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Analysis of the sustainable production of hydrogen as an energy vector in Colombia

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"I believe there is a force in this world that lies beneath the surface, something primal and wild that awakens when we need that extra push to survive like those wildflowers that bloom after the fire has blackened an entire forest. Most people fear it and keep it locked deep inside, but there will always be those who dare to love what they carry within them, which is untamed." One of those people is my father."

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Maria Camila Garcia Vallejo

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Abstract

Analysis of the sustainable production of hydrogen as an energy vector in Colombia

The first step towards the energy transition that promotes a carbon-neutral society is the implementation of renewable energy sources, accompanied by the development of new energy carriers with lower pollution rates and higher energy efficiencies. Based on this, the energy transition requires several efforts in the processes of transformation, generation, and consumption of energy. Therefore, discovering new alternative energy resources and systems has become a priority, and multiple governments and major industries, such as the IEA, have already recognized the role of hydrogen in this task. However, given the diversity of pathways for converting raw materials into energy products, it is only possible to formulate sound decisions with preliminary conceptual design and multi-criteria evaluation.

To date, the transformation pathways for hydrogen production have focused on petrochemical and thermochemical schemes and have been analyzed as single processes, discounting the relevance of other production schemes such as electrolytic and biological processes. In addition, there are no rigorous studies that analyze all the production pathways. Therefore, this work begins with a heuristic analysis of technologies and raw materials for hydrogen production. This analysis was based on objective criteria such as environmental impact, economic aspects, and operational and energetic parameters of the process. The main results were that the schemes with the highest level of development, economic and environmental advantages were (i) steam methane reforming, (ii) biomass gasification, (iii) alkaline electrolysis, and (iv) dark fermentation. Then, a heuristic analysis was developed considering the potential of the main agricultural and agro-industrial wastes in obtaining hydrogen, considering the pathways mentioned above. Once the raw materials and technologies with the greatest opportunity for development were established, the schemes were evaluated at the experimental level and scaled up in simulation schemes using Aspen Plus.

At the experimental level, it was evaluated (i) anaerobic digestion of cassava stalk to produce biomethane for steam reforming (SBMR), (ii) gasification of corn stover, (iii) alkaline electrolysis, and (iv) dark fermentation using rice straw and the microorganism T. *thermosaccharolyticum* W16. The experimental schemes did not contemplate the gas separation and purification stage. The experimental results were used to simulate and evaluate the sustainability of the biorefineries. In the separation and purification stages, widely developed technologies such as Pressure Swing Adsorption (PSA) were proposed to obtain hydrogen. Then, a comparative analysis of the sustainability of the main hydrogen production technologies was carried out. For this purpose, techno-energy, economic, environmental, and social indicators were used to calculate a global sustainability index (S_{Id}).

Steam biomethane reforming (SBMR) and electrolysis with solar power (EL), were the systems with the highest S_{Id} regarding techno-energy and environmental dimensions, respectively. Moreover, thermochemical, and biological technologies require further research to decrease the environmental load and improve the mass efficiency of the process.

Finally, once it was established that SBMR was the technology with the highest sustainability index, it was evaluated considering a life cycle assessment. For this purpose, the Sucre region and a highly available agricultural residue were considered: the cassava stalks. Cassava is a highly distributed crop in Colombia. Like other crops, cassava generates different usable residues, such as cassava stalk, which can be valued by producing energy carriers that meet the needs of the process. Therefore, this work also included evaluating the environmental impact of the cassava value chain for the Sucre region and analyzed the possibility of including residue processing stages to produce energy carriers of low (biomethane) and high (hydrogen) complexity. As the main results, the influence of the processing stage in the value chain can be highlighted, contributing more than 90% of the impact due to energy demands and waste generated. In addition, when the production of energy carriers was included, biomethane and hydrogen could supply the energy needs of the biorefinery and between 72% and 58% of the energy demand of the transformer stage, respectively. Finally, it was established that the value chain without the valorization of cassava residues produced 1.22 kg CO_2 eq/kg cassava. In comparison, when including the valorization stages, the value chain generated 1.20 kg CO_2/kg of cassava, where raw materials, especially sludge for anaerobic digestion, presented the greatest contribution to the environmental impact in the biorefineries. Thus, agricultural residues and the production of energy carriers become established as a processing alternative for generating usable energy within the links of the production chain, mitigating, in turn, the overall impact of the value chain.

Keywords: *Heuristic analysis, sustainability analysis, hydrogen, value chain, life cycle assessment.*

Resumen

Análisis de la producción sostenible de hidrógeno como vector energético en Colombia

El primer paso hacia la transición energética que promueve una sociedad neutra en carbono es la implementación de fuentes de energía renovables, acompañadas del desarrollo de nuevos vectores energéticos con menores índices de contaminación y mayores eficiencias energéticas. En base a ello, la transición energética requiere numerosos esfuerzos en los procesos de transformación, generación y consumo de energía. Por lo anterior, el descubrimiento de nuevos recursos y sistemas energéticos alternativos se ha convertido en una prioridad y el papel que desempeña el hidrógeno en esta tarea ya ha sido reconocido por múltiples gobiernos y grandes industrias, tales como la IEA. No obstante, dada la multiplicidad de vías de conversión de materias primas en productos energéticos, es imposible formular decisiones sólidas sin un diseño conceptual preliminar y una evaluación multicriterio.

Hasta la fecha, las rutas de transformación para la producción de hidrogeno se han centrado en esquemas petroquímicos y termoquímicos, y se han analizado como procesos unitarios, desconociendo la relevancia que presentan otros esquemas de producción como los procesos electrolíticos y biológicos. Adicionalmente, no existen estudios rigurosos que analicen todas las rutas de producción en conjunto. Por lo tanto, este trabajo inicia como el planteamiento de un análisis heurístico aplicado a tecnologías y materias primas para la producción de hidrogeno. Este análisis se basó en criterios objetivos como el impacto ambiental, aspectos económicos y los parámetros operacionales y energéticos del proceso. Como principales resultados se obtuvieron que los esquemas con mayor nivel de desarrollo, ventajas económicas y ambientales fueron el (i) reformado de metano con vapor, (ii) gasificación de la biomasa, (iii) electrolisis alcalina y (iv) fermentación oscura. Luego, se desarrolló un análisis heurístico considerando el potencial que presentaban los principales residuos agrícolas y/o agroindustriales en la obtención de hidrogeno considerando las vías anteriormente mencionadas. Una vez se establecieron las materias primas y las tecnologías con mayor oportunidad de desarrollo, los esquemas fueron evaluados a nivel experimental y escalados en esquemas de simulación utilizando Aspen Plus.

A nivel experimental se evaluó (i) la digestión anaerobia del tallo de yuca para la producción de biometano aprovechable en reformado con vapor (SBMR) (ii) la gasificación de la tusa de maíz (iii) la electrólisis alcalina y (iv) la fermentación oscura utilizando paja de arroz y el microorganismo T. *thermosaccharolyticum* W16. En los esquemas experimentales no se contempló la etapa de separación ni purificación del gas. Los resultados experimentales se utilizaron para simular y evaluar la sostenibilidad de las biorrefinerías y en las etapas de separación y purificación se propusieron tecnologías ampliamente desarrolladas como Adsorción por cambio de presión (PSA) para la obtención del hidrogeno. Luego, se realizó un análisis comparativo de la sostenibilidad de las principales tecnologías de producción de hidrógeno. Para ello, se utilizaron indicadores tecno energéticos, económicos, medioambientales y sociales para calcular un índice de sostenibilidad global (S_{Id}). El reformado de biometano con vapor (SBMR) y la electrólisis con energía solar (EL) fueron los sistemas con el S_{Id} más alto en función de las dimensiones tecno energética y medioambiental, respectivamente. Por otro lado, las tecnologías termoquímica y biológica requieren más investigación para disminuir la carga medioambiental y mejorar el rendimiento másico del proceso.

Finalmente, una vez se estableció que el SBMR fue la tecnología con mayor índice de sostenibilidad, esta tecnología se evaluó considerando un análisis de ciclo de vida. Para ello, se consideró la región de Sucre y un residuo agrícola altamente disponible: el tallo de yuca. La yuca es un cultivo altamente distribuido en Colombia y al igual que otros cultivos, la yuca genera diferentes residuos aprovechables, como el tallo de yuca, que pueden ser valorizados mediante la producción de vectores energéticos que satisfagan las necesidades del proceso. Por lo tanto, este trabajo también incluyó la evaluación del impacto ambiental de la cadena de valor de la yuca para la región de Sucre y analizo la posibilidad de incluir etapas de procesamiento de residuos para producir vectores energéticos de baja (biometano) y alta (hidrógeno) complejidad. Como principales resultados, se puede destacar la influencia de la etapa de transformación en la cadena de valor, aportando más del 90% del impacto ambiental, derivado de la alta demanda de energía y la generación de residuos. Además, cuando se incluyó la producción de vectores energéticos, el biometano y el hidrógeno pudieron abastecer las necesidades energéticas de la biorrefinería y entre el 72% y el 58% de la demanda energética de la etapa de transformación, respectivamente. Por último, se estableció que la cadena de valor sin la valorización de los residuos de yuca produjo 1,22 kg CO_2 eq/kg de yuca. En comparación, con la cadena de valor que incluyo las etapas de valorización, la cadena de valor generó 1,20 kg CO_2/kg de yuca, donde las materias primas, especialmente los lodos para digestión anaeróbica presentaron la mayor contribución al impacto ambiental en las biorrefinerías. De esta forma, se puede concluir que los residuos agrícolas y la producción de vectores energéticos se establecen como una alternativa de procesamiento para la generación de energía aprovechable dentro de los eslabones de la cadena productiva, mitigando, a su vez, el impacto global de la cadena de valor.

Palabras clave: *Análisis heurístico, análisis de sostenibilidad, hidrógeno, cadena de valor, evaluación del ciclo de vida.*

Content

Figures

Supplementary material-Appendix A

Tables

Nomenclature

Symbol	Definition	Unit
Heuristic analysis of pathways, technologies, and raw materials		
η_{En}	Energy efficiency	%
ψ	Exergy efficiency	%
TRL	Technological readiness level	
IPCC	Intergovernmental Panel on Climate Change	
AC	Availability of existing crops and productivity	
TI	Technical indicators and yields	
RU	Raw material costs	
RC	Raw material for direct consumption or use in other production processes	
SR	Social impact of raw material production	
CC	Chemical characterization of raw materials	
Experimental and simulation schemes		
SBMR	Steam biomethane reforming	
SMR	Steam methane reforming	
EL	Electrolysis	
GF	Gasification	
DF	Dark fermentation	
S_{Id}	Sustainability index	%
D_j	Dimension	
α_i	Level of relevance for each indicator	
T	Technical dimension	
Ec	Economic dimension	
Ev	Environmental dimension	
S	Social dimension	
WGS	Water gas shift reaction	
PSA	Pressure swing adsorption	
VSA	Vacuum displacement adsorption unit	
HPWS	High-pressure water scrubbing	
VFA	Volatile fatty acids	
BMP	Biochemical methane potential	
Chemical characterization		
NREL	National Renewable Energy Laboratory	
ASTM	*American Society for Testing and Materials*	
TS	Total solids	%
VS	Volatile solids	%

VM	Volatile matter	%
FC	Fixed carbon	%

Techno-energetic assessment

Y_H	Product yield	g Hydrogen/ kg Raw materials
PMI	Process mass intensity	kg Inlet streams/ kg Products
MLI	Mass loss index	kg Waste streams/ kg Product
SEC	Specific energy consumption	kW/ kg Raw materials
SGI	Self-generation index	

Economic assessment

NEW	Net energy value	MJ/h
MPSEF	Minimum processing scale for economic feasibility	kg/h
NPV	Net present value	M-USD/year
CapEx	Capital expenditures	
OpEx	Operating expenses	

Environmental assessment

eLCA	Environmental life cycle assessment	
eLCI	Environmental life cycle inventory	
CC	Climate change	kg CO_2 eq
TA	Terrestrial acidification	kg SO_2 eq
FE	Freshwater eutrophication	kg P eq
ME	Marine eutrophication	kg N eq
HT	Human toxicity	kg 1,4-DB eq
POF	Photochemical oxidant formation	kg NMVOC
FET	Freshwater ecotoxicity	kg 1,4-DB eq
IR	Ionizing radiation	kBq U235 eq
ALO	Agricultural land occupation	m^2a
ULO	Urban land occupation	m^2a
WD	Water depletion	m^3
MD	Metal depletion	kg Fe eq
FD	Fossil depletion	kg oil eq

Social assessment

sLCA	Social life cycle assessment	
PSILCA	Product social life cycle assessment	
M_W	Minimum wage	
H_W	Working hours per employer	h/week
LW_H	Industrial water use – extraction	%
LW_R	Industrial water use – renewable water	%
E_B	Biomass extraction	ton/km^2
E_F	Extraction of fossil fuels	%

J_G	Employment generation	Jobs/year
P_{CO_2}	CO_2 eq footprint	%
sLCI	Social life cycle inventory	

Research disseminations

Research papers

Published

M. C. Garcia-Vallejo, T. A. Patiño, A. Poveda-Giraldo, S. Piedrahita-Rodríguez, C. Ariel, and C. Alzate, "Alternatives for the Valorization of Avocado Waste Generated in the Different Links of the Value Chain Based on a Life-Cycle Analysis Approach," Agronomy 2023, Vol. 13, Page 2229, vol. 13, no. 9, p. 2229, Aug. 2023, doi: 10.3390/AGRONOMY13092229.

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Submitted

M.C. Garcia-Vallejo, and C.A. Cardona Alzate, "Sustainability of hydrogen production towards a neutral carbon society" International Journal of Hydrogen Energy, Submitted date: 11/10/23

M.C. Garcia-Vallejo, and C.A. Cardona Alzate, "Prefeasibility analysis of biomass gasification and electrolysis for hydrogen production" Environmental research, Submitted date: 11/10/23

M. C. Garcia-Vallejo, and C. A. Cardona Alzate, "Comparative analysis of renewable technologies for hydrogen production using primary crop residues"**.** Energy, Submitted date: 08/11/23

M. C. Garcia-Vallejo, and C. A. Cardona Alzate, “Life cycle assessment of the cassava value chain in Colombia and the possible use of cassava residues as energy carriers". Industrial Crop and Product, Submitted date: 08/11/23

Under review - Articles

M. C. Garcia-Vallejo, and C. A. Cardona Alzate, "Comparative analysis of biological and electrolytic process for hydrogen production”**.**

M. C. Garcia-Vallejo, Jhonathan Moncada and C. A. Cardona Alzate, “Hydrogen overview”.

M. C. Garcia-Vallejo, Jhonathan Moncada and C. A. Cardona Alzate, “Energy balance in the replacement of the Colombian vehicle fleet by alternative energy carriers such as hydrogen”**.**

Books chapter

C.A. Cardona Alzate, C.E. Orrego Alzate, M. Ortiz-Sanchez, S. Piedrahita-Rodriguez, T. Agudelo Patiño and **M. C. Garcia-Vallejo**, " Samaná en la época de postconflicto: historia y restauración del tejido social," in Samaná, paraíso agroindustrial. Una sociedad progresando en el postconflicto.

C.A. Cardona Alzate, C.E. Orrego Alzate, M. Ortiz-Sanchez, S. Piedrahita-Rodriguez, T. Agudelo Patiño and **M. C. Garcia-Vallejo**, " Alternativas de aprovechamiento de la cadena de valor del plátano para un desarrollo sostenible," in Samaná, paraíso agroindustrial. Una sociedad progresando en el postconflicto.

Conference participation

M. C. Garcia-Vallejo, J.C. Solarte-Toro, and C. A. Cardona Alzate, “Bioenergy solutions for decentralized rural areas based on avocado waste conversion,” in World Sustainable Energy Days 2022, oral presentation, physical presence (Linz-Austria), 2022.

M. C. Garcia-Vallejo, J.A. Poveda-Giraldo, and C. A. Cardona Alzate, “Valorization alternatives of tropical forest fruits based on the açai (Euterpe oleracea) processing in small communities,” in World Sustainable Energy Days 2023, oral presentation, physical presence (Linz-Austria), 2023.

M.C. Garcia-Vallejo and C. A. Cardona Alzate, “Prefeasibility analysis of biomass gasification and electrolysis for hydrogen production,” 10th International Conference on Sustainable Solid Waste Management, oral presentation, physical presence (Chenia-Greece), 2023

Participation in research projects

Program: Reconstrucción del tejido social en zonas de posconflicto en Colombia" in the project "Competencias empresariales y de innovación para el desarrollo económico y la inclusión productiva de las regiones afectadas por el conflicto colombiano. 2022-2023. Funding: MinCiencias Position: Monitor and Co-researcher.

Project: Aprovechamiento y valorización sostenible de residuos sólidos orgánicos y su posible aplicación en biorrefinerías y tecnologías de Residuos-a-Energía en el departamento de Sucre". BPIN project 2020000100189, Contract CPSP No. 145-2022. 2022-2023. Funding: MinCiencias and Universidad de Sucre. Position: Co-researcher.

Project: Análisis de sostenibilidad de diferentes alternativas para la valorización de residuos de aguacate generados en diferentes eslabones de la cadena productiva con un enfoque de análisis de ciclo de vida. 2022-2023. Funding: Universidad Nacional de Colombia sede Manizales. Position: Co-researcher.

Thesis structure

Throughout this thesis, the reader will find the main and most important research project results framed in the Master of Engineering - Chemical Engineering program. For this purpose, six chapters structure the document and fulfill the objectives described in the initial proposal. Considering that the results of each objective are the input or starting point for the following objective, this research work was developed considering the following scheme: (i) to perform a literature review, (ii) to heuristic analysis of the main pathways and technologies available for hydrogen production, (iii) to heuristic analysis considering three potential raw materials for Colombia, specifically the Sucre region, (iv) evaluate at an experimental level four hydrogen production schemes, (v) propose and assessment four simulation schemes for hydrogen production considering experimental results and (vi) establish the sustainability of the simulation schemes considering technical, energetic, economic, social and environmental assessment. Therefore, the first two sessions (item (i) and (ii)) are characterized by a bibliographic analysis; then, in session (iii), experimental work is carried out to provide first-hand information for the development of the simulation schemes that are part of the session (iv) and end with a complete sustainability analysis of the scenarios, to establish the best hydrogen production scheme in the Colombian context. The writing of each chapter was based on original research articles published or currently submitted for journal acceptance to different publishers such as the Multidisciplinary Digital Publishing Institute (MDPI), Springer, and Elsevier. Therefore, besides the literature review, each chapter has an abstract, keywords, introduction, methodology, results, discussion, conclusions, and references. Finally, the paper includes general conclusions and future perspectives. The appendices at the end of the paper are part of the Supplementary Material enclosed with the research article (if applicable).

- Chapter 1: Hydrogen as an emerging energy carrier: An overview.
- Chapter 2: Heuristic analysis of pathways, technologies, and raw materials for hydrogen production.
- Chapter 3: Comparative analysis of renewable technologies for hydrogen production using primary crop residues.
- Chapter 4: Comparative analysis of biological and electrolytic processes for hydrogen production.
- Chapter 5: Sustainability of hydrogen production towards a neutral carbon society.
- Chapter 6: Life cycle assessment of the cassava value chain in Colombia and the possible use of cassava residues as energy carriers.

Introduction

The dependence over the years on fossil fuels as the main energy source has caused an energy crisis and multiple environmental problems [1]. United Arab Emirates has estimated the natural gas demand deficit in 2042, and the depletion of fossil fuels in Egypt in the coming decades [2],[3]. Excessive emissions of gases and other pollutants trigger significant environmental consequences. Based on reports by the International Energy Agency (IEA), in 2021, CO_2 emissions from combustion processes increased to 36.3 gigatons [4]. On the other hand, the Fourth Assessment Report (AR4) of the United Nations Intergovernmental Panel on Climate Change (IPCC) reports that since the middle of the 20th century, the constant increase in the concentration of greenhouse gases (GHG) has generated a global increase in the earth temperature [4]. Therefore, there is an effort to explore clean and renewable alternatives for sustainable development. These efforts potentialize changes directly associated with what different authors call "energy transition" [5]. The energy transition sets the basis for the exponential increase of new studies and the development of public debates to mitigate the global climate crisis and adapt to new energy scenarios.

Nowadays, discovering new alternative resources and systems of energy has become a challenge for academia and industry. The role played by hydrogen in this task was recognized by the IEA at the beginning of the 21st century [6]. Hydrogen is one of the most abundant elements on earth and combines easily with other chemical elements [7]. Currently, hydrogen is mainly used to produce methanol and ammonia. However, hydrogen production has become a topic of interest for multinational and international companies. Hydrogen is a clean fuel that does not generate toxic emissions and allows for reducing the environmental impact generated by the fossil fuel-based industry. Hydrogen demand reached 94 million tonnes (Mt) in 2021 and contained energy equal to about 2.5% of global final energy consumption [8]. Hydrogen can be produced from a wide range of feedstocks and processes, making hydrogen an important energy carrier for contributing to energy security. More than 95% of the hydrogen produced is derived from fossil fuels; the rest is from water electrolysis [9]. However, it is necessary to investigate other processes, such as biological and thermochemical processes, considering the environmental impact of petrochemical processes and the low energy efficiency of electrolytic processes.

Several technologies can be used to produce hydrogen, such as (i) fossil-fuel-derived technologies (steam reforming, partial oxidation, desulfurization), (ii) electrolytic (electrolysis and photoelectrolysis of water), (iii) thermochemical (gasification, pyrolysis, and co-pyrolysis), (iv) biological processes (direct and indirect bio photolysis, photo fermentation and dark fermentations) and (v) the catalytic processes. The last technologies are alternatives to fossil fuels and represent an opportunity for environmental improvement. However, it is only possible to consider the environmental perspective. For example, the water electrolytic process does not pollute, but its energy efficiency is low [10]. For this reason, processes must be evaluated from an environmental perspective and an economic and social perspective. In economic terms, thermochemical processes based on the use of biomass have advantages over other processes because they use and valorize as raw materials, materials considered waste by other industrial sectors [10]. In addition, thermochemical processes such as pyrolysis allow obtaining hydrogen and other high-value-added by-products (bio-oil, synthesis gas, and biochar) [11]. Biological processes focused on biomass treatment are also promising. Biomass is one of earth's most abundant renewable resources and has multifaceted importance. Biomass research is receiving considerable attention due to the possibility of converting waste into energy. Currently, biomass contributes approximately 12% of the world's energy supply. However, in many developing countries, this contribution is 40-50% [12].

Based on this, this work proposes a critical analysis of hydrogen transformation pathways, considering some technical, economic, and environmental aspects. It presents the development of a research project that begins with the heuristic analysis of the pathways, technologies, and raw materials available for hydrogen production. Then, four “technology + raw material” schemes were established and evaluated at the experimental level. With the data provided by the experimental tests, simulation schemes were developed in different software (Aspen, MatLab, and others), and an assessment of the sustainability of these scenarios was performed considering technical, energetic, economic, environmental, and social dimensions. Finally, the results of the evaluations allowed us to establish the feasibility of implementing such schemes in the Colombian context.

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Hypothesis

The use of process engineering strategies will demonstrate that there are more sustainable hydrogen production pathways than those currently used by industry.

Objectives

General Objectives

To propose sustainable hydrogen production schemes in the Colombian context

Specific Objectives

1) To evaluate under heuristic analysis strategies the transformation pathways for hydrogen production.
2) To evaluate the potential raw materials for hydrogen production based on different technology schemes.
3) To simulate and assess the selected hydrogen pathways.
4) To validate the selected technologies experimentally.
5) Assess and compare the proposed technology schemes based on technical, economic, energetic, and environmental perspectives.

Chapter 01: Hydrogen as an emerging energy carrier: An overview.

Abstract

The crucial to the energy transition that promotes a carbon-neutral society is the implementation of renewable energy sources, which requires numerous transformation processes in energy generation and consumption. At present, hydrogen is mainly used for the synthesis of chemicals. However, hydrogen presents numerous advances as a renewable energy carrier. Furthermore, with the growth of hydrogen-based studies and projects, its energy potential is expected to expand and be successfully applied in numerous industrial sectors in the coming decades. This article reviews the hydrogen production technologies and storage methods proposed so far. Additionally, some economic, environmental, and social aspects of hydrogen deployment are presented. Finally, hydrogen-producing countries and their energy development policies are discussed.

Keywords: *Hydrogen, renewable energies, energy transition, energy security, carbon-neutral society.*

1.1 Energy transitions throughout history

Throughout the ages, one of humanity's primary tasks has been the relentless quest for energy sources to harness. From prehistoric times, when humanity discovered fire, through the Middle Ages to the present day, fuels have played a central role in the development of society. However, in today's world, this society faces increasing dependence on fossil fuels, which are one of the largest contributors to the environmental crisis that we are facing. This situation compels the adoption of new energy sources that align with contemporary economic models, fostering energy security and reducing environmental impact.

1.1.1. The first energy transition: from wood to fossil fuels

The transition from wood products to fossil fuels, particularly oil, was driven by the urban and commercial development of the United Kingdom, notably after the discovery of substantial oil, gas, and coal reserves [1]. This shift began in the early 18th century and took over two centuries to establish fossil fuels as the world's primary energy source, completely replacing wood by the late 19th century. The adoption of fossil fuels varied across sectors, with British cities rapidly embracing coal during the first Industrial Revolution. Simultaneously, technological advances like the steam engine, initially powered by wood and coal, catalyzed industrial mechanization and automotive technology development [2], [3].

In the 20th century, internal combustion engines replaced inefficient and large steam engines, reshaping transportation through technological advancements. The transportation industry and oil extraction mutually fueled each other's growth. Major oil discoveries in the early 20th century lowered liquid fuel prices, increasing dependence on petrochemical-based fuels in various sectors, especially transportation, due to their widespread availability and distribution infrastructure. This dominance continued until the early 1970s, when environmental concerns related to fossil fuels became evident [1]. The global climate crisis prompted the establishment of commissions to explore renewable fuel options for reducing environmental impact. Additionally, the 1973-1974 "oil embargo" by OPEC members caused global economic repercussions, leading different countries, including Brazil, France, and the United States, to launch programs to reduce their energy sector's reliance on foreign oil to avoid similar crises.

1.1.2. Global energy transition efforts

Countries have sought to reduce fossil fuel dependence through energy transitions. For example, Brazil has used ethanol, derived mainly from sugarcane, as a transport biofuel since 1925 [4]. The 1970s oil crisis prompted Brazil, which imported 80 % of its oil, to focus on ethanol production. These moves not only decreased fossil fuel imports but also positioned Brazil as a major ethanol exporter. From 1975 to 2009, ethanol production grew from 0.9 million to 27 billion liters, creating over 700,000 jobs by 2004 and saving 110 million tons of carbon compared to gasoline [5]. In 1970, oil constituted 70 % of France's energy, with 72 % imported from the Middle East [6]. Post-energy crisis, France prioritized nuclear energy, constructing 58 reactors between 1971 and 2001, making it the world's second-largest nuclear energy producer. However, public concerns about safety and environmental effects led to widespread opposition. Regardless, France aimed to become a fully nuclear society. Following the 1977 energy recession, the U.S. introduced the "Independence Project" during Jimmy Carter's presidency to achieve energy self-sufficiency. The project focused on increasing domestic energy supply, developing new technologies, and emphasizing energy conservation. Despite significant efforts, the project didn't achieve its goals due to rising national oil and gas production, leading to increased oil imports [7].

1.2. Hydrogen: A versatile energy carrier

Hydrogen is considered an alternative fuel, but unlike fossil fuels, it is not a primary energy source. Hydrogen's role is defined as a "secondary energy carrier." Initially, hydrogen is produced from another energy source and then transported for consumption. Various renewable and non-renewable technologies can be employed to obtain hydrogen, and it has various applications in sectors such as transportation, industry, heating, electricity generation, and distribution systems utilizing internal combustion cells or turbines [8]. Furthermore, it can serve as a storage medium, thanks to its high energy density, providing three times more energy than gasoline per unit of mass [9].

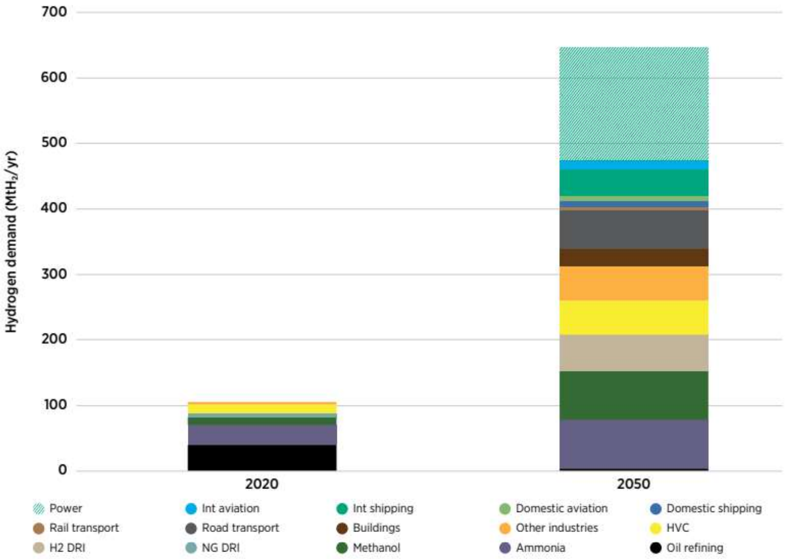
The importance of hydrogen as a potential energy carrier has grown in recent years. As a result, the most recent studies aim to investigate and optimize hydrogen production processes and systems [10]. Therefore, all these efforts are crucial for developing new technologies capable of addressing environmental issues without compromising global energy security. Hydrogen can be produced through processes like electrolysis of water, thermochemical processes at high temperatures, and biological processes involving biomass [11]. The diversity in production methods significantly contributes to energy supply security. Using hydrogen as an energy carrier could establish an unconventional energy chain encompassing production, storage, distribution, and energy utilization. However, for this chain to be considered renewable, it must include solar or other energy sources for hydrogen production. Following hydrogen production, a crucial aspect is its storage [12]. Consequently, research efforts emphasize improving hydrogen storage capacity. Several authors highlight that current hydrogen storage technologies do not meet the techno-economic feasibility of the process, and alternatives such as liquid, gas, or solid-phase hydrogen storage should be explored [13].

Once the issues related to hydrogen storage and safety are resolved, it becomes possible to ensure that a hydrogen-based economy can bring numerous environmental and economic benefits. The most compelling argument for promoting a hydrogen-based energy economy is its global potential to reduce CO_2 emissions. However, transitioning to a hydrogen-based energy system involves numerous scientific, technological, and socioeconomic challenges. A report published by the U.S. National Research Council and the National Academy of Engineering identifies three primary barriers to achieving a hydrogen-based economy, including (i) developing the necessary infrastructure for hydrogen supply to end-users, (ii) reducing hydrogen production costs from renewable sources over the long term, and (iii) capturing CO_2 as a by-product of certain hydrogen production processes [14]. These aspects pose significant challenges to the implementation of a hydrogen-based economy. Nevertheless, numerous efforts advocate resolving these difficulties to establish a sustainable energy system.

1.3. Hydrogen demand worldwide

The global demand for hydrogen is steadily increasing at an annual rate of 4 % to 6 % [15]. This increase in hydrogen consumption can be attributed to the refining and chemical synthesis sectors, where hydrogen plays a key role in lowering the sulfur content of conventional fuels and in the methanol and ammonia production processes, respectively. In addition, the increasing adoption of hydrogen contributes to reducing CO_2 emissions, as this long-term strategy aims to decouple economic and social growth from increased GHGs emissions by considering the use of low-carbon fuels such as renewable hydrogen. As a result, the hydrogen generation market is expected to exceed \$200 billion by 2023, up from \$115.25 billion generated in 2017 [16].

The development of alternative fuels as a global energy source is gaining widespread attention, particularly from the industrial sector. The focus on alternative fuels is also a response to the fluctuating value of oil, which creates uncertainties, particularly for industries heavily reliant on non-renewable fuels [17]. For this reason, demand for hydrogen in end-use sectors is expected to increase almost fivefold by 2050 (see **Figure 1.1**). Although there is a wide range of users for this demand, chemicals and transportation will be the main consumption sectors. First, demand for ammonia and methanol could increase three to four-fold, driven by growth in developing economies and their currently negligible use as fuels. In addition, for the transportation sector, uses of pure hydrogen to supplement electricity are emerging in the land transportation sectors, where the use of ammonia for international shipping and synthetic fuels for international aviation have become a priority. The remaining demand of 614 Mt H_2/year would come from the power sector to meet the need for flexibility and thermal generation to offset fluctuations in variable renewable energy and complement other flexibility measures. Finally, for steel, demand remains uncertain as key decarbonization technologies, such as direct hydrogen-reduced iron and carbon capture and storage, have yet to be tested and deployed on a large scale [18].



Note: Hydrogen demand for 2020 excludes hydrogen as part of the mix of off-gases for steel production. DRI = direct reduced iron; HVC = high-value chemicals; Int = international; NG = natural gas.

Figure 1.1. Hydrogen demand by application in 2020 and 2050 [18].

Today, China is the world's largest hydrogen consumer, with some 24 Mt H_2/year in 2020 [19]. In addition, the country produces about a quarter of the world's hydrogen used for refining, hosting a quarter of the world's ammonia production and more than half of the world's methanol and steel production. By 2050, China is expected to remain a leading country in the industrial sector, including developing new applications for emerging energy carriers such as hydrogen. This way, China could retain about a quarter of the world's hydrogen demand driven by its industrial sector. In addition to China, the second country with the highest demand would be India, where steel production is expected to quadruple by 2050; combined with one of the world's largest iron ore reserves and low-cost renewable electricity, it opens the opportunity to use electrolytic hydrogen for direct iron reduction [20]. Finally, the third country with the highest demand would be the United States of America, which would increase from 10 Mt H_2/year to more than 30 Mt H_2/year in 2050, focusing on the transportation sector. Thus, hydrogen demand in 2050 is expected to be concentrated in the world's top ten countries, accounting for about two-thirds of global consumption (see **Figure 1.2**).

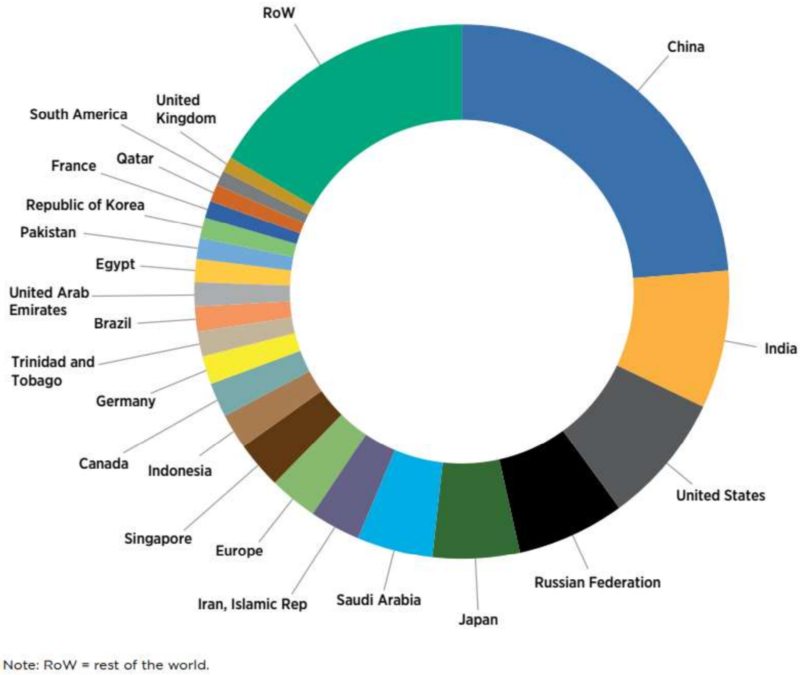


Figure 1.2. Hydrogen demand by country in 2050 in a 1.5°C scenario [18].

1.4. Hydrogen production technologies

Hydrogen production can be achieved through several technologies. The first one involves hydrogen production from fossil fuels, the primary source of natural gas. Moreover, "green" hydrogen production is linked to the electrolytic decomposition of water, as well as thermochemical and biological processes. This so-called "green" hydrogen necessitates production from renewable energies like solar, geothermal, wind, and sea (tidal) sources. **Table 1.1** displays the most extensively researched hydrogen production technologies and their corresponding efficiencies.

Table 1.1. Technologies used for hydrogen production and their efficiency.

Technology	Raw materials	Yield (Y_{H_2O})	Remarks	Ref.
		Hydrogen production from fossil sources		
Steam methane reforming (SMR)	Methane	84.5% at 700°C	Hydrogen and syngas production using Zr, Co, and Ca-based catalysts.	[21]
Partial oxidation (POX)	Hydrocarbons	55.0% at 230-300°C	Hydrogen production using ZnO-based catalysts.	[22]

Autothermal Reforming (ATR)	Hydrocarbons	30.0% at 430-530°C	Autothermal reforming is optimal at 730°C and with molar ratios of air: methane/steam at 2.	[23]
Plasma reforming	Hydrocarbons	50-75% at 700-800°C	Using plasmatrons with better thermal insulation, efficient heat regeneration, and improved plasma catalysis can reduce the specific energy consumption in the process.	
Hydrogen production from the electrolysis process				
Electrolysis	Water	50-60%	Hydrogen production with proton exchange membrane	[24]
Photoelectrolysis	Water	55-70%	Hydrogen production by TiO_2 photoelectrodes	[25]
Thermochemical water splitting	Water	20-45%	Hydrogen production using nuclear heat from a high-temperature gas-cooled reactor (HTGR)	[26]
Hydrogen production from thermochemical processes				
Pyrolysis	Biomass	51.0% at 750-800°C	Hydrogen production from waste biomass with fixed-bed reactors	[27]
Co-pyrolysis	Biomass	89-97% at 600°C	Utilization of highly oxygenated and volatile pyrolysis oils from biomass residues as sustainable liquid fuels for conversion to a hydrogen-rich gas	[28]
Gasification	Biomass	15% at 800°C	Hydrogen production by catalytic Gasification of biomass at low to high temperatures	[29]
Hydrogen production from biological processes				
Biophotolysis	Biomass	16.8 %	Hydrogen production by Microalgal photosynthesis	[30]
Photofermentation	Biomass	25.0 %	Hydrogen production by photo fermentation of tequila vinasses	[31]
Dark fermentation	Biomass	4.4 %	Hydrogen production by dark fermentation using mixed cultures and anaerobic sludge from wastewater	[32]
Microbial electrolysis cells	Biomass	0.1%	Production of hydrogen from residues biomass in a pilot-scale	[33]

* Mass yield

A more detailed explanation of the different processes from various sources is presented below.

1.4.1. Hydrogen from petrochemical processes

Technologies for hydrogen production from fossil fuels convert hydrocarbon-rich materials into hydrogen-enriched streams. The most widely applied commercial hydrogen production technology is steam methane reforming (SMR). On the other hand, gaseous hydrogen can be produced from hydrocarbon combustion using two technologies: (i) partial oxidation (POX) and (ii) autothermal reforming (ATR), accompanied by desulfurization processes. This last process is justified due to the considerable amount of sulfur contained in hydrocarbons. The technologies mentioned above are characterized by the production of high levels of carbon monoxide (CO). These significant amounts of CO are treated by processes such as (i) water gas shift (WGS) and methanation to transform CO into CO_2. Finally, the last noteworthy technology is plasma reforming, where the energy source is electric.

a. Steam methane reforming (SMR)

SMR is the most widely used and cost-effective process for hydrogen production, owing to its high efficiency and low operating costs. In this process, natural gas and low molecular weight hydrocarbons serve as feedstock. The process can be divided into two stages. In the first stage, hydrocarbons are introduced into a tubular reactor with temperatures ranging from 500°C to 900°C [34]. This reactor is equipped with a catalyst, either non-precious (nickel) or precious (group VIII) metals, selected based on the process's heat and mass transfer limitations. It's important to note that the initial raw material should not contain significant sulfur content, as such amounts of sulfur can adversely affect the catalytic process and, consequently, the overall performance. Hence, a desulfurization process is conducted before the hydrocarbons are converted into hydrogen [35]. During this first stage, synthesis gas and small amounts of CO_2 are produced (Eq. 1.1 and 1.2). Subsequently, the second stage involves taking the products from the first stage to a boiler to generate steam and a condenser to convert CO into CO_2, considering the water gas shift reactions (WGS) (Eq. 1.3).

$$C_mH_n + mH_2O_{(g)} \rightarrow mCO + (m + 0.5n)H_2 \qquad \text{Endothermic} \qquad \text{(Eq. 1.1)}$$

$$C_mH_n + 2mH_2O_{(g)} \rightarrow mCO_2 + (2m + 0.5n)H_2 \qquad \text{Endothermic} \qquad \text{(Eq. 1.2)}$$

$$CO + H_2O_{(g)} \rightarrow CO_2 + H_2 \qquad \text{Exothermic} \qquad \text{(Eq. 1.3)}$$

b. Partial oxidation (POX)

Hydrocarbon POX has been regularly proposed as a technology for hydrogen production. The feedstocks employed in this process include methane, biogas, and hydrocarbon fractions with high molecular weights. The feedstock undergoes gasification within an oxygen and steam-rich environment (as per Eq. 1.4 to 1.6) [36]. The process is conducted at elevated temperatures (1300°C to 1500°C) and high pressures (between 3 MPa and 8 MPa). The high temperatures and safety-related issues render this technology less suitable for manufacturing portable devices, as these challenges are often linked to thermal management concerns.

$CH_4 + O_2 \rightarrow CO + 2H_2$ Exothermic (Eq. 1.4)
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(g)}$ Exothermic (Eq. 1.5)
$CH_4 + H_2O_{(g)} \rightarrow CO + 3H_2$ Endothermic (Eq. 1.6)

In the POX process, the resulting gaseous mixture contains CO, CO_2, H_2O, H_2, CH_4, and small traces of H_2S. Compared to the SMR method, the POX process produces a higher amount of CO. Additionally, the process yield, similar to SMR technology, relies on the H/C ratio of the feedstock. The higher this value, the greater the process yields. The thermal efficiency of the industrial-level process is comparable to that of the SMR process, reaching between 60 % and 75 % [37].

c. Autothermal Reforming (ATR)

The ATR process is a derivation of the POX process, but contrary to POX, steam is added to the oxidation process, and catalysts are used. The ATR process is a combination of the SMR and the POX process (Eq. 1.7). Among the advantages of this process are that (i) it does not require external heat, (ii) it is an operationally simpler process, and (iii) it has lower costs than the SMR process [38]. However, in the ATR process, the selection of the operating conditions depends on the specific objective of the process. Among the current expectations of this technology is its applicability in producing gas-to-liquid fuels. The thermal efficiency of the process is comparable to the efficiency of the POX process and can reach values between 60 % and 75 % [39].

$CH_4 + H_2O_{(g)} + O_2 \rightarrow 3CO + 7H_2$ Exothermic (Eq. 1.7)

d. Water-gas shift (WGS)

The above processes can be modified by adding gas or eliminating CO. In the WGS process, H_2O and CO are transformed into CO_2 and H_2 using a steam reaction at high temperatures (400°C to 500°C). The presence of catalysts allows the consumption of CO until concentrations below 0.5% molar are achieved (Eq. 1.8) [38]. Kinetic parameters govern this process and involve an increase in temperature to achieve close to 90 % CO conversions. Finally, the resulting trace CO can be used as catalysts in mechanization processes (Eq. 1.9 and 1.10). These reactions allow the highest CO consumption. However, these reactions also involve a moderate consumption of H_2, which can lead to a lower overall yield.

$CO + H_2O_{(g)} \rightarrow CO_2 + H_2$ Exothermic (Eq. 1.8)
$CO + 3H_2 \rightarrow CH_4 + H_2O_{(g)}$ Exothermic (Eq. 1.9)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O_{(g)}$ Exothermic (Eq. 1.10)

e. Plasma reforming

The reactions that occur during the plasma reforming process are the same reactions performed in the SMR process (Eq. 1.1 to 1.3). However, the free radicals and energy used during the reactive steps come from plasma. This plasma is generated with heat or electricity [40]. Once steam is introduced to the reactor where the hydrocarbons are located, H·, O·, and OH· radicals are produced. Additionally, electrons are released into the reactive medium, and the presence of these electrons, together with free radicals, causes oxidation and reduction reactions. Two scenarios can occur during plasma reforming: (i) thermal plasma reforming and (ii) non-thermal plasma reforming [41].

Plasma reforming often uses equipment called "plasmatrons." These devices can reach temperatures over 1,900°C. The heat generated during the process is independent of the operating conditions of the reactive medium. This phenomenon is made possible by the high energy density associated with the plasma and the reaction times used. Generally, in these processes, the reaction time is sufficiently short. Plasmatrons can produce hydrogen-rich gas streams from various hydrocarbons, achieving values close to 99.9 %. Plasma reforming technology has competitive advantages over conventional technologies, focusing on process conditions that allow high temperatures and high conversion rates because the reactions are thermodynamically favored. Additionally, the devices used under this technology are usually low cost, low weight, and have short response times. This gives them some flexibility and ease of transport [57]. Among the disadvantages of this process are (i) the dependence on electricity and (ii) the operational difficulty encountered in processes requiring high pressures. These problems derive from the possible electrode erosion due to technical problems, reducing its useful life.

1.4.2. Hydrogen from electrolytic processes

Electrolysis, photoelectrolysis, and thermochemical water splitting are promising technologies for long-term hydrogen production. About 5 % of the hydrogen produced worldwide is obtained from electrolysis processes. The electrolysis process involves a direct current of electricity through two electrodes (anode and cathode), causing the breaking of bonds in the water molecule (Equation 1.11).

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \text{Endothermic} \qquad \text{(Eq. 1.11)}$$

Electrolytic processes that focus on the breakdown of the water molecule occur at room temperature. The most frequently used electrodes are stainless steel or platinum. The process is characterized by zero-emission of pollutant gases, significantly mitigating the greenhouse effect. However, this technology presents one of the major disadvantages at the operational level: high energy consumption and the energy efficiency of electrolysis processes range from 50 % to 70 % [42].

a. Electrolysis

Electrolysis is one of the few technologies currently used at the industrial level. Water decomposition (Eq. 1.12 and 1.13) is a method that has been known for many years. However, its energy efficiency is low compared to previously described methods (technologies derived from petrochemical processing). This low energy efficiency is due to energy conversion. In electrolysis processes, electrical energy is converted into chemical energy (H_2), which leads to high electricity consumption. The most used electrolysis technology is alkaline. However, new technologies such as solid oxide electrolysis (SOEC) and proton exchange membranes (PEM) have been developed [43]. Electrolysis using PEM is the technology with the best electrical efficiency and the least corrosion problems. However, alkaline electrolysis is still the most widely used due to its lower capital investment cost.

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ Cathode (Eq. 1.12)

$4OH^-_{(aq)} \rightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$ Anode (Eq. 1.13)

b. Photoelectrolysis

Photoelectrolysis is one of the renewable technologies that are still under experimental development. Nevertheless, it is currently considered the least expensive and most efficient electrolysis method for hydrogen production. In this process, the electrodes used are called photoelectrodes. They are devices that absorb sunlight, converting it into available energy to generate a voltage used in water decomposition (Eq. 1.12 and 1.13) [44]. Photoelectrodes are composed of semiconductor layers, a catalyst, and protective layers. These layers can be fabricated from different materials; however, each layer directly influences the overall efficiency of the process, so an appropriate choice of materials must be made. Nevertheless, since this process has no direct dependence on electrical energy, it presents a better renewable alternative for hydrogen production.

c. Thermochemical water splitting

Thermochemical water splitting, also called thermolysis, is based on the same principle of water decomposition. As in electrolysis, chemical reactions decompose water into H_2 and O_2. These chemical reactions start under the medium's induction of heat or electrical energy, and water decomposes at elevated temperatures (>2,500°C). These temperatures cannot be reached with currently available materials. Therefore, high pressures are used to lower the operating temperature. Different thermochemical cycles have been developed to describe the water decomposition process. However, despite their variability, all agree that the chemical reagents are reused during the process, and only the raw material (water) is continuously fed. During the decomposition of the water, H_2, O_2, and a small fraction of heat are obtained as by-products. Several authors report that this process can achieve efficiencies close to 40-50% [45]. Compared to the traditional electrolysis process, this process has advantages concerning electrical efficiency. However, thermochemical cycles have serious disadvantages; among them, the high operating conditions and the corrosion problems associated with the acids produced prevent this technology from competing economically. For this, it is necessary to develop new materials that are more resistant and do not have high initial investment costs.

1.4.3. Hydrogen from thermochemical processes

Biomass is a renewable resource that can be transformed into energy. Biomass is usually divided into four categories: (i) energy crops (woody, agricultural, industrial, and aquatic crops), (ii) agricultural residues, (iii) forestry residues, and (iv) industrial and municipal residues. These renewable resources present different types of composition and characteristics, which can be used for energy production. Among the processes used for biomass utilization are thermochemical processes, including pyrolysis and gasification. Thermochemical processes often involve the combustion of biomass in an oxygen-limited environment. The purpose of this process is to transform the chemical energy of the biomass into heat, electricity, or mechanical energy. These processes are characterized by low energy efficiencies (15% -60 %) [46]. For this reason, the by-products of the process tend to be valorized (bio-oil, synthesis gas, and biochar), and in recent years, catalysts have been used to improve hydrogen production. **Table 1.2** presents various feedstocks used during thermochemical processes for hydrogen production.

Table 1.2. Hydrogen production from the thermochemical processing of biomass.

Raw material	Catalyst used	Hydrogen production	Ref.
Pyrolysis and co-pyrolysis*			
Rice straw	Cr_2O_3	15.3% at 500°C 22.7% at 850°C	[47]
Sawdust	Cr_2O_3	17.6% at 500°C 28.8% at 850°C	[48]
Agricultural and forest residues	UCI G-91	60.0% at 750°C	[49]
Gasification**			
Sawdust	Na_2CO_3	48.3% at 700°C 59.8% at 900°C	[50]
Wood	Not used	7.70% at 550°C	[51]
Almond shell	Perovskite	63.7% at 900°C	[52]
Aqueous Phase Reforming			
Wheat straw	Pt 5% on activated carbon	44.5% at 250°C	[53]
Wood	Pt/Al_2O_3	0.02% at 280°C	[54]
Sorghum	Cr	0.24% at 270°C	[55]

NR: Not reported * Mass yield ** Volumetric yield

a. Pyrolysis and co-pyrolysis

Pyrolysis is heating biomass from 450°C to 800°C without oxygen and under moderate pressures of 0.1 MPa to 0.5 MPa [46]. Pyrolysis can be classified as (i) slow pyrolysis, (ii) flash pyrolysis, and (iii) fast pyrolysis. Slow pyrolysis is characterized by the fact that it is used for charcoal production. Therefore, this technology is not considered for hydrogen production. Then, there is fast pyrolysis, a high-temperature process that generates different products. The main products of fast pyrolysis are (i) gaseous products such as H_2 and CH_4, (ii) liquid products such as bio-oil, and (iii) solid products such as charcoal and biochar. Fast and flash pyrolysis allows hydrogen to be obtained directly under specific operating conditions. These conditions are associated with high temperatures and short reaction times. Biomass is exposed to high temperatures, generating gaseous products. Among these gaseous products is methane, which can be converted to hydrogen by steam reforming (Eq. 1.1), and to increase hydrogen productivity, WGS reactions can also be carried out (Eq. 1.8). Additionally, to gaseous products, liquid products can also be processed for hydrogen production [56].

b. Gasification

Gasification technology is classified as a variation of pyrolysis because it occurs in the presence of O_2 and is understood as a partial oxidation process of biomass. The main product of this process is a mixture of gases enriched in $H_2, CH_4, CO_2,$ and N_2, known as syngas [51]. The gasification process requires biomass with a moisture content of less than 35 % because the high moisture content in the feedstock is directly associated with low thermal efficiency. In gasification processes, one of the main problems is tar formation. The formation of this product favors polymerization reactions that do not promote hydrogen formation. Currently, different methodologies have been developed to reduce tar formation. These methodologies are based on the control of operating conditions and the addition of catalysts. Another problem associated with gasification processes is ash formation. High ash content in the reactor can cause fouling, deposition, sintering, and agglomeration problems. These problems are usually solved using reactor ash fractionation and leaching processes. Despite these drawbacks, hydrogen can be obtained among the gaseous gasification products, and hydrogen productivity is associated with steam reforming and WGS reactions in the reactor. To optimize hydrogen production, many authors suggest using a fluidized bed reactor, where it is possible to reach yields of 60 % for hydrogen [57]. These conversion levels make the gasification process an attractive alternative for hydrogen production from biomass. Additionally, the operating costs for hydrogen production by gasification are competitive with the SMR process, which is the most widely applied at the industrial level.

c. Aqueous Phase Reforming (APR)

Aqueous phase reforming is a technology that is still under development. This technology processes oxygenated hydrocarbons from biomass to produce hydrogen. APR reactions occur at low temperatures from 220°C to 270°C [58]. Low temperatures minimize decomposition reactions, which are undesirable during the process, and WGS reactions are favored at low temperatures, increasing hydrogen productivity. An operational advantage of the APR process is the formation of H_2 and CO_2 with small fractions of CO. Proponents of this technology focus on using platinum (Pt) and nickel (Ni) catalysts to maximize the hydrogen yield. The Pt catalyst is considered for its high catalytic activity, and the Ni catalyst for its low cost [59]. The correct selection of this catalyst allows for minimizing the methanation reactions that promote the formation of undesirable products. Additionally, the catalyst must be stable since APR reactors are usually large, and the durability of the catalyst can have serious economic and environmental effects. Finally, these processes can achieve yields of up to 55 %, as reported by Cortright et al. [60].

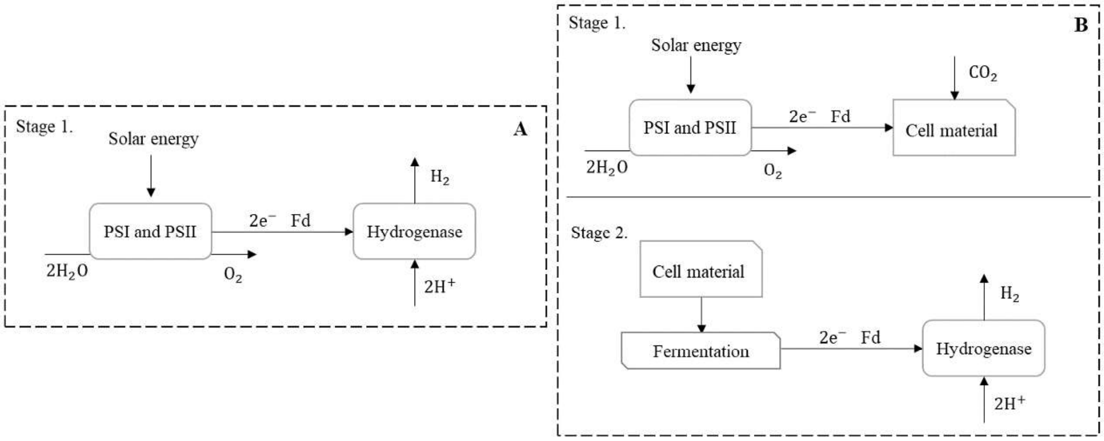
1.4.4. Hydrogen from biological processes

The biological production of hydrogen is a process that has been known for a long time. However, these processes have generally been carried out at a laboratory scale and occasionally scaled up to industrial processing. Biological hydrogen production can be realized using different technologies: (i) direct or indirect biophotolysis, (ii) biological water gas shift, (iii) photofermentation, (iv) dark fermentation, and (v) microbial electrolysis. The enzymatic behavior of hydrogenases and nitrogenases governs these processes. Hydrogenases are enzymes capable of producing and consuming hydrogen simultaneously, whereas nitrogenases only produce hydrogen (Eq. 1.14-1.16). These processes need to be commercially developed, and further research needs to be conducted to apply them easily.

$H_2 \rightarrow 2e^- + 2H^+$	Hydrogenase (absorption)	(Eq. 1.14)
$H_2 \leftarrow 2e^- + 2H^+$	Hydrogenase (reversible)	(Eq. 1.15)
$4ATP + 2H^+ + 2e^- \rightarrow H_2 + 4ADP + 4Pi$	Nitrogenase	(Eq. 1.16)

a. Direct or indirect bio photolysis

The production of hydrogen by photosynthetic processes is called biophotolysis. This photosynthetic system uses microalgae to take advantage of solar energy and turn it into chemical energy. The chemical energy is then used to fractionate the water molecules to produce hydrogen (Eq. 1.17). Hydrogen production by photosynthetic processes can be classified as direct or indirect (see **Figure 1.3**) [61].



A) Direct B) Indirect

Figure 1.3. Schematic of the biophotolysis process [46].

The direct processes are divided into two stages: (i) a system (PSI) and (ii) a system (PSII). The first system is responsible for the reduction of CO_2, and the second is responsible for the fractionation of water molecules. The most used microorganisms for these processes are cyanobacteria containing hydrogenase enzymes. However, these processes usually present low efficiencies (around 5 %) because the enzyme is sensitive to the amount of O_2 in the medium. To improve hydrogen productivity by hydrogenases, the O_2 concentrations must be less than 0.1 % [62]. This condition is satisfied when mutant microorganisms, which present greater tolerance to the presence of O_2 in the medium, are used. However, even with mutant microorganisms, the highest efficiency reported has been 15 % [63]. These values are low compared to other hydrogen production processes. Given the above, it is considered a technology still in development.

$$H_2O \rightarrow^{\text{Solar energy}} 2H_2 + O_2 \qquad \text{(Eq. 1.17)}$$

Indirect biophotolysis processes usually involve more steps than direct processes (Eq. 1.18 and 1.19). These stages are usually referred to as (i) biomass production from photosynthetic processes, (ii) biomass concentration, and (iii) dark and anaerobic fermentation. The last stage involves the production of hydrogen and acetates. Then, these produced acetates are also converted into hydrogen. Different from direct processes, indirect processes depend on the medium's pH. Several authors have reported that the optimum pH for hydrogen production is between 6.8 and 8.3 [64]. Currently, the major disadvantage of this process is the high investment costs. However, it is expected that these costs will be reduced with the optimization of the process due to advances in research.

$$6H_2O + 6CO_2 \rightarrow^{\text{Solar energy}} C_6H_{12}O_6 + 6O_2 \qquad \text{(Eq. 1.18)}$$
$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2 \qquad \text{(Eq. 1.19)}$$

b. Biological water-gas shift

The water-gas shift process at the biological level is a process that is still under development. So far, this process has only been performed on a laboratory scale. These processes take advantage of the ability of some microorganisms to survive in environments where only CO is available as a carbon source. Among these microorganisms is the heterotrophic bacterium *Rhodospirillum rubrum*. This microorganism can survive in the dark by using CO to produce ATP. The hydrogen production process occurs under anaerobic conditions and is initiated by the oxidation of CO. The electrons produced during this oxidation are utilized by hydrogenase for hydrogen production. The process occurs at low temperatures and is conditioned by thermodynamic phenomena resulting from the production of H_2 and CO_2 [65]. The rate of transformation of substrates into products is high in comparison with other biological processes. However, the limiting step of the process is microbial growth. Biomass concentration requires the presence of light, which suppresses hydrogen production. Another disadvantage of the process is ensuring the sterility of the medium; if the reactor becomes contaminated, aseptic processes must be carried out in the shortest possible time.

c. Photo fermentation

Photofermentation processes are based on the conversion of biomass into H_2 and CO_2. These processes are developed from photosynthetic bacteria that use solar energy to convert carbohydrates. Photosynthetic bacteria use nitrogenases to produce hydrogen from biomass and hydrogenases to recycle some of the hydrogen produced to support microbial growth. The operating conditions of the processes are anaerobic environments; temperatures range from 30 °C to 35 °C and require a neutral pH [38]. Recently, feedstocks from waste biomass have been used for photofermentative hydrogen production. Some examples of hydrogen production from industrial and agricultural wastes are given in **Table 1.3**. The efficiency of these processes differs in wide ranges, largely due to the availability of the substrate present in the biomass. Despite the possibility of using residual biomass, it is not a technology that presents competitive results. The major difficulties with photofermentation are (i) the use of the enzyme nitrogenase, which presents high energy demand; (ii) the demand for large equipment for the photofermentative process; and (iii) the low efficiency in solar energy conversion. These drawbacks suggest that the technology is still under development.

Table 1.3. Hydrogen production from residual biomass.

Raw material	Bacterial System	Hydrogen yield	Ref
Rice straw	*Rhodopseudomonas palustris*	0.014% w	[66]
Cornstalk	*Rhodospirillum rubrum*, *R. pulastris*, *Rhodobacter sphaeroides*, *R. capsulata*, and *Rhodobacter capsulatus*	0.012% w	[67]
Corn cob	*Rhodospirillum rubrum*, *Rhodopseudomonas palustri, and Rhodobacter capsulatus*,	0.008% w	[68]
Corn straw	*Rhodospirillum rubrum*, *Rhodopseudomonas capsulate*, and *Rhodopseudomonas palustris*	0.012% w	[69]
Sorghum stover	Photosynthetic bacteria isolated from silt sewage, pig and cow manure	3.34 %vol	[70]
Soybean stalk	Photosynthetic bacteria isolated from silt sewage, pig and cow manure	2.90% vol	[70]
Bagasse	*Rhodobium marinum* (Sanur)	0.005% vol	[71]
	Rhodobacter sphaeroides S10	0.0224% vol	[72]

d. Dark fermentation

These fermentations are carried out with anaerobic bacteria, microalgae, and green algae that survive in a very wide temperature range (30 °C and 80 °C) and can produce hydrogen in dark conditions [73]. The most efficient microorganisms for hydrogen production are *Clostridium* sp, *Bacillus* sp, *Enterobacter aerogenes*, and *Enterobacter cloacae*. The biomass used during fermentation must be biologically easy to degrade and have a high carbohydrate content (an example is glucose, which has as end products acid acetate Eq. 1.20 and butyrate Eq. 1.21). The main products of dark fermentation are H_2 and CO_2. In smaller quantities, other gases, such as CH_4 and H_2S, can also be produced. The productivity of hydrogen depends on the operating conditions of the medium. Among these conditions, pH has a very important role to play. To promote the production of H_2, it is necessary to maintain the pH at values between 5 and 9 [74]. On the other hand, once H_2 starts to concentrate in the medium, it is necessary to extract it to inhibit the production of reduced substrates. The efficiencies reported for dark fermentative processes are higher than those reported for other biological processes (Biophotolysis). This suggests an increase in commercial value, even though it is not widespread technology on an industrial scale.

$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$ (Eq. 1.20)
$C_6H_{12}O_6 + 2H_2O \rightarrow (CH_2)_3OOH + 2H_2 + 2CO_2$ (Eq. 1.21)

e. Microbial electrolysis cells (MEC)

Microbial electrolytic cells are one of the most recent biological processes for hydrogen production. These processes are carried out in microbial reactors, which transform the raw material directly into hydrogen using electrochemical phenomena. A MEC is recognized as a modified fuel cell. This cell can decompose organic matter in an anaerobic environment to produce hydrogen. During the process, protons, electrons, and CO_2 are produced. The protons travel through the proton membrane, and the electrons travel through the electrical resistance to the cathode, where hydrogen is produced (Eq. 1.20 to 1.23). Among the advantages of this technology is the production of pure hydrogen. Some authors report the possibility of obtaining hydrogen with a purity of 99.5 % [75].

$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^-$ Anode (Eq. 1.22)
$8H^+ + 8e^- \rightarrow 4H_2$ Cathode (Eq. 1.23)

1.4.5. Hydrogen from alternative processes

a. Hydrogen production from non-conventional feedstocks

During biodiesel production, glycerol is one of the most produced by-products. Given the above, authors like Dave et al. [76] have reported processes to produce hydrogen by steam reforming glycerol using Ni-based catalysts promoted by Zr and supported on Ce. This opens the possibility of using glycerol as a feedstock for hydrogen production. Another unconventional feedstock that has demonstrated its applicability for hydrogen production is urea. Some authors have reported using this feedstock to produce hydrogen and other value-added compounds, such as nitrogen, by electrochemical oxidation processes in alkaline media [77]. The process of oxidation of urea to hydrogen presents a beneficial alternative in economic terms since pure hydrogen can be obtained with low energy consumption and moderate operating conditions. Additionally, these processes involve the production of nitrogen and water as non-polluting and commercially valuable by-products.

Moreover, cheese whey is a waste product of the dairy industry, rich in soluble carbohydrates that can be used as a raw material for hydrogen production. Lactose contains proteins, lipids, and mineral salts. Given its composition, some studies suggest using cheese whey for hydrogen production using continuous reactors such as CSTR. Venetsaneas et al. [78] explore the potential exposure of cheese whey for energy recovery in gaseous fuels such as H_2 and CH_4. Finally, hydrogen sulfide (H_2S) is a common by-product of the petrochemical industry arising from natural gas processing and other processes associated with refineries. To treat H_2S, the

Claus process, where the hydrogen produced during the partial oxidation of H_2S to S is wasted, has been used. Given the above, some authors have proposed recycling hydrogen, avoiding direct water oxidation. Another option studied for hydrogen production is the catalytic decomposition of H_2S on semiconductor photocatalysts. Authors such as Bai et al. developed CdS nanoparticles to decompose H_2S with hydrogen production rates of 24 mmol/g h [79].

b. Ammonia Reforming

A final process recently used for hydrogen production is Ammonia reforming. This process is most frequently applied in manufacturing fuel cells for portable energy functions. Ammonia is known for its use in fertilizer production, and this phenomenon ensures a comprehensive distribution system in the world, circumventing logistic and feedstock supply problems. However, PEM fuel cells face a technological challenge involving reducing ammonia concentration to ppb in the acid electrolyte to ensure its lifetime. Prolonged exposure of the electrolyte to ammonia at high concentrations causes severe impairments in battery performance as the damage is cumulative because of ammonia agglomerates in the electrolyte [80].

c. Power to hydrogen

Power to Hydrogen (PtH) is based on using electrical energy to drive electrolysis, separating water into its constituent hydrogen and oxygen molecules. The hydrogen can then be stored as a high-pressure gas, cryogenic liquid, or metal hydride for transport and subsequent use in fuel cells or combustion technologies for power generation. In addition, PtH serves as a precursor to electrify the production of chemicals such as methanol and ammonia. Power to Methanol (PtM) extends the PtH concept by combining hydrogen with CO_2 to synthesize methanol. Methanol is easily stored in liquid form and can produce energy by decomposing it into hydrogen or using it directly in fuel cells. In addition, CO_2 for PtM can be obtained from several sources, including capturing pollutant gases from conventional processes or directly from the air. Additionally, Power to Ammonia (PtA) is another PtH extension that combines hydrogen with nitrogen separated from the air. Like methanol, ammonia can be easily stored in liquid form to generate electricity and heat using fuel cells or combustion technologies [81]. **Figure 1.4** outlines the relevant PtA and PtM technologies described and their interconnections.

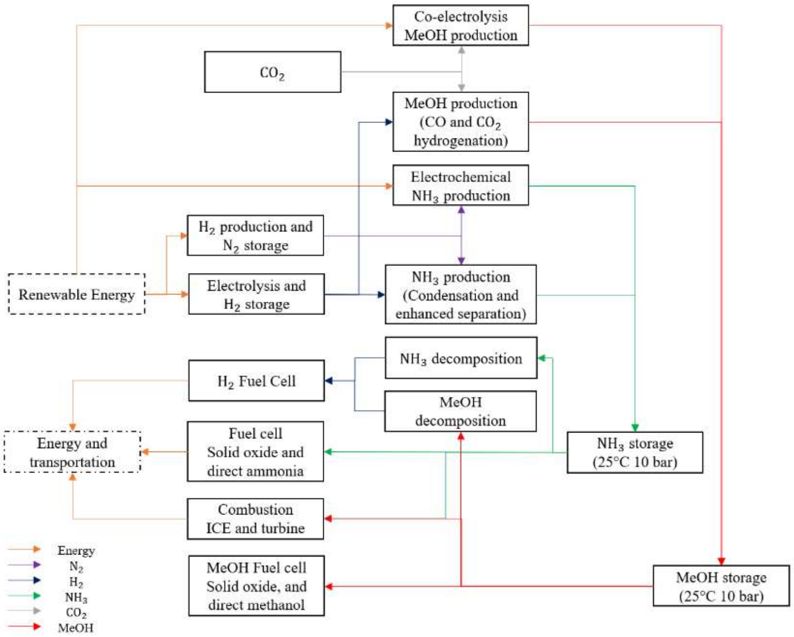


Figure 1.4. Conceptual technology outline for electrified ammonia and methanol production and utilization in energy and transportation.

1.5. Technology for hydrogen separation and recovery

Separating and recovering the main product in chemical processing is usually one of the costliest steps. Technologies such as pressure swing adsorption (PSA), cryogenic distillation, and membranes are used for hydrogen recovery. The PSA process is directly dependent on the adsorbents used, and the higher the adsorption capacity, the higher the contaminant capture and the purer the main product. PSA processes can reach purities of 99.99 % for hydrogen. However, the major disadvantage of PSA processes is their operability only at medium and large scales [82]. The cryogenic distillation process is performed at temperatures below 0 °C and takes advantage of the difference between the boiling temperatures of the fed substances to perform their separation. However, compared to PSA processes, cryogenic distillation achieves limited hydrogen purities. The hydrogen purity reported for cryogenic distillation is 90 % to 98 % [83].

Meanwhile, membrane-based technology allows hydrogen recovery from low-or high-pressure streams. Membrane technology has the lowest capital cost due to its low energy consumption, and the most used materials for fabricating these membranes are polymers such as (i) polysulfide and (ii) cellulose acetate. The development of polymeric membranes focuses on improving the selectivity of the material towards the product based on the size difference of the molecules [84]. However, one of the disadvantages of polymeric membranes is their inability to resist aggressive chemical environments characterized by high pressures and temperatures. Furthermore, extreme operating conditions cause compaction of the polymer, reducing its permeability and accelerating its deterioration. Given the above, membranes based on inorganic compounds have been proposed recently. These membranes can be of two types: (i) Cerami porous (zeolites and silica) or (ii) dense membranes (which include metallic or ceramic compounds). Ceramic membranes present high porosity, selectivity, and stability against operating conditions, while dense membranes, especially those based on palladium alloys, allow the recovery of hydrogen streams with high purity levels. This recovery occurs using solution-diffusion mechanisms that allow hydrogen to be absorbed and deposited on only one membrane side [85].

1.6. Hydrogen storage

Hydrogen storage is a technical problem that slows its application as fuel or renewable chemicals. Hydrogen contains more energy per unit mass than other substances. Additionally, it is lightweight and has the highest energy density per unit volume (see **Table 1.4**). Based on these properties, it is necessary to design two types of storage for hydrogen. The first storage should focus on using hydrogen as a renewable fuel, and the second as a chemical for other synthesis processes. Hydrogen storage must meet minimum requirements to ensure the safety of hydrogen as a product. These requirements are set as a scientific challenge for the development of a safe storage system. One problem during hydrogen storage processes is the materials used for stationary storage tanks. Currently, high-pressure containers with steel cylinders are used. These containers can store hydrogen at 200 bars with a gravimetric density of 1 %w (1 %w equals 186 Wh/kg of contained energy). On the other hand, high-quality carbon cylinders are available. These cylinders can tolerate pressures between 700 and 1000 bar, with gravimetric densities up to 10 %w [86]. However, this type of storage is a risk due to the high flammability of this gas. Therefore, it is important to consider the materials used during hydrogen storage since they must minimize interactions with the gas. These interactions can be (i) the physical adsorption of hydrogen molecules on the surface of the material, (ii) the formation of chemical hydrides, and (iii) the chemical adsorption of hydrogen [87].

Table 1.4. Properties of hydrogen and other fuels [88].

Fuel	Boiling point (°C)	Lower heating value (MJ/kg)	Lower flammability limit (%vol.) *	Upper flammability limit (%vol.) **	The energy density (kWh/dm^3)
Hydrogen	-252.7	120	4.0	75.0	2.37 (liquid) 0.53 (gas)
Gasoline	77-127	44.4	1.0	6.0	9.2
Methanol	64.0	20.1	7.0	36.0	4.4
Methane	-161.0	50.0	5.0	15.0	2.3
Propane	-42.0	46.4	2.0	10.0	6.9

* In air ** At 0°C and 1 bar in the air

Additionally, for transport, hydrogen requires 300 times more space than gasoline to store an equivalent amount of energy under standard conditions. Therefore, pressure is used to increase the energy density per volume and reduce the size of the storage tanks. As a result, the size of the tanks is reduced, but their weight increases drastically [88]. Hydrogen in the liquid phase entails energy losses, and its boiling point increases. This is a risk to the safety of the process. Given the above, hydrogen storage processes require further technological advances. For all these reasons, hydrogen storage processes require new technological advances, and alternatives include (i) compressed gas, (ii) subway storage, (iii) liquid hydrogen, (iv) solid hydrogen, and (v) other systems [13].

1.6.1. Types of hydrogen storage

a) Hydrogen as a compressed gas

It is necessary to perform compression processes to store hydrogen in smaller space volumes. The most used method to compress hydrogen is gas cylinders at high pressure (700 bar). When hydrogen is compressed at this pressure, it reaches volumetric densities of 36 kg/m^3 and loses between 10 % and 15 % of its energy content. Therefore, this type of storage is used to transport hydrogen. However, another problem during this type of storage is the temperature increase. During the compression process, the temperature rises, promoting the degradation of the compound [89]. For this reason, the development of lightweight materials with a low thermal conductivity that allows the safe transport of hydrogen is currently being encouraged.

b) Underground Hydrogen Storage

Underground hydrogen storage is a methodology applied in large-scale production processes. Suggested locations for underground hydrogen storage include (i) oil and natural gas reservoirs, (ii) salt caverns, and (iii) aquifers. However, these locations are often conditioned by geological and structural aspects. Recently, salt caverns have been receiving some interest as hydrogen storage areas due to their stability and impermeability. The volumes that these caverns can tolerate range from 100,000 to 1,000,000 m^3 of hydrogen [90]. However, the development of these storage spaces is limited by technical issues. Any space for hydrogen storage must also comply with environmental regulations and safety standards.

c) Hydrogen in the liquid and solid phase

Hydrogen can change from gaseous to liquid when subjected to low temperatures. The liquid storage of hydrogen ensures small volumes and moderate energy densities (about 70.8 kg/m^3). However, this method must gain more interest since the liquefaction process is energy-intensive and time-consuming. During liquefaction processes, hydrogen can lose more than 30 % of its energy content [91]. Currently, liquid-phase hydrogen is only used for specific applications such as aeronautics. Hydrogen storage in the solid phase is based on its combination with other materials. This combination occurs through adsorption or absorption processes. During adsorption processes, hydrogen is stored in the bulk of the material and allows the synthesis of other chemical compounds (metal hydrides). An example of this process is palladium. Palladium can absorb 900 times its volume in hydrogen under standard conditions [92]. Additionally, absorption processes involve the deposition of hydrogen in porous materials. These processes present better thermal control of the process, and although it is not a commercially available technology, it may present a viable alternative.

d) Other systems

Inorganic materials have certain advantages over organic materials. These materials are usually less expensive, lighter, and more environmentally friendly. Liquid fuels have advantages over gas-phase hydrogen, notably high energy density and short charging and discharging times. Liquid hydrogen storage systems are proposed to preserve these properties. These systems must be capable of storing and releasing as much hydrogen as possible at temperatures between 80 °C and 150°C. A candidate for this task is ammonia. This chemical compound can store 18 %w of hydrogen, and its processing is established in the industry. As a hydrogen carrier, ammonia requires a Haber-Bosh-type synthesis, followed by a controlled thermal decomposition process. However, among the limitations of this process is the toxicity of ammonia. This characteristic does not allow its public use. Given the above, applications as liquid hydrogen carriers focus on using ammonia borane and lithium amido borane. These compounds can release 11 %w of hydrogen at temperatures of 908 °C [13].

1.6.2. Hazards in hydrogen storage

Under standard conditions, hydrogen is a colorless and odorless gas whose weight is lower than that of air. Additionally, to these characteristics, hydrogen has a low density due to its smaller particle size, allowing it to penetrate metals and alloys such as steel and iron. The penetration of hydrogen particles into the metal can generate cracks, decreasing the strength of the material and generating a possible fracture. Then, hydrogen reacts violently with oxidizing agents such as nitrous oxide and halogens, causing many exothermic reactions. Also, hydrogen forms different mixtures with other fuels, many of which are explosive in the presence of atmospheric oxygen in a wide range of concentrations [93]. Given the above, although hydrogen is not toxic, it does present high fire and explosion hazards. **Table 1.5** presents a comparative analysis of the hazards of using three fuels, including hydrogen. Thus, future applications derived from the use of hydrogen should consider preventive aspects to avoid accidents and promote safe products to the consumer.

Table 1.5. Hydrogen, methane, and gasoline storage hazards [93].

Storage	H_2	CH_4	Gasoline
As transport fuel			
Safety			Safer, lower volatility, and lower flammability and detonation limits.
Energy density	Highest		
Size of molecules	Smallest (permeable materials)		
Fuel spills causing a fire hazard	Highest	Medium	Lowest
Fire duration for the same liquid fuel volume	Shortest	Medium	Longest
Odorization	Not odorized	Odorized	Normally smelly

Buoyancy	14.5 times lighter than air	1.8 times lighter than air	Gasoline vapor is heavier than air.
The energy of explosion for equal volume storage	Least explosive potential		
Ignition energy	0.25 of CH_4 and 0.08 of gasoline		
Auto-ignition energy	585°C	540°C	227°C – 447°C
Flame visibility	Invisible in daylight, visible at night	Visible	Visible
Hazardous smoke	Lower	Medium	Severe
Qualitative aspects			
Fuel toxicity	***	**	*
Combustion products toxicity	***	**	*
Diffusion coefficient	***	**	*
Specific heat	***	**	*
Flammable energy	*	**	***
Flammable temperature	***	**	*
Explosion energy	***	**	*

***More safety **Intermediate safety *Less safety

1.7. Hydrogen safety

The safety issues associated with using hydrogen limit its implementation as a renewable fuel. However, the risks posed by hydrogen are at the same level as those assumed while using other fuels. Hydrogen can be safely harnessed if the appropriate mechanisms and infrastructure are in place. Hydrogen's main sources of insecurity are (i) its flammability and (ii) high pressures for its storage. Given the properties of hydrogen, safety mechanisms should include early detection systems. These systems should be portable and have alarms that allow the identification of hydrogen in the environment before it exceeds 20 % to 40 % of the lower flammability level. The National Fire Protection requires hydrogen supply companies to use this type of detector [94]. Presently, there are different types of safety sensors on the market that allow the use of hydrogen in different industrial sectors.

Since hydrogen provides more energy per unit mass, it is important to consider the autoignition temperature (585 °C). Additionally, it is important to consider the flame speed, which is usually higher than other volatile compounds and is in the range of 265 to 325 cm/s. According to the NASA department, the ignition sources include (i) short circuits, (ii) sparks, (iii) fracture of metals, (iv) heating of substances by high velocities, (v) welding, (vi) friction and friction phenomena, (vii) impacts and mechanical vibrations. When hydrogen is mixed with large amounts of air, combustion is initiated as a detonation or deflagration. The power of the initiator depends directly on the volume of hydrogen and the presence of turbulence-inducing structures in front of the initial flame. The minimum range that can generate a detonation is between 18.3 %vol. And 59 %vol. of hydrogen [95].

So far, only scenarios where hydrogen is mixed with other gases have been discussed. However, its contact with workers must also be considered. In case of skin contact, it may cause freezer burns or signs of hypothermia. Inhalation may cause asphyxiation or respiratory problems associated with icing. The hazards associated with contact with hydrogen can be distributed according to their nature. There are physiological hazards (respiratory conditions), physical hazards (damage to equipment), and chemical hazards (ignition). Based on the above, there are initiatives such as the European Hydrogen Safety Panel (EHSP) and projects such as Hydrogen Safety for Energy Applications (HySEA) [96]. These initiatives develop regulations to promote safety when handling hydrogen. Safety is not only an aspect focused on technical design. Additionally, it is necessary to guarantee the consumer that the products and services offered by hydrogen do not threaten their integrity. The development of these confidence levels allows the incorporation of hydrogen in multiple applications. These applications range from using hydrogen in residential and transportation to manufacturing fuel cell-powered equipment. One of the methodologies to promote high levels of confidence in a product is the establishment of international standards accepted by the community in general. The implementation of these standards becomes part of the engineering used during the processes of obtaining, distributing, and transporting hydrogen.

1.8. Economic aspects of hydrogen production

The most cost-effective process for hydrogen production is SMR. This technology accounts for more than 90% of the world's hydrogen production, and the price of this product is around USD 7/GJ [97]. Competitive pricing, such as that offered by SMR, is obtained by POX. However, these technologies are often recognized for their high environmental impact. This impact is sanctioned by economic measures, increasing the price of hydrogen by up to 25 %. Gasification and pyrolysis are the most cost-effective processes among thermochemical processes. Gasification allows for obtaining hydrogen between USD 10/GJ and 14/GJ, and pyrolysis has a price between USD 8.9/GJ and 15.5/GJ [98]. The final price of hydrogen is governed by the equipment used, the raw material, and availability. Water electrolysis is one of the simplest technologies, but its efficiency is moderate due to high electricity costs (see **Table 1.6**). Biological processes consume less energy and can be applied to small-scale decentralized hydrogen production due to the availability of residual biomass rich in carbohydrates digestible by microorganisms. Regarding biophotolysis, some authors report hydrogen prices of USD 10/GJ and USD 20/GJ for indirect and direct processes, respectively [62]. Based on the above, the methods with the greatest opportunity for future development are SMR processes and catalyzed biomass gasification. The use of solar energy in fermentation processes is also possible if improvements in substrate consumption are made.

Table 1.6. Efficiency and technological maturity of the technologies used for hydrogen production.

Technology	Efficiency	TRL	Technological maturity
Steam methane reforming (SMR)	70-85%	>7	Commercial
Partial oxidation (POX)	60-75%	>6	Commercial
Autothermal Reforming (ATR)	60-75%	>6	Short-term development

Plasma reforming	9-85%*	>7	Long-term development
Electrolysis	50-70%	4-7	Commercial
Photolysis	0.50%*	<4	Long-term development
Thermochemical water splitting	NA	<4	Long-term development
Biomass gasification	35-50%	>6	Commercial

*Purification processes are not included

1.9. Environmental aspects of hydrogen production

The environmental impact of hydrogen production depends on the technology implemented. Current hydrogen production is based on SMR processes and biomass gasification, and this hydrogen is called "gray hydrogen." The production of gray hydrogen does not contribute to environmental impact mitigation. On the contrary, about 10 kg of CO_2 is emitted to the environment for each H_2 produced. The environmental problems derived from this constant emission of gases cause harmful effects on human health and can also generate massive displacement. Based on the above, one of the viable alternatives to mitigate these problems is the implementation of green hydrogen. However, the energy transition to these processes requires time and investment. Therefore, other medium-term alternatives, such as "blue and yellow hydrogen," are emerging. Blue hydrogen is obtained through SMR processes with integrated carbon capture systems. These processes reduce carbon release by up to 90 %, reducing the volume of pollution to 1.5 kg CO_2/kg of H_2 produced [99]. Yellow hydrogen has zero carbon emissions. This hydrogen is derived from nuclear energy and is competitively priced with current processes (USD 2/kg H_2) [100]. The carbon footprint is one way to establish the environmental impact caused by each production technology (see **Table 1.7**).

Table 1.7. Carbon footprint generated by technologies for hydrogen production [11].

Technology	Primary energy	kg CO_2/ kg H_2
Steam methane reforming (SMR)	Thermal	8.0-10.0
Autothermal Reforming (ATR)	Thermal	4.0-6.0
Plasma reforming	Thermal	10.0-12.0
Electrolysis	Electrical	8.0
Photoelectrolysis	Photonic	2.0
Biophotolysis	Photonic and biochemical	2.0-4.0
Thermochemical water splitting	Thermal	0.0-2.0
Biomass gasification	Thermal	4.0-6.0
Dark fermentation	Biochemical	0.0-2.0
Photo fermentation	Photonic and biochemical	0.0-2.0

An additional aspect to consider is hydrogen emission as a greenhouse gas and the waste generated after the hydrogen production, environmental impacts generated by the disposal of polluting materials such as waste from electrodes and batteries in the electrolysis process. Additionally, production, transport, and distribution processes can release between 0.2 % and 10 % of the hydrogen produced. The released hydrogen can react with free radicals and disrupt the oxidation reactions of other gases present in the atmosphere [101]. Hydrogen oxidation in the stratosphere can trigger decreases in the temperature of this environment and cause larger holes in the ozone layer. For this reason, ensuring minimal emissions in hydrogen production, storage, and supply processes is important. These processes must be rigorously evaluated before the mass deployment of hydrogen production worldwide.

1.10. Social aspects and political implications of hydrogen production

Generally, energy policies focus on managing and directing energy production, distribution, and consumption processes. Thus, energy policies include legislation regulating energy activities, international alliances, research and development of energy sources, economic fluctuations, energy diversification, risk factors in the face of a possible energy crisis, and the different modalities of resources and incentives for energy source development projects. Additionally, current energy policies also focus their objectives on environmental issues. These include technologies that promote the responsible and efficient use of various energy sources, reducing the environmental impact mainly in atmospheric pollution [102]. Under the above scenario, biofuels are attracting interest in the scientific community, and multiple governments have announced their commitment to energy-sustainable programs. However, national policies vary depending on the raw material and technology applied. Additionally, the objectives and expectations of bioenergy projects are driven by the national situation and foreign dependence on oil. Thus, political interest is moving towards the possibility of a hydrogen-based economy. However, before initiating an energy transition, it is important to ask whether hydrogen can satisfy the main energy needs and whether this product can play a relevant role in a sustainable energy future. Despite the multiple efforts of different organizations seeking to include hydrogen in their energy structure, it is important to strengthen the commitment of international organizations to help countries create a policy framework for hydrogen and other less polluting energy systems. International organizations should provide capital in recognition of objectives focusing on hydrogen as a possible means to meet the demand for clean energy. Some agreements exist, such as the Kyoto Protocol, British Petroleum (BP), and Royal Dutch Shell [103]. BP and Shell are companies focused on hydrogen energy projects around the world. On the one hand, Shell has committed to contributing USD 1 billion to i+D activities and the commercialization of hydrogen energy in 2006. BP also provides infrastructure for projects focusing on hydrogen supply with applications in the transportation sector in more than ten cities worldwide, including the CUTE (Clean Urban Transport for Europe) buses operating in London [104].

Finally, financial support is one of the main challenges facing hydrogen production technologies at the societal level. Although private companies make the largest monetary contributions, support from the government's policies is necessary to facilitate the energy transition [103]. Additionally, subsidized projects must be clear that these initiatives aim to reach a carbon-neutral society. The possibility of reaching this minimum level of emissions is one of the reasons that should weigh most heavily during energy debates. Decisions must be made across the board, even though the development of technologies on a global scale takes different forms. This variability in project expansion is due to the diverse conditions and demands of multiple communities. However, this variability should not be separated from the final objective.

1.11. Development strategies in hydrogen production worldwide

To achieve a smooth energy transition, it is important to consider the political participation of different governments worldwide. This way, national strategies can be developed to establish a methodology, with development objectives feasible at different timeframes. Such planning would allow rapid progress in implementing hydrogen as a new renewable resource. Several governments have already undertaken this task worldwide, with countries like the U.S., Canada, and Croatia standing out. In recent years, hydrogen production technologies have been spreading worldwide, from low-scale plants in urban areas to large-scale plants where hydrogen is produced with a high degree of purity.

A. European Union (EU)

The first advances in hydrogen production technologies were made in Europe. Europe formed the "EU Hydrogen Strategy" to turn its allies into carbon-neutral zones. Thus, its priority is the production of green hydrogen derived from the use of renewable energies. This European project is divided into three stages. The first stage covers the period between 2020 and 2024. During this period, the main goal is the production of 1 million tons of green hydrogen. In the second stage, from 2024 to 2030, 10 million tons of green hydrogen production is proposed. In the last stage, which extends to 2030, the energy transition to renewable fuels is expected to be deployed in the world's most important countries. To speed up these processes, financial resources will be managed by the European Hydrogen Alliance and the European Commission [105].

B. Croatia

Multiple projects focused on hydrogen production are being developed in Croatia in various institutes and universities. Croatia has an energy potential derived from solar energy, concentrated in its coastal area. Thus, photovoltaic systems for hydrogen production are favored. In recent decades, Croatia has conducted several studies on alkaline and PEM electrolyzers. These studies evaluate the possibility of coupling these energy systems with the electricity distribution network in the country. This coupling would solve several problems, including the imbalance of the power grid. Additionally, the Croatian National Government, to encourage the development of renewable fuels, has made interventions in its energy legislation and has previously presented frameworks for the development and application of renewable energies, focused on the use of hydrogen [106]. The Croatian national strategy toward energy transition is based on three pillars. The first pillar is a development strategy progressively oriented towards producing green hydrogen. The second pillar sets out the main applications for hydrogen production. Additionally, an alternative route for the acquisition of hydrogen in other countries is planned. This is if the national product fails to meet the local energy demand. Finally, the third pillar is based on forming critical knowledge in the community. Educational institutions will provide educational plans that will allow the population to be adequately informed about the energy transition.

C. Benelux ((The Netherlands, Belgium, and Luxembourg)

The Benelux agreement exemplifies international cooperation toward an energy transition to a carbon-neutral society. As a member country, the Netherlands aims to reduce natural gas consumption and transition to using other renewable fuels, including hydrogen. The Dutch Hydrogen Strategy recognizes the potential of hydrogen as a renewable fuel and has adjusted its energy policy to promote its production. To this end, it has developed programs to enable the Netherlands to enter the new energy market. This program is based on several stages. Among these stages are (i) the formulation of public and private policies that promote the reduction of green hydrogen production costs and (ii) the creation of international support policies for the integrated development of efficient hydrogen production technologies. The renewable energy that has the greatest potential based on the exosystemic reality of the Netherlands is centered on the use of wind energy. Different authors have conducted studies in which it is reported that 4.6 % of service stations in the Netherlands are suitable for installing wind turbines [107]. Using the energy from these turbines would allow the production of green hydrogen. Although Belgium does not present progress equivalent to that of its allies regarding hydrogen production, it is immersed in energy transition initiatives. Among the initiatives present in Belgium is H_2-Mobility Belgium. This mobility plan was developed to create a National Hydrogen Implementation Plan in Belgium. This plan is based on the experiences of neighboring countries, and therefore, it is expected that more than 100 HRS will be installed in Belgium by the end of 2030 [107].

D. Germany

Germany is recognized as one of the leading European countries in hydrogen production technology investment. Based on Germany's National Hydrogen Strategy, many countries have followed suit and developed their energy policies. The main objective of this German initiative is to incorporate hydrogen into industry and society, promoting their country as a carbon-neutral society. Germany's National Hydrogen Strategy envisages implementing more than 30 actions to promote the research, construction, and commissioning of hydrogen-producing plants [108]. These actions go hand in hand with European and international collaborations. This first stage of the energy transition will end in 2023, and the second phase is expected to involve significant changes. These changes suggest strategies to stabilize the world market based on emerging economic, environmental, and social changes.

E. U.S and Canada

The American government's interest in promoting renewable energy use is an initiative that dates to the 1973 oil crisis. For this, the International Hydrogen Energy Association was created, and the first conference was held in Florida, in the U.S. Thus, the U.S. Energy Research and Development Administration (ERDA) expressed its support for hydrogen energy research as part of the country's energy self-sufficiency project. However, financial support for the initiatives never exceeded USD 24 million per year until 1970. Then, in 1980, financial support decreased and was not resumed until 1990 because of growing concern about global climate change. Based on recent developments related to the depletion of fossil resources and the consequences of global warming, the U.S. Department of Energy (DOE) proposed programs such as the hydrogen roadmap, which assumes that 90 % of the fuel is produced from fossil fuels and the remainder by nuclear-powered electrolysis technologies. Additionally, DOE supports research efforts to produce hydrogen from natural gas, coal, and nuclear energy. Thus, support for hydrogen-related programs comes from the Offices of Science and Technology, the Office of Energy Efficiency and Renewable Energy, and the Office of Fossil and Nuclear Energy. Since 2002, new offices have also been created to integrate hydrogen sectors and applications. Thus, the Hydrogen Office, the Fuel Cell, and Infrastructure Technologies Program, and the FreedomCAR (Cooperative Automotive Research) program were created. The objectives of the FreedomCAR program are to create affordable fuel cells and improve hydrogen storage systems [104].

Canada has also been one of the most active American countries in developing renewable energies, especially those related to hydrogen, and has numerous leading companies. The Department of Industry is one of the government agencies that, together with the Department of Natural Resources, has established plans to strengthen programs for deploying and progressively commercializing hydrogen production technologies. 2003 financial aid was also announced to improve air quality and reduce pollutant gas emissions. Likewise, the federal government allocated over USD 80 million to i+D, including innovation projects in hydrogen production and partnerships with fuel cell producers in the country. Sustainable Development Technology Canada coordinates all these efforts to promote an energy transition [104].

F. Colombia

Colombia is one of the Latin American countries that stands out in coal production and the high availability of biomass and water resources. First, its water supply is six times above the world average and three times above the Latin American average, and the great wind and solar potential in the northern part of the country is an attractive potential for electricity generation. The great wind and solar potential and the reduction in taxes accelerate the participation of renewable energies in the national energy matrix. The participation of renewable technologies in the energy matrix plans to reach 12 % by the end of 2022, thus reaching 2,400 MW installed [109]. Additionally, Colombia's geographic location facilitates trade with five other countries and has access to two oceans, which positions it as a commercial node. This positional advantage facilitates the creation of a distribution and transportation network for hydrogen and its derivatives.

The Colombian government has developed different laws to encourage the development of competitive technologies in hydrogen production and to mediate international agreements. These laws allow attracting collaboration and investment processes between different industrial sectors. An example is the Energy Transition Law 2099, published on July 10, 2021. This law seeks to establish a fiscal framework that encourages investment in projects related to renewable energy production. This investment is relevant based on the economic aid that accompanies it. These economic aids may include (i) the exemption of payment of customs duties, (ii) the exclusion of consumption tax, and (iii) the deduction of income tax for the value of 50 % of the investment [109]. These economic aids are intended to support the emergence of projects that produce hydrogen with low emission levels (green and blue hydrogen).

Finally, in recent years, the Ministry of Mines and Energy proposed "The Roadmap for Hydrogen in Colombia," a roadmap aimed at contributing to the development and installation of hydrogen in Colombia. This project is derived from the national government's commitment to the 2015 Paris Agreement. Within this route, goals are established for the years 2030 and 2050. In the first period, which includes until 2030, the main objectives are to produce 1 GW of energy derived from electrolytic processes under green hydrogen. The possibility of reaching a unit cost of USD 1.7/kg H_2 is also proposed, and to produce blue hydrogen, a production of 50 kton is expected by constructing new plants that allow the capture and storage of the CO_2 produced [109].

1.12. Applications derived from hydrogen utilization

Hydrogen is an energy carrier that can be used for multiple energy applications. Additionally, it is a chemical product involved in synthesizing other compounds with high added value. The main application of hydrogen in industry is energy. Some of these energy applications include their use in energy storage, gas production, and co- and tri-generation systems.

1.12.1. Applications in power systems

With the accelerated development of renewable energies, generating systems that capture and store the energy produced is important. Renewable energies are often dependent on climatic and environmental conditions. For this reason, the energy produced must be stored safely and in supports that can guarantee stability in the face of consumption fluctuations. Based on the above, some hydrogen energy storage projects have been carried out worldwide. One example is DATAZERO, which aims to integrate renewable energy with data science. This integration is done to apply optimization cycles and ecological control to supply the energy demand through renewable energy generation under optimal conditions [110].

Electrolyzers and fuel cells can be used as services in electric grids. The service offered by this equipment is to make the inclusion of renewable energies in electricity grids more flexible and easier. Among the benefits offered by this equipment are (i) the reduction of grid congestion, (ii) autogenous start-up, and (iii) frequency and voltage regulation [111]. Although other equipment fulfills these functions, the versatility of hydrogen allows greater benefits without resorting to greater operational risks. In most of the reported studies, the coupling of this equipment in the electric grids generates a decrease in operating costs, which triggers a decrease in the cost in the market, favoring the inclusion of renewable energies in the production plants.

1.12.2. Production of gas from electrical energy

Fuel gas is generally produced from the conversion of electrical energy into gas. Since hydrogen is a fuel gas with high energy density, its applications in this sector have gained relevance. Hydrogen produced by electrolytic processes can undergo mechanization and be injected into the natural gas grid. According to statistical studies, about 85 % of energy conversion to gas projects are in Europe, Japan, and the United States. In Europe, one of the major contributors is Germany, which has installed 40 MW and expects to have a plant generating gas at a rate of 100 MW for industrial use in the short term [112]. Additionally, gas conversion projects are being carried out in several parts of the world where the solar and wind potential is promising. However, the projects currently installed for energy conversion to gas are pilot-scale projects, and their duration is at most three years. For this reason, it is pertinent to seek more social and political support to boost the use of renewable energies and guarantee global energy demand.

1.12.3. Co and trigeneration

Fuel cells can be used in larger engines to generate CHP (heat and power) or CCP (cooling and power) energy. CHP power is also known as cogeneration, and the combination of CHP+CCP and CCHP power is known as tri-generation. In cogeneration, electricity is produced as the main product of the system. Then, the heat released during the process is used for other applications, such as heating. Several commercial projects have been developed to couple different fuel cells into cogeneration systems. As a world leader in technology, Japan has managed to promote projects such as ENE-FARM. These projects produced 300,000 units in 2018, providing residential services [13]. Additionally, micro-CHP projects for domestic applications have been carried out in Europe. Between 2012 and 2017, 1,000 micro-CHP units were successfully installed in more than ten countries [13]. However, using fuel cells is not unanimously justified in energy utilization, and the life cycle assessment (LCA) of the operation of this equipment elucidates a lower production of toxic gases compared to standard processes.

The tri-generation processes are a more complex derivation of the cogeneration processes. For tri-generation processes, the main engine produces electricity. Then, a heat pump produces cold from a heat sink thanks to a thermal coupling. Finally, the extracted steam passes through a condenser for heat generation. If a comparative analysis is made between traditional tri-generation processes and processes using fuel cells, a decrease in gas emissions and a higher overall efficiency can be evidenced. Some authors report overall efficiencies of 75 % for fuel cell-based tri-generation processes used on a large scale [113]. Additionally, in other applications, it is possible to take advantage of the heat generated by the fuel cell to reduce the energy consumption of the compressor and to allow the storage of the cold current when it is not being used. In this way, the simultaneous tri-generation processes coupled to fuel cells allow the optimization of the processes and, in turn, reduce the environmental impact.

1.12.4. Application of hydrogen in the transportation sector

Given the efficiency and energy savings of electric vehicles, it is expected that by 2030, 3 % of global sales will be hydrogen-based fuel cell vehicles. Several companies worldwide are developing propulsion systems based on fuel cells due to their operational advantages. These operational advantages include (i) higher quality, (ii) increased safety, and (iii) reduced environmental impact [13]. Also, fuel cells can be applied to other means of transportation, such as shipping vessels. Ships generate multiple gas emissions to the environment when using fossil fuels. Given the above, this sector is beginning to lean towards renewable energy sources like hydrogen. Thus, the initiative to add fuel cells to the energy systems of ships arose [114]. The same is true for trains using hydrogen. In Europe, multiple hydrogen trains have been operated. Given the above, hydrogen represents a great energy application scheme that meets maritime and land transportation needs.

1.13. Conclusions

Hydrogen production is expected to become an important integrated system that can mitigate environmental impacts while meeting global energy demand. Important advances have been made in using hydrogen in several industrial sectors. Among these sectors, hydrogen transportation and power generation systems stand out. Hydrogen is an abundant compound and can be produced from many raw materials. This versatility facilitates the implementation of multiple production technologies. Additionally, renewable technologies for hydrogen production have a minimal environmental impact. Given the above, it is expected to reduce dependence on fossil fuels and promote an economic and energy transition towards renewable energy sources. Although it has been many years since the concept of the "hydrogen economy" first appeared, it is only in the last few years that this value chain has been given greater prominence. This recent interest stems from the multiple energy applications of hydrogen. However, proper infrastructure development and the global supply chain for the deployment of hydrogen as fuel still present many technological challenges. The main challenges stem from the low efficiency and high operating costs of some technologies. Given the above, the industrial development of these processes requires a series of research advances to improve them. These research advances should focus on (i) reducing operating costs, (ii) improving efficiency, (iii) improving safety and durability systems, and (iv) optimizing the transportation chain and storage systems. These advances can also be promoted with the support of public policies. Strategies derived from energy policies should set global targets for the transition from fossil fuels to renewable energy sources, such as hydrogen.

1.14. References

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Chapter 02: Heuristic analysis of pathways, technologies, and raw materials for hydrogen production.

2.1. Introduction

Hydrogen can be produced from several feedstocks and technologies; however, establishing which is the best alternative is challenging because it offers multiple advantages and disadvantages. Therefore, this work developed a heuristic analysis of the hydrogen production pathways considering technical, energetic, economic, and environmental aspects. A comparative analysis was also developed for the main hydrogen production technologies, considering design and operation indicators. After the pathways and technologies assessment, a heuristic analysis was carried out considering three raw materials of high economic impact in Colombia: corn stover, cassava stalk, and rice straw, to evaluate the hydrogen production potential of these raw materials considering composition, production, and supply logistics factors.

2.1.1. Methodology: Heuristic analysis of pathways and technologies

a. Hydrogen production pathways

The heuristic analysis of the transformation pathways was based on global indicators such as environmental impact, economic, and energy aspects. Considering that the pathways are composed of different technologies, the three most developed technologies at the research level were defined for each pathway based on literature reports. Then, a search was done for at least five bibliography sources that reported the indicators considered. The same flow rate basis was used for all indicators: kg of hydrogen. Then, each indicator was evaluated, and a level of importance was assigned to that indicator to obtain a weighting as an overall result in each pathway.

i) Environmental impact

The first step towards a carbon-neutral economy is studying and analyzing the environmental impact generated by each production process. A life cycle analysis (LCA) must be carried out to understand and evaluate the environmental impact of the process. Therefore, the Leiden Center for Environmental Sciences published an operational guide to perform LCAs according to ISO standards [1]. For this study, the categories associated with global warming potential (GWP, kg CO_2 eq) and acidification potential (AP, kg SO_2 eq) were considered since these indicators measure CO_2 emissions and the impact of SO_2 on soil and water, respectively [2]. The LCA results published by Bhandari et al. [3] and Ozbilen et al. [4] were used in this study.

ii) CO_2 ratio emissions

It has long been known that CO_2 emissions cause various damages and harm human health and ecosystems. Thus, industrial activities are regulated by national legislation within the framework of CO_2 emissions. Therefore, this indicator considered the ratio between the CO_2 production flows of each transformation pathway and the hydrogen flows produced.

iii) Economic analysis

The cost associated with hydrogen production generates uncertainty, considering that this indicator is strongly influenced by the technology readiness level presented by each pathway. Additionally, these costs are affected by the raw materials and the available infrastructure. The average cost of hydrogen production for the electrolytic and thermochemical pathways was taken from Parthasarathy et al. [5]. The costs previously reported by Nassir Uddin et al. [6] were used for the petrochemical and biological processes. The production costs used correspond to high-scale processes.

iv) Analysis of energy and exergy efficiencies.

Efficiency is defined as the ratio of the product energy to the feedstock energy, as shown in equation (2.1), where ṁ is the mass flow rate of hydrogen produced, LHV is the Lower heating value of hydrogen (121 MJ/kg), and E_{in} is the rate of energy input to the process. Exergy efficiency is the product exergy ratio to feedstock exergy. The exergetic efficiency was calculated with equation (2.2), where $ex_{H_2}^{ch}$ is the hydrogen chemical exergy, and Ex_{in} is the rate of exergy input to the process [7].

$$\eta_{En} = \frac{\dot{m}LHV_{H_2}}{\dot{E}_{in}} x100 \qquad \text{Eq. (2.1)}$$

$$\psi = \frac{\dot{m}ex_{H_2}^{ch}}{\dot{Ex}_{in}} \text{x100} \qquad \text{Eq. (2.2)}$$

The data used for the evaluation of energy and exergy efficiency were based on the studies previously reported by Ismail et al. [8], Bičáková et al. [9], Singh et al. [10], and others [11]–[13].

v) Key aspects for development

The main key aspects of hydrogen development are listed in **Table 2.1**. This indicator was qualitative and associates each pathway with the challenges faced in developing a high level of commercialization. For this purpose, the i+D needs they require to optimize their processes and increase production scales were considered [7]. One of the most relevant aspects was the technological readiness level (TRL), considering that a pathway with TRL values lower than 4 does not present applications at the pilot scale. Then, a pathway with TRL values between 4-6 refers to processes still in the development phase and subject to modifications at the design and infrastructure level. When technologies are at TRL 7 or higher, they are categorized as a system or subsystem. Therefore, high TRL's are ideal to avoid drawbacks associated with designing and implementing production schemes due to the need for previous studies applied in the industrial sector.

Table 2.1. Key aspects for transformation pathway development.

Indicator	
Lower capital costs	High product purity
Lower operating and maintenance costs	High production rate
Raw material availability	Lower temperature and pressure requirements
Operational safety	Technological maturity level (TRL)
Existing infrastructure	

Overall comparison

The results associated with environmental impact, economic analysis, energy, and exergy efficiencies, and CO_2 ratio emissions follow a standardized equation (2.3), where "Worst" was considered as the value of the least favored scenario and "Best" as the value of the best-performing scenario. Therefore, the ranking was between 0 and 1, where 0 means a lower value, and 1 would be the ideal case (minimum emissions and costs). This expression was previously reported for value normalizations [14]. The qualitative evaluation of the development aspects was considered informative and is not computed with the overall comparison.

$$\text{Rank (Pathway}_\text{i}) = \frac{\text{Route}_\text{i} - \text{Worst}}{\text{Best} - \text{Worst}} \qquad \text{Eq. (2.3)}$$

b. Hydrogen production technologies

Decision-making in technology assessment is complex due to the multiple options available, each based on different characteristics. Therefore, a heuristic analysis was proposed considering the design and operating conditions indicators. The methodology reported by Chau et al. [15] was considered for designing the heuristic model of hydrogen technologies.

a) Design: Three sub-indicators were established: (i) commercial availability of the technology, (ii) availability of raw materials, and (iii) cost of hydrogen production. The commercial availability of the technology was based on the amount of time since it has been available on the market for use by industries. Therefore, the reports published by Shiva Kumar et al. [16] and Rice et al. [17] were used. The second sub-indicator examined the costs associated with the supply of raw materials and their subsequent transport to the production site. The data reported by Carapellucci et al. [18] and Liu et al. [19] were considered. Finally, the third sub-indicator was based on reports previously made by Dincer et al. [7], where the variation of the hydrogen production price as a function of the implemented technology was analyzed.

b) Operating conditions: Regarding the operating conditions, the following were considered as sub-indicators: (i) process temperature and pressure, (ii) process energy efficiency, (iii) product purity, and (iv) process production rate. The first sub-indicator evaluated the level of complexity of the operating conditions, considering data previously reported by Brauns et al. [20], Riedel et al. [21], Jaouen et al. [22] and others [23], [24]. The second sub-indicator considered the energy efficiency of the process, defined as the ratio between the energy supplied and produced. Multiple reports were considered for the evaluation of this sub-indicator, including Timmerberg et al. [25], James et al. [26], and Mehmeti et al. [27]. The third sub-indicator examines the purity level at which the hydrogen was obtained to guide its application. The data reported by Zeng et al. [28], Kalamaras et al. [29], and Wang et al. [30] were considered. Finally, the fourth sub-indicator considered the hydrogen production rate associated with different process yields, as reported by Lane et al. [31] and Khojasteh Salkuyeh et al. [32].

Based on the literature data, each sub-indicator received a score (from 0 to 1), which was then weighted at the global level according to **Tables 2.2** and **2.3**. Technologies with higher commercial availability, higher raw material availability, lower temperature and pressure requirements, higher energy efficiencies, and higher production rates will receive scores close to 1.

Table 2.2. Ranges and normalized values for the analysis of production technology sub-indicator.

Sub-indicator	Score 0.00-0.25	 0.26-0.50	 0.51-0.75	 0.76-1.00	Unit
Commercial Availability	New-25	26-50	51-75	76-100	years
Availability of Resource	Used in other industries	Frequently used	Little used	No apparent use	kg
Production cost	4.00-2.99	3.00-1.99	2.00-0.99	1.00-0.01	USD/kg H_2
Operating conditions					
Temperature	1600-1201	1200-801	800-401	400-0	°C
Pressure	100-76	75-51	50-26	25-0	bar
Energy Efficiency	0-25	26-50	51-75	76-100	kWh/ m^3 of H_2
Product Purity	50-62	63-75	76-88	89-100	%
Production Rate	0-200	201-400	401-600	600-1000	x10^3kg/day

Overall comparison

Based on the assumption that not all indicators and sub-indicators have the same relevance and units, each will have a relative relevance level. Therefore, the relative weights are presented in **Table 2.3.**

Table 2.3. Relative weights assigned to each criterion for the evaluation of the technologies.

Main indicator	Main indicator weights	Main sub-indicator	Main sub-indicator weights
Design	0.45	Commercial Availability	0.35
		Availability of Resource	0.35
		Production cost	0.30
	0.55	Operating conditions	0.30

Operating conditions	Energy Efficiency	0.20
	Product Purity	0.20
	Production Rate	0.30

2.1.2. Methodology: Heuristic analysis of raw materials

Considering the results of the heuristic analysis of the technologies and transformation pathways, this analysis focused on evaluating the coupling between the best-performing technologies and different feedstocks available in Colombia. Colombia is a multi-diverse country with a great variety of productive zones, where the region of Sucre stands out as a major contributor to the national production of grains and horticultural products for human consumption. For the petrochemical, thermochemical, and biological processes, the production of agricultural residues in the department of Sucre was considered. For the petrochemical processes, the biomethane production potential of each feedstock was evaluated. At the regional level in the department of Sucre, different agricultural value chains represent the starting point for the analysis of raw materials. Agriculture is one of the most important economic activities in the region; however, this activity is often not technified and focuses on small-scale production, which leads to a reduction in product quality and the generation of a considerable volume of residues during the cultivation, harvesting, transportation, and marketing stages. As a result, there is a great economic loss, low productivity, and limited competitiveness of the department production chains. Therefore, crops such as cassava, corn, and rice were established, which generate more than 50,000 tons/year of waste, including corn stover, rice straw, and cassava stalk [33]. This residual biomass has been previously studied due to its potential chemical composition, which is usable in hydrogen production processes. Thus, each technology (excluding electrolytic processes) was evaluated considering the three feedstocks (corn stover, cassava stalk, and rice straw) to identify the best technology and feedstock couplings.

The heuristic analysis of raw materials considered six indicators, including technical, productivity, economic, social impact, and logistic parameters, and considered the methodology described by Arias et al. [34]. For this purpose, each indicator received a score from 0 to 5, according to the relationship between the calculated value and the best possible value; thus, after analyzing all the indicators, each raw material received an overall value based on the weight of the different indicators.

The information used to analyze the indicators was derived from bibliography reports and, in the absence of studies on the technologies coupled to the raw materials, approximate calculations were made considering mass balances based on the main raw material platform. The indicators used for the heuristic analysis of raw materials are described below.

A. Availability of raw material: This indicator considered the number of hectares of the crop needed to satisfy a continuous flow of 25 tons/day to a plant for hydrogen production. This indicator considered the mass balances and crop productivity yields reported in the Ministry of Agriculture and Development databases.

B. Technical indicators and yields: This indicator evaluated the level of feedstock conversion into hydrogen, considering literature reports, such as those described by Lesme Jaén et al. [35], Murugan et al. [36], and Dalmiş et al. [37] for thermochemical processes, Ren et al. [38], Zong et al. [39] and Dong et al. [40] for biological processes, and Zhu et al. [41], Jekayinfa et al. [42] and Mussoline et al. [43] for anaerobic digestion processes.

C. Raw material costs: This indicator refers to the cost of each raw material in terms of transportation. For this purpose, the point of origin of the raw material was the municipality in the Sucre region, where there is the largest production. An approximate calculation was made of the distance to the city where the biorefinery was proposed to be located, and the transportation cost was calculated considering a value of 0.046 USD/ton/km based on quotations made in the region.

D. Demand for raw material in other agroindustrial sectors: This indicator considers other raw material uses. For this purpose, other industries or sectors that demand raw material use were considered, and the reports made by Lesme Jaén et al. [35] and Sarnklong et al. [44] were used.

E. Social impact of raw material production: This indicator relates to the labor demand for the different crops according to the hectares required, considering agricultural reports or crop manuals. For this purpose, the reports made by Ortigoza et al. [45] and Lizarralde et al. [46] were considered, where the number of workers required per hectare of crop per day is specified.

F. Chemical characterization of raw materials: The raw material comprises different recoverable fractions such as the amount of sugars, extractives, ash, volatile matter, and calorific value. Therefore, it is important to consider the amount of each raw material and elemental analysis to determine ratios such as C/H and C/O, information relevant to thermochemical processes. These data were extracted from the literature, considering reports by Zhu et al. [41] for corn stover, Ismail et al. [47] for cassava stalk, and Kalra et al. [48] for rice straw.

Overall comparison

Based on the assumption that not all categories have the same relevance and units, relative importance will be assigned to each. The relative weights are presented in **Table 2.4.**

Table 2.4. Evaluation indicator for raw material.

	Indicator	Importance
AC	Availability of existing crops and productivity	0.10
TI	Technical indicators and yields	0.30
RC	Raw material costs	0.15
RU	Raw material for direct consumption or use in other production processes	0.15
SR	Social impact of raw material production	0.10
CC	Chemical characterization of raw materials	0.20

2.2. Results and discussions

a. Hydrogen production pathways

i) Environmental impact

The environmental impact generated by the different hydrogen production pathways can be observed in **Figure 2.1**. The pathway based on fossil fuels and thermochemical processes greatly impacts GWP and AP. This result is congruent with the by-products generated during the process, where gases such as carbon monoxide, carbon dioxide, hydrogen sulfide, and methane prevail. Carbon dioxide and methane are GHGs that can have diverse consequences regarding an increase in global temperature [49]. In contrast, biological and electrochemical pathways have the least environmental impact. In electrolytics, the environmental contribution is mainly due to the primary electricity source, assumed to be the conventional sources (hydro and thermal), and biological process; the environmental impact is associated with the generation of waste flows with a high organic load [50].

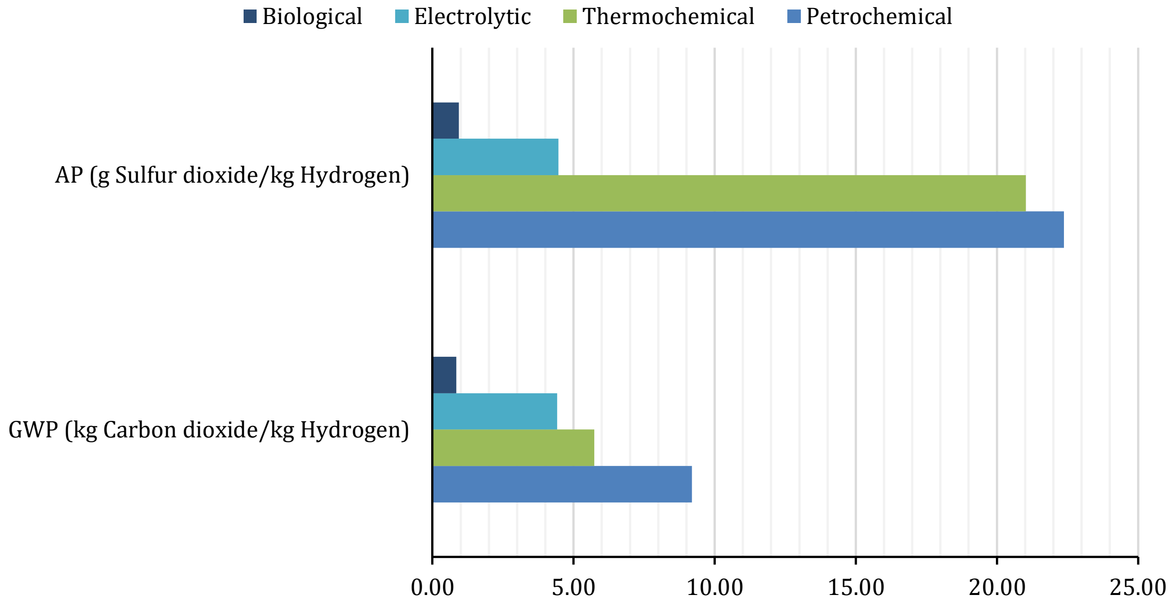

Figure 2.1. Environmental impact (GWP kg CO_2/kg H_2 and AP g SO_2/kg H_2) of selected hydrogen production pathways based on heuristic analysis.

ii) The ratio of CO_2 emissions

The pathways with the highest CO_2 ratio associated with the industrial sector are the petrochemical, thermochemical, and electrolytic pathways, with 9.19, 5.74, and 4.43 kg CO_2/ kg H_2, respectively. The petrochemical pathways have the highest contribution, followed by the thermochemical represented by gasification. The electrolytic pathways associate their contribution because conventional electricity comes from hydroelectric or thermochemical plants, affecting the dynamics of ecosystems, such as local flora and fauna. In addition, their construction triggