in Fig. 4 and briefly explained in the following.

First, the theoretical ability for carbon dioxide removal and the permanence of carbon dioxide storage is checked. This is obtained according to the guidelines for eligibility check on technology level as described by Full et al. (2022) [15]. Second, GHG emission flows are calculated following ISO 14040/44 [40,41]. It focuses on the impact category of global warming potential over 100 years (GWP$_{100}$) and thus aims at quantifying

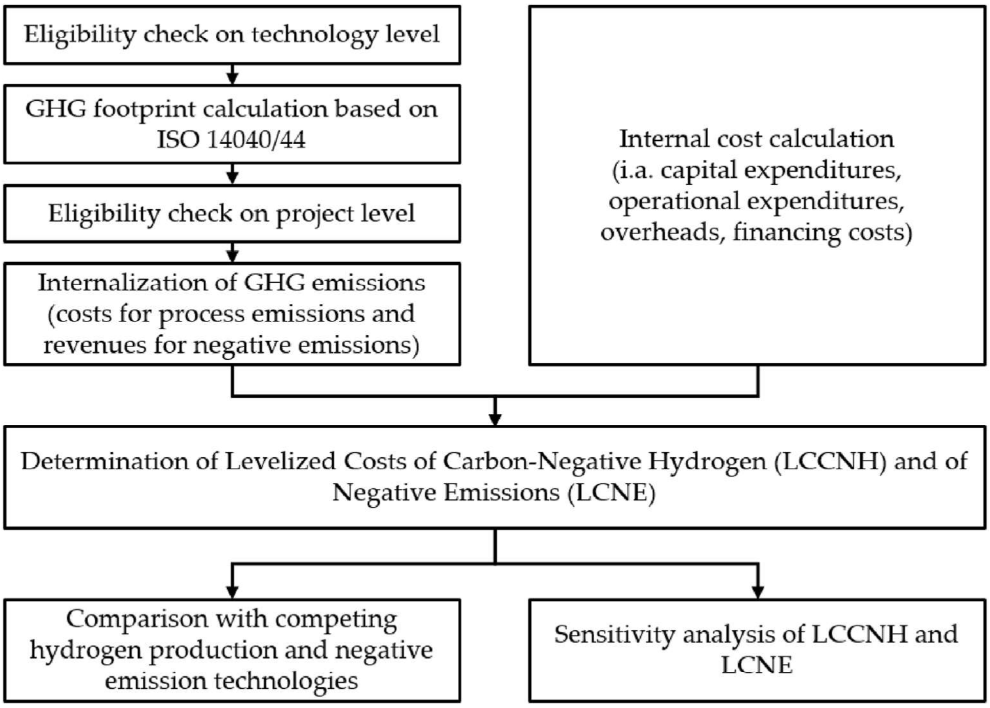

Fig. 4 – Schematic overview of the methodology of the work based on [15].

the GHG footprint of the example project and its subsystems. A "cradle-to-grave" system boundary is applied. The functional unit is chosen depending on the product under consideration. It is defined as one ton of CO_2eq permanently (>1000a) removed or one kWh (net calorific value) of generated biohydrogen. Carbon removal certificates (CRC) are assumed to be paid for negative emissions, thus for the net-amount of carbon dioxide permanently removed from the atmosphere. Here, further risk deductions for long-term carbon storage leakages of 1% are considered [22]. The emissions for the construction of the infrastructure required are drawn from the ecoinvent database for the construction of a factory for synthetic gas with facilities for gas production and processing. The dataset includes materials for construction and operation of the building machines, as well as waste materials, such as waste concrete and reinforced steel. The output capacity of this factory of 5 MW is scaled down to the output capacity of the biohydrogen production plant of 3.409 MW by factor 1.47 and referenced from the factory lifetime of 50 years to the evaluations' scope of one year. The substrates assumed to be used in the HyBECC facility are waste or residue streams from fruit processing, i.e., a waste stream from the upstream product system of fruit juice production. Therefore, they enter the system without a CO_2eq burden [28,41]. If the amount of permanently stored biogenic carbon dioxide is higher than the GHG emissions caused by the example project, the eligibility on the project level is confirmed [15]. Costs for GHG process emissions and revenues for negative emissions are estimated based on the GHG balance applying the simplified basic model for regulatory systems in net-zero emission economies [15]. External costs and benefits on the climate are assumed to be entirely internalized.

Factorial cost estimation is applied for the calculation of capital expenditures (CapEx). Operational expenditures (OpEx) are calculated based on plant dimensions, experimental data, experience values from biogas plants in Germany and surcharge factors [27,29]. Both internal and internalized costs and revenues are included in the calculation of three central key performance indicators (KPIs): the levelized costs of carbon negative hydrogen (LCCNH), the levelized costs of stored carbon dioxide (LCSC) and the levelized costs of negative emissions (LCNE). Those KPIs allow the comparison of different HyBECCS approaches with other hydrogen production technologies and NETs concerning their economic competitiveness and environmental performance in terms of GHG emissions.

The LCCNH (in EUR/kWhH_2) constitute the costs incurred to produce 1 kWh (net calorific value) of CNH in a climate-neutralized way. They are determined according to Equation (1) by summing up all costs (C3) incurred within system boundary B3, the estimated internalization costs (C_{int}) of all process GHG emissions, and the assumed revenues (R2) from the internalization of the external benefits of generating negative emissions, divided by the hydrogen production in kWh (yH_2). C_{int} can be divided into $C_{int,E1}$ and $C_{int,E2b}$, referring to the internalized process emissions occurring within HyBECCS system boundary B1 and B2, respectively. R2 are obtained by internalizing the external benefits of negative emissions, for example through carbon removal certificates. The LCSC (in EUR/tCO_2stored) are defined as the costs that occur to permanently store one ton of carbon dioxide using a carbon-neutralized process. They are determined according to Equation (2) by the sum of C3, C_{int}, revenues (R1) obtained from the sales of hydrogen, divided by the absolute value of stored carbon dioxide E2a. The LCNE (in EUR/tCO_2removed) are the costs that occur to achieve one ton (CO_2eq) negative emissions, i.e., to permanently remove one ton of carbon dioxide from the atmosphere, in a carbon-neutralized way. As shown in Equation (3) they are calculated by summing up the costs of C3 and C_{int} and deducting the revenues obtained from the sales of hydrogen (R1), divided by the absolute value of negative emissions E3, which is the absolute value of E2a minus process GHG emissions within system boundaries B1 (E1) and B2 (E2b). Capital expenditures, cash flows of revenues and expenses over the plant lifetime as well as the product yields for hydrogen, biogenic carbon dioxide and negative emissions (yH_2, E2a, E3) in Equations (1)–(3) are all discounted to a common reference point in time for the calculation of the levelized costs, i.e., annualized values.

$$LCCNH = (C3 + C_{int,E1} + C_{int,E2b} - R2) / yH_2 \quad (1)$$

$$LCSC = (C3 + C_{int,E1} + C_{int,E2b} - R1) / |E2a| \quad (2)$$

$$LCNE = (C3 + C_{int,E1} + C_{int,E2b} - R1) / |E3| \quad (3)$$

Only in case of negative emissions (E3<0), the hydrogen qualifies as carbon negative and its LCOE can be referred to as LCCNH. Also, only in the case of negative emissions, the term LCNE can be used. According to Equation (4), this prerequisite can be examined by determining the emission factor (EF), which has to be smaller than one. The GHG emissions of HyBECCS can be divided, according to the system boundaries, into process GHG emissions (E1) emitted within system boundary B1, process GHG emissions (E2b) emitted during the carbon storage or carbon utilization process, and the amount of CO_2stored in the long term (E2a).

$$EF = (E1 + E2b) / |E2a| \quad (4)$$

To investigate the impacts on the main KPIs LCCNH and LCNE, they are subjected to a sensitivity analysis. This analysis is conductetd in order to determine how uncertainties and risks affect economic and environmental performance factors. Therefore, the following parameters are varied in an interval of ±50% of their value and examined for their influences on the KPIs: H_2/CO_2 yield, GHG internalization costs/revenues, process emissions of HyBECCS, total CapEx, total OpEx, process leakages, and (in the case of LCNE) the hydrogen sales price. Concluding the evaluations, the example process is compared with competing hydrogen production and negative emission technologies to evaluate its economic and environmental competitiveness.

5. Results

5.1. *Environmental assessment*

5.1.1. *Eligibility on technology level*

The first assessment step evaluates the eligibility on a technology level given under two conditions: (a) The theoretical ability for carbon dioxide removal and (b) the theoretical permanence of carbon dioxide storage [15]. For the HyBECCS project under evaluation, waste or residues from the processing of fruit, a renewable, fast-growing biomass, are used as substrate. Therefore, the carbon dioxide in the product gas is considered to be of biogenic origin and the theoretical ability for carbon dioxide removal is given. The theoretical permanance of carbon dioxide storage is given due to the technology choice made for CS. The selected carbon dioxide storage in saline formations can be considered to be permanent for over 1000 years in the case of a careful site selection [22]. Thus, the projects' eligibility on a technology level is given.

5.1.2. *Carbon footprint*

The process scheme for the calculation of the global warming potential over 100 years (GWP_{100}) in tCO_2eq per functional unit (carbon footprint) is depicted in Fig. 5. It shows the scope of the assessment. Following the "cradle-to-grave" approach, the system boundary of the LCA embraces all essential process steps described in section 2.

Table 1 summarizes the GHG emissions for the example project. The total carbon footprint for the example project is derived by subtracting the amount of CO_2stored per functional unit from the process emissions, resulting in a negative carbon footprint of −0.53 $kgCO_2eq/kWhH_2$. The main share of 74.72% in the total GHG emissions of the example project (system boundary B3) is due to the provision of heat for hygienization. Electricity from the German grid accounts for 15.66%, while emissions from the CS process chain contribute another 9.38%. The shares for the construction and carbon dioxide transport remain at 0.24% and 0.01%, respectively.

The GHG emissions resulting from CS are drawn partially from an LCA conducted by Gassnova. Process emissions along the CS process chain, including storage, maintenance and monitoring of injected CO_2, as well as infrastructure construction emissions are assumed to be 10.81 kg CO_2eq/tCO_2stored, according to their work [24]. As GHG emissions from carbon dioxide capture are not included in that value, they are taken into account within the evaluation of system boundary B1 and its corresponding emission flow E1. GHG emissions from carbon dioxide transportation to the storage site are associated with system boundary B2 (cf. Fig. 2) and are calculated at 0.009 $kgCO_2eq/tCO_2$stored. The GHG emissions generated from the construction and operation of the CS plant drawn from Ref. [24], together with the carbon footprint for carbon dioxide transportation, sum up to a total carbon footprint of 10.82 $kgCO_2eq/tCO_2$stored.

5.1.3. *Eligibility on project level*

Even though the example project has the theoretical ability for carbon removal on a technology level (cf. 5.1.1.), this does not mean that it can actually deliver negative emissions. The actual ability on a project level is estimated ex-ante considering the carbon footprint of the process (cf. 5.1.2) and has to be monitored during its operation [15]. As the example project does not exist in reality, the ex-post evaluation of the eligibility on the project level is not part of this work. According to equation (4), the EF expresses the ratio between the GHG process emissions and the amount of stored carbon dioxide in tCO_2eq/tCO_2stored. For the example project, the EF is calculated at 0.12 tCO_2eq/tCO_2stored. This means that for each ton of biogenic carbon dioxide permanently stored, 0.12 tCO_2eq

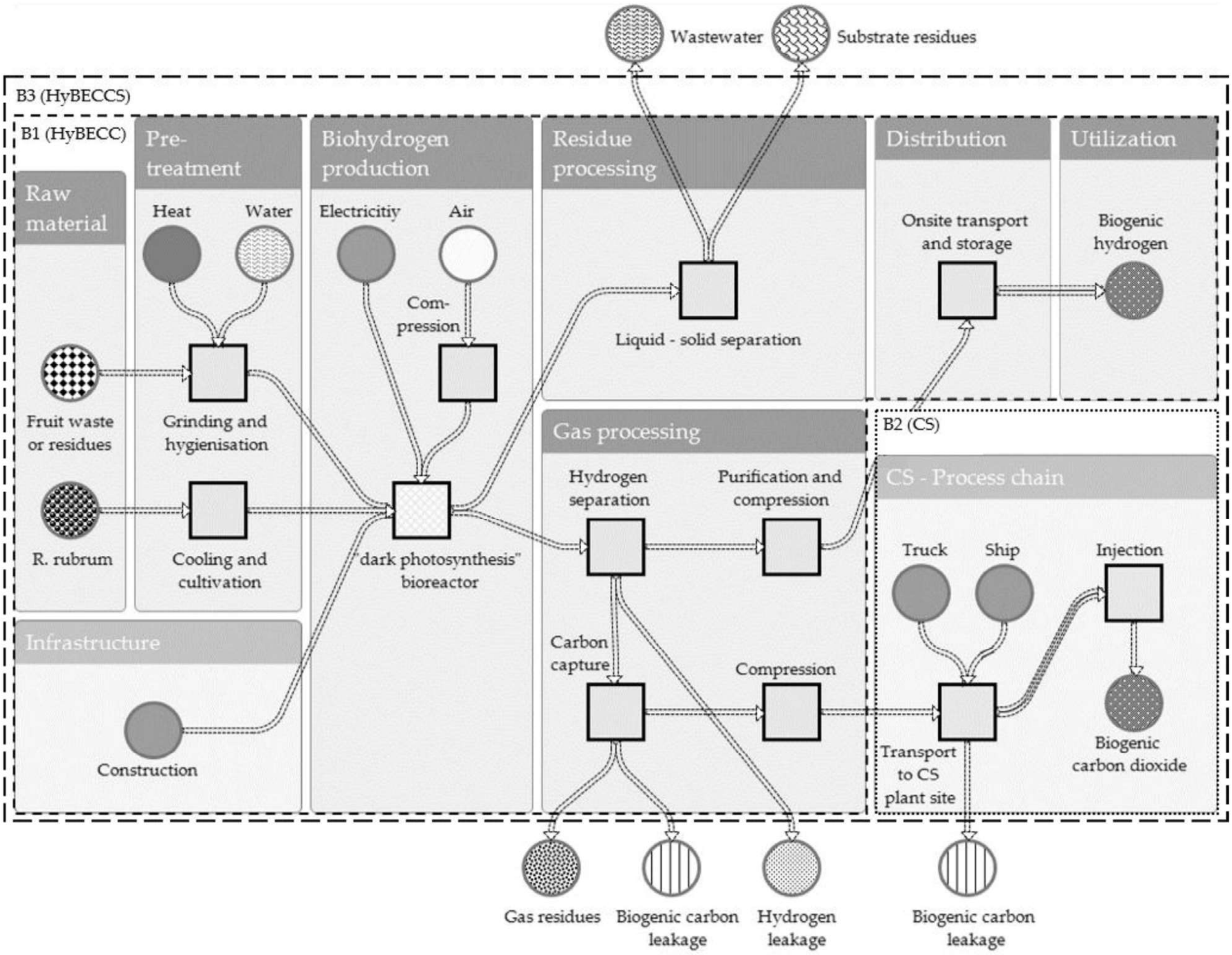

Fig. 5 – Process scheme for life cycle assessment (own representation).

are emitted throughout the whole life cycle of the HyBECCS project, including the process emissions from CS. In reverse, this means that 0.88 tCO_2 are actively removed from the atmosphere for each ton of biogenic carbon dioxide permanently stored. Considering biohydrogen production, 20.03 kg of carbon dioxide are removed for each kg (0.60 $kgCO_2$ for each $kWhH_2$) produced in the example project. As the EF is smaller than 1 (EF < 1), the analyzed example project produces CNH and qualifies as a NET on a project level, according to Ref. [15].

5.2. *Techno-economic assessment*

5.2.1. *Capital expenditures (CapEx)*

Table 2 summarizes the composition of the CapEx. The total plant costs (TPC) for the HyBECC system element contain the total equipment costs, including the substrate management, bacteria management, bioreactor system, sterile compressed air system, digestate processing, and gas processing. They are estimated at 2,763,450 EUR. Direct and indirect costs (DIC)

Table 1 – GHG footprints of the respective system elements. (HyBECC = hydrogen bioenergy with carbon capture, CS = carbon storage, HyBECCS = hydrogen bioenergy with carbon capture and storage, own calculation according to ISO 14040/44).

System Element (boundary)	Functional Unit	Process Emissions	Carbon Footprint	Unit
HyBECC (B1)	1 tCO_2stored	104.57	–	$kgCO_2eq/tCO_2$stored
CS (B2)	1 tCO_2stored	10.82	–	$kgCO_2eq/tCO_2$stored
HyBECCS (B3)	**1 tCO_2stored**	**115.39**	**−884.62**	**$kgCO_2eq/tCO_2$stored**
HyBECC (B1)	1 $kWhH_2$	0.0628	–	$kgCO_2eq/kWhH_2$
HyBECC (B2)	1 $kWhH_2$	0.0065	–	$kgCO_2eq/kWhH_2$
HyBECCS (B3)	**1 $kWhH_2$**	**0.0693**	**−0.53**	**$kgCO_2eq/kWhH_2$**

Table 2 – Absolute values and percentage of the different CapEx components. (HyBECC = hydrogen bioenergy with carbon capture, CS = carbon storage, Own Calculation based on factorial cost estimation, all sources are listed in Appendix A, Table A1).

Cost position (system element)	Value	Unit	Percentage of total CapEx
Substrate management	1,175,200	EUR	12%
Bioreactor system	706,300	EUR	7%
Digestate processing	506,500	EUR	5%
Bacteria management	145,450	EUR	1%
Sterile compressed air system	140,850	EUR	1%
Gas processing system	89,150	EUR	1%
Sum total plant costs (HyBECC)	2,763,450	EUR	28%
Direct and indirect costs (HyBECC)	2,686,050	EUR	27%
CapEx Carbon Storage (CS)	4,422,000	EUR	45%
Sum total CapEx (HyBECCS)	**9,871,500**	**EUR**	**100%**

include costs for equipment installation, piping, engineering, supervision, and legal expenses. They are estimated at 2,686,050 EUR in dependence of the TPC (cf. assumptions made in section 3). The CapEx of the system element CS are estimated at 4,422,000 EUR, resulting into a total CapEx of the example project of 9,871,500 EUR.

The CapEx for the HyBECCS project can be split into 55% on the system element HyBECC and 45% on the system element CS. TPC and DIC of system element HyBECC account for 28% and 27% of the total CapEx respectively. The substrate management has the largest share of the TPC with 43%, and third largest share of total CapEx with 12%.

5.2.2. *Operational expenditures (OpEx)*

OpEx estimations for the example project are summarized in Table 3. The variable costs, estimated at 1,412,800 EUR per year, include expenses for electricity, heat, process water, activated carbon, as well as for the transportation, storage, and monitoring of biogenic CO_2. Fixed production costs comprise expenses for taxes and insurance, maintenance, and personnel costs. They are estimated at 776,200 EUR per year, thus resulting into total OpEx of 2,189,000 EUR per year.

Heat accounts for the largest share of OpEx with 32%, followed by personal expenses with 22%, process water with 14% and CS with 12%.

Table 3 – Absolute values and percentage of annualized OpEx (CS = carbon storage). (Own Calculation based on plant dimensions, experimental data, experience values from biogas plants in Germany and surcharge factors, all sources are listed in Appendix A, Table A1).

Cost position	Value	Unit	Percentage of total OpEx
Electricity	101,700	EUR/a	5%
Heat	696,100	EUR/a	32%
Process water	307,000	EUR/a	14%
Activated carbon	46,100	EUR/a	2%
CS (transport, storage, monitoring)	261,900	EUR/a	12%
Sum variable costs	**1,412,800**	**EUR/a**	**65%**
Taxes and insurance	98,700	EUR/a	5%
Maintenance	197,400	EUR/a	9%
Personnel expenses	480,100	EUR/a	22%
Sum fixed costs	**776,200**	**EUR/a**	**35%**
Sum OpEx	**2,189,000**	**EUR/a**	**100%**

5.2.3. *Levelized costs*

Table 4 summarizes the levelized costs. They can be divided into the internal levelized costs and the key performance indicators LCCNH, LCNE and LCSC (cf. section 4). The three KPIs are derived according to equations (1)–(3) taking into account the external costs and benefits of GHG emissions and removals.

The internal LCOE for system boundary B3 are higher than for system boundary B1. This is due to the additional costs for CS infrastructure and operations as well as the revenues generated from selling the co-product biogenic carbon dioxide. These revenues lower the internal LCOE in B1. However, they do not influence the internal LCOE in B3, as they occur in the same magnitude as a cost position in B2 and are thus offset against the revenues generated in B1. Internal LCSC in B2 are 385.02 EUR/tCO_2 higher compared to LCNE in B3. This is due to the revenues obtained from the hydrogen sales as part of the internal LCNE calculation. Considering LCCNH, the internalization of external effects leads to a reduction of about 0.11 EUR/kWhH_2 compared to the internal LCOE in B3. The LCNE is around 25.69 EUR/tCO_2 higher compared to the internal LCNE in B3. LCSC are reduced by about 322.40 EUR/tCO_2 compared to internal LCSC (B2).

5.3. *Sensitivity analysis*

Fig. 6 illustrates the results of the sensitivity analysis for the KPIs LCCNH and LCNE, as described in section 4.

The GHG internalization costs and revenues, H_2/CO_2 yield and the total OpEx can be identified as the parameters with the greatest impact on the LCCNH, as shown in Fig. 6 (a). The H_2/CO_2 yields have the greatest effect on the LCCNH, when being reduced. A reduction of the yields causes the LCCNH to converge to infinity. Increasing total OpEx and decreasing GHG internalization costs and revenues also have a comparatively high impact driving up the LCCNH. The highest value

Table 4 – Levelized costs, divided into internal levelized costs and key performance indicators (KPIs).

Internal levelized costs	Value	Unit
Internal LCOE (B1)	0.08 | 2.59	EUR/kWh | EUR/kgH_2
Internal LCOE (B3)	0.12 | 3.85	EUR/kWh | EUR/kgH_2
Internal LCSC (B2)	62.64	EUR/tCO_2stored
Internal LCNE (B3)	−322.38	EUR/tCO_2removed
KPIs		
LCCNH	0.013 | 0.43	EUR/kWh | EUR/kgH_2
LCNE	−296.69	EUR/tCO_2removed
LCSC	−259.76	EUR/tCO_2stored

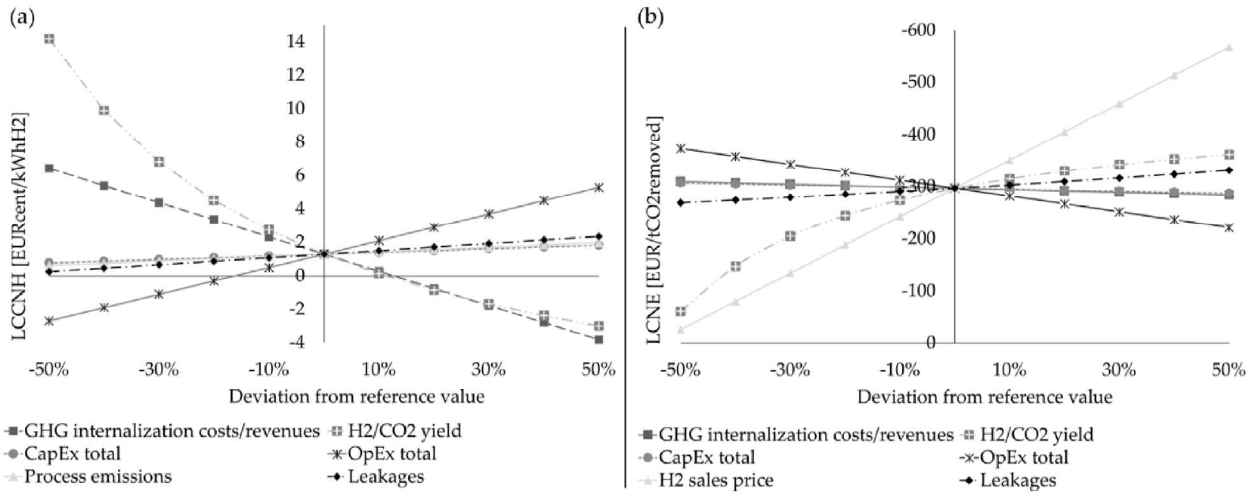

Fig. 6 — Sensitivity analysis of LCCNH (a) and LCNE (b) (own representation).

for LCCNH is calculated at 14.17 EURcent/kWh for reducing H_2/CO_2 yield by 50%. The lowest value for LCCNH is calculated at −3.84 EURcent/kWh for increasing GHG internalization costs and revenues by 50%. Fig. 6 (b) shows the influences of the parameters on the LCNE. The graph shows that the hydrogen sales price has the greatest impact on the LCNE. While a 50% reduction would lead to a cost increase of 91% to −25.89 EUR/tCO_2removed, a 50% increase would reduce the LCNE by 91% to −567.48 EUR/tCO_2removed. Further, the H_2/CO_2 yield and the total OpEx have a considerably high impact on the LCNE. Corresponding to the influence on the LCCNH, decreasing H_2/CO_2 yields leads to a disproportionate increase in the LCNE, converging to infinity. The impact of process emissions is not included in Fig. 6 (b) as the values correspond to the curve for GHG internalization costs and revenues.

6. Discussion of the exemplary results

6.1. *Comparison with competing hydrogen generation technologies*

In the following, the GHG emissions of the example project are compared to competing hydrogen production technologies. For each technology, the GHG emissions that occur throughout the production processes are indicated in Fig. 7 without CCS or, if applicable, with CCS. As shown in section 5.1.2., the example project causes GHG emissions of 0.0628 $kgCO_2eq/kWhH_2$ in system boundary B1, which is within the same magnitude as the GHG emissions of green hydrogen from electrolysis using renewable energy (0.05 $kgCO_2eq/kWhH_2$). This value is considerably lower than the GHG emissions of hydrogen generated via electrolysis using the EU electricity mix (0.72 $kgCO_2eq/kWhH_2$), as well as steam methane reforming (SMR) from both biogas (0.23 $kgCO_2eq/kWhH_2$) and natural gas (0.32 $kgCO_2eq/kWhH_2$) [42,43].

The GHG balance of the example project, including carbon storage (B3) is negative and amounts to −0.53 $kgCO_2eq/kWhH_2$.

Hydrogen production through biogas SMR can also be extended to HyBECCS systems [14]. If the biogenic carbon dioxide occurring in the biogas as well as reformed gas is permanently stored (see e.g. Ref. [43]), the GHG intensity of a HyBECCS project based on biogas SMR (−0.45 $kgCO_2eq/kWhH_2$) is within the same magnitude as the example project considered in this work. Application of CCS in natural gas SMR processes could reduce the carbon footprint from 0.32 to 0.17 $kgCO_2eq/kWhH_2$.

Fig. 8 shows the LCCNH of the example project compared to the levelized costs of energy (LCOE) of other hydrogen generation technologies. The internal LCOE constitute the levelized costs without internalization of the external effects of the process due to GHG emissions and removals. The internal LCOE of biohydrogen from the example project (0.12 $EUR/kWhH_2$ or 4.00 EUR/kgH_2) are lower compared to green hydrogen from electrolysis using renewable electrical energy (0.17 $EUR/kWhH_2$ or 5.67 EUR/kgH_2). This indicates that the example project could already be competitive to green hydrogen production from electrolysis under the assumptions made. The second bar from the left shows the assumed internalization costs and revenues for GHG emissions and carbon dioxide removal of the example project (cf. 5.1.2.).

For the example project, the LCCNH is 0.013 $EUR/kWhH_2$ (0.43 EUR/kgH_2). The comparison of the LCCNH with the total LCOE (including GHG internalization costs) of the alternative technologies underlines the high ecological benefit of CNH. Including all positive and negative effects in the calculations, the fossil alternative grey hydrogen from natural gas (0.12 $EUR/kWhH_2$ or 4.00 EUR/kgH_2) loses its competitiveness [42,44]. A direct comparison to the conventional fossil energy carrier natural gas (not part of Fig. 8) comes to the same conclusion: The internal LCOE of 0.02 EUR/kWh would rise to 0.06 EUR/kWh when including the external costs of GHG emissions [42,44]. In comparison to hydrogen from electrolysis using renewable electricity, the positive impact of the negative emissions also provide a considerable advantage to the example project. Overcompensating its GHG emissions with carbon dioxide removals leads to a net income of 0.107

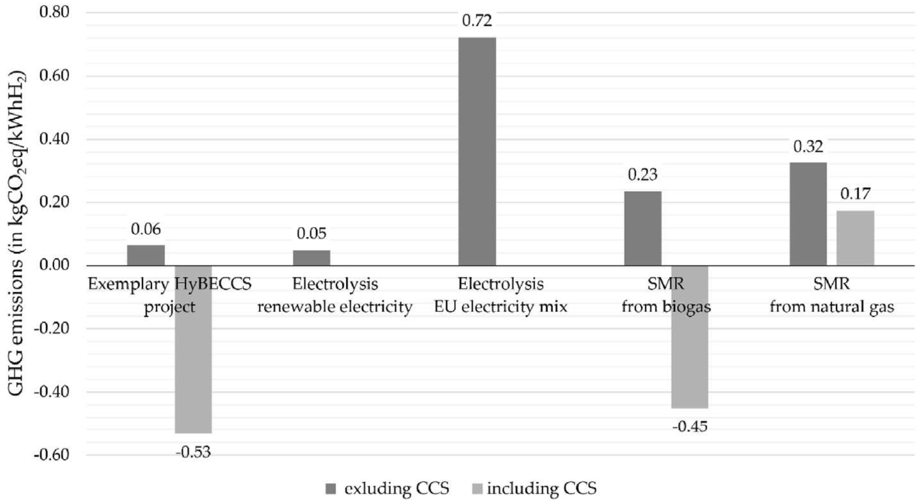

Fig. 7 – GHG emissions from biohydrogen generated via the exemplary HyBECCS project and from other hydrogen production technologies. Own elaboration including data from Refs. [42,43].

EUR/kWh (3.57 EUR/kgH_2), whereas green hydrogen from electrolysis has to account for 0.01 EUR/kWhH_2 (0.33 EUR/kgH_2) of GHG internalization costs. As elaborated by Full et al. (2021), the production costs for CNH in 2030 would have to be below 4.30 per kg in a worst-case scenario to be competitive in Germany, taking into account hydrogen market forecasts [13]. All estimated levelized costs of the example project are below this value.

6.2. *Comparison with competing negative emission technologies*

Changing the point of view from biohydrogen to the negative emissions as main product of the example project, its comparison with other NETs is possible. The EF of the example project is estimated to be 0.12 tCO_2eq/tCO_2stored (cf. 5.1.3.). According to Fajardy et al. (2019) an average emission factor of 0.5 tCO_2eq/tCO_2stored for BECCS can be obtained [45]. Borchers et al. (2022) indicate an emission factor between 0.1 and 0.9 tCO_2eq/tCO_2stored for BECCS, depending on the technology chosen [10]. The example project is, thus, at the very low EF range of BECCS approaches, as shown in Fig. 9. Considering DACCS approaches, the emission factors vary significantly depending on the type of energy provision and their location. According to an analysis of Terlouw et al. (2021), the EF of DACCS lies between 0.03 tCO_2eq/tCO_2stored for DACCS plants in Norway using waste heat and grid electricity and 0.91 tCO_2eq/tCO_2stored for DACCS plants in Greece using high-temperature heat pumps and grid electricity [46]. Borchers et al. (2022) indicate an EF of 0.6 tCO_2eq/tCO_2stored for both decentralized and centralized DACCS options [10]. The EF of the example project is, thus, comparable to DACCS plants at the lower end of their EF range.

The internal LCNE for the example project are estimated at −322 EUR/tCO_2removed (cf. 5.2.3.). Thus, even without internalizing any externalities, the removal of one ton of

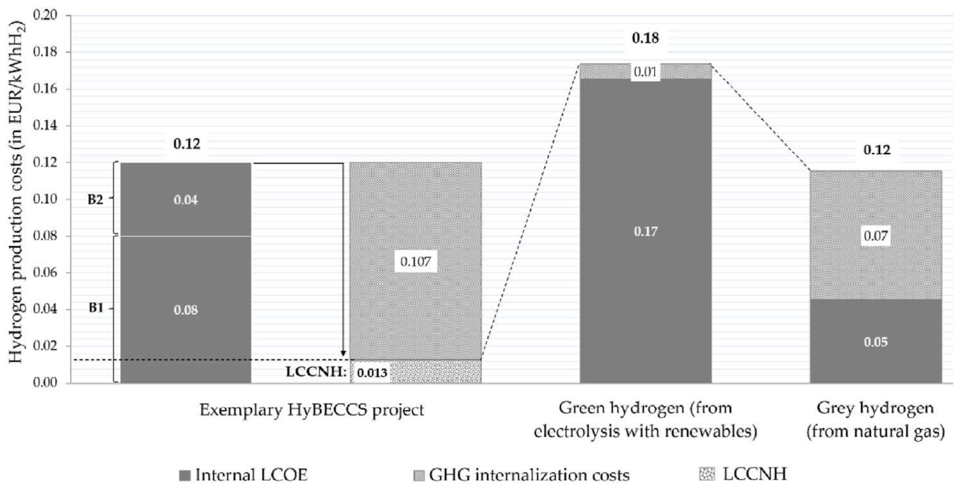

Fig. 8 – Comparison of the levelized costs of carbon-negative hydrogen (LCCNH) from the exemplary HyBECCS project with the LCOE of other hydrogen production technologies. B1: system boundary B1 (HyBECC system element), B2: system boundary B2 (CS system element). Own elaboration including data from Refs. [42,44].

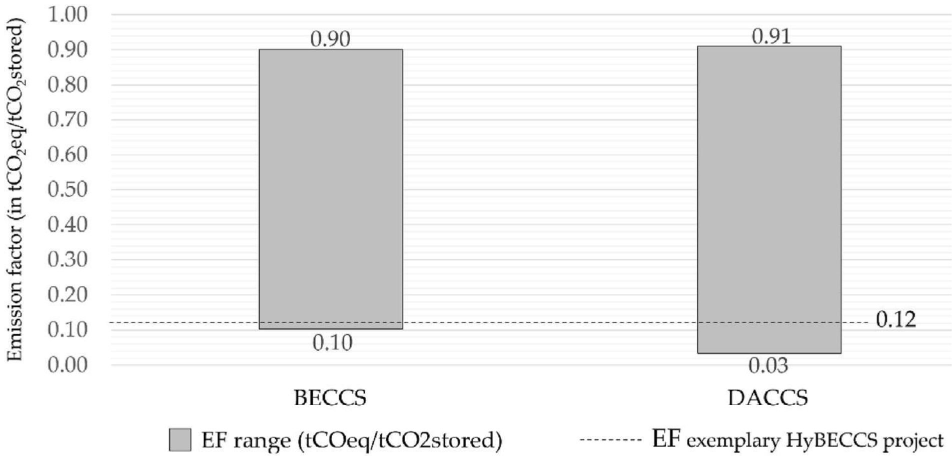

Fig. 9 – Emission factors from the exemplary HyBECCS project compared to the EF ranges of other BECCS approaches and DACCS. Own elaboration including data from Refs. [10,46].

carbon dioxide from the atmosphere generates an income of 322 EUR due to the sales of the co-product biohydrogen. Other BECCS approaches generally show a wide range of internal LCNE due to the variety of the underlying technologies. Möllersten et al. (2020) indicate approx. 19.40 to over 97 EUR/tCO_2removed, whereas the IPCC (2018) indicates a minimum of approx. 194 EUR/tCO_2removed [23]. DACCS approaches also show a wide cost range. For DACCS, Möllersten et al. (2020) indicate internal LCNE of approx. 39–581 EUR/tCO_2removed, whereas the IPCC (2018) indicate approx. 19.40–969 EUR/tCO_2removed [23]. The LCNE of the example project is estimated at −297 EUR/tCO_2removed. This states that removing one ton of carbon dioxide from the atmosphere generates an income of 297 EUR, even after internalizing all externalities from GHG emissions. When applying internalization, the LCNE cost range is approx. 39–367 EUR/tCO_2eq for BECCS. For DACCS, the LCNE cost range is 25–1127 EUR/tCO_2eq. Fig. 10 summarizes the comparison of the LCNE of the example project to the Internal LCNE cost range as well as to the LCNE cost ranges of BECCS and DACCS. It can be seen that the Internal LCNE as well as the LCNE of the example project is within the BECCS cost range.

7. Limitations

As the example project considered in this work is not fully implemented, the results rely on the assumptions made. However, all assumptions are associated with uncertainties. The sensitivity analysis (cf. 5.3.) revealed that the performance of the KPIs is especially susceptible to the parameters H_2/CO_2 yield, hydrogen sales price, and OpEx with heating costs and personnel expenses showing the highest impacts. These parameters should be given particular attention when verifying the assumptions made. However, some assumptions and their uncertainties should be noted additionally.

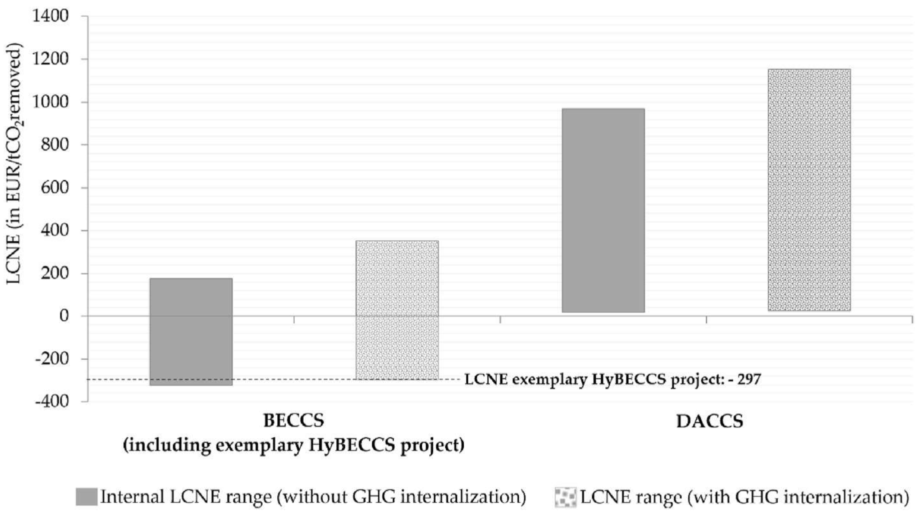

Fig. 10 – LCNE (with GHG internalization) from the exemplary HyBECCS project based on "dark photosynthesis" compared to the (Internal) LCNE range of BECCS and the (Internal) LCNE range of DACCS. Source: Own elaboration including data from Refs. [23,47].

An important point of discussion from the authors' perspective is the waste or residual material used as substrate material. On the one hand, the large quantity considered must be available. On the other hand, its processing may involve environmental impacts or costs, which have been neglected in this work. Direct damages to ecosystems or indirect damages through increased competition for land use, with substantial risks to biodiversity, can occur. In this work, a one-sided focus is placed on GHG emissions. However, all impact categories of LCAs, especially conflicts with food production and biodiversity must be analyzed. Further, considering the economic impacts of the substrate material used, revenues or costs can arise for their acceptance or disposal. Thus, the price for the substrate used can be a significant factor in terms of costs. In Germany, for instance, the waste receipt of sewage sludge can generate revenues of about 30 EUR/t, whereas the use of sugar beet leaf silage can lead to costs of around 28 EUR/t [48]. In this work, the substrate residues from "dark photosynthesis" are considered a product of equal value to the originating residues from fruit juice production. They can be used e.g. as fertilizer. However, it must be highlighted, that whether the substrate used is associated with costs or even revenues. This has to be determined carefully for each specific substrate used. Another limitation concerns the bulk density of the material. Fruit waste consists of materials of different compositions and densities that in turn depend on the moisture content of the substance. For apple pomace as an example, the bulk density ranges from 251 kg/m^3 for dry matter to about 1017 kg/m^3 for fresh matter [49]. Since the product yields are linked to the amount of the used substrate, a higher bulk density results in higher yields assuming constant fructose content. At the same time, the amount of substrate to be processed increases. Besides moisture, pre-treatment of biomass is an important aspect of biohydrogen production [50]. Pre-treatment may lead to the formation of toxins and inhibitors, affecting bacterial conversion of the substrate to biohydrogen. Therefore physical, chemical, physiochemical and biological pre-treatment methods as well as subsequent detoxification have to be implemented carefully for optimal feedstock quality. The neglected feedstock price (cf. section 3) and the annually needed amount may be bottlenecks for HyBECCS projects and must be carefully determined for each HyBECCS project.

Additionally, it should be noted that the assumed GHG internalization price of 195 EUR/tCO_2eq does not comply with reality but represents an idealized scenario representing an appropriate GHG internalization price for the ecological damage from climate change [39]. It also has to be underlined that the exemplary "dark photosynthesis" process analyzed in this paper is one technological approach amongst many HyBECCS approaches. Therefore, the example project and the results of this analysis are not representative for HyBECCS technologies in general. They only apply to the technology combination considered under the assumptions made. Generally, biotechnological process routes for biohydrogen production like "dark photosynthesis", face major challenges in their industrial implementation and scale up due to slow conversion rates [51]. In this regard, "dark photosynthesis" is no exception, existing yet only at a laboratory scale. Measures for scale up, such as continuous production, are highly encouraged and will pave the way for faster development [52,53].

8. Summary and conclusion

In this paper, a techno-economic and environmental analysis is performed for an exemplary HyBECCS project. The evaluation is based on the methodological assessment approach presented by Full et al. (2022) and conducted primarily to validate this approach [15]. The methodology allows to compare HyBECCS technologies with other hydrogen production technologies and NETs. Therefore, in addition to conventional economic criteria, the specific key performance indicators integrate macroeconomic effects resulting from the GHG emissions and reductions as a special feature. The example project chosen combines the production of biohydrogen and biogenic carbon dioxide using fructose-containing waste or residues from fruit processing with storage of the carbon dioxide in saline formations.

First, an estimation of the carbon footprint is conducted. It indicates that the overall process chain of the example project is a carbon sink under the assumptions made. For every kg of biohydrogen produced, 17.72 kg of carbon dioxide (0.53 kgCO_2/kWhH_2) could be removed from the atmosphere. With this information, the eligibility check on the project level is fulfilled and the example project qualifies as HyBECCS technology being capable of delivering carbon-negative hydrogen. For the techno-economic analysis, the capital and operational expenditures are estimated. Considering CapEx, the estimations result in a total of 9,871,500 EUR. 55% of these costs are related to the production of biohydrogen and carbon dioxide capturing. Carbon storage accounts for the other 45% of the costs. Total OpEx sum up to 2,189,000 EUR per year with the highest shares of 32% for heating costs, 22% for personnel expenses, 14% for process water, and 12% for carbon dioxide transport, storage, and monitoring of the CS plant. The levelized costs of carbon-negative hydrogen are estimated at 0.013 EUR/kWhH_2 (0.43 EUR/kgH_2). They represent the costs incurred to produce hydrogen with negative emissions in a climate-neutralized way. The comparison of the LCCNH with the LCOE including GHG neutralization costs of alternative hydrogen production technologies, shows that the example project can provide hydrogen with the lowest costs under the assumptions made. The value for grey hydrogen from natural gas is estimated at 0.12 EUR/kWhH_2, for instance. Also, in comparison to green hydrogen from electrolysis using renewable electricity (0.18 EUR/kWhH_2), the positive climatic impact of the negative emissions provides a considerable advantage. Even without the assumed internalization of GHG impacts, the calculations show an economic advantage of the example project (0.12 EUR/kWhH_2) over green hydrogen (0.17 EUR/kWhH_2) [42,44]. To make a comparison with other NETs, the GHG removal efficiency represented by the emission factor EF is considered first. The EF of the example project is estimated at 0.12 tCO_2eq/tCO_2stored. This value is at the lower end of the EF ranges both from other BECCS and DACCS approaches, as literature shows. Additionally, the levelized costs of stored carbon dioxide LCSC are obtained. They represent the costs that occur to permanently store one ton of carbon dioxide with a carbon-neutralized process. The LCSC of the example project are estimated at about −260 EUR/tCO_2stored. To further compare the costs of the example project with other NETs, the levelized costs of negative emissions LCNE are examined. They represent the costs that occur to achieve one ton (CO_2eq) of negative emissions in a carbon-neutralized way. The LCNE of the example project are estimated at −297 EUR/tCO_2removed. This means that an income of 279 EUR due to the sales of the co-product biohydrogen could be generated. For BECCS, the LCNE range is approx. 39–367 EUR/tCO_2-removed, for DACCS, 25–1127 EUR/tCO_2removed. The internal LCOE of the example project is estimated at −322 EUR/tCO2removed. This indicates that even without internalizing any externalities, the removal of one ton of carbon dioxide from the atmosphere would generate an income of 322 EUR through biohydrogen sales.

A sensitivity analysis is carried out in order to determine uncertainties and risks affecting economic and environmental performance. It is shown that the GHG internalization costs and revenues, H_2/CO_2 yield, and the total OpEx have the greatest impact on the LCCNH of the example project. Further, the hydrogen sales price has the greatest impact on the LCNE of the example project. A 50% reduction would lead to a cost increase of 91% to −25.89 EUR/tCO_2removed. Further, the H_2/CO_2 yield and the total OpEx have a considerably higher impact on the LCNE than the total CapEx, GHG internalization costs and revenues, and leakages.

Finally, it has been shown that the theoretical fundamentals elaborated by Full et al. (2022) are applicable in practice. A comparability of the example project with other NETs and hydrogen production technologies has been achieved. It has also been shown that it is possible to specifically evaluate the economic influences of the technologies considered for society coming from GHG emissions or removals.

9. Outlook

Further investigations should be conducted based on the results. For example, CS technologies and NETs are associated with different time horizons of storage and risks of reversal [23,47]. In the present evaluations, these two factors are not considered. However, to raise the comparability of different NETs and CS technologies, they have to be taken into account. Additionally, the ability of HyBECCS to deliver negative emissions and its potential economic competitiveness indicated by the results of the analysis in this paper are based on assumptions and are thus insecure. Further investigations on the potential of HyBECCS on a technology-specific, national and global level are necessary. Therefore, different biohydrogen production technologies should be subjected to the method and extended to HyBECCS facilities. Suitable options could include, for example, dark fermentation [54–57], biomass gasification [58–61] or biogas steam reforming [43,62,63].

Author contributions

Conceptualization, methodology, formal analysis: J.F.; writing (original draft), investigation, data curation, visualization: J.F., M.G., S.Z. and T.S.; writing (review and editing): R.M. and A.S.; funding acquisition: J.F:, R.M. and A.S. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2023.09.252.

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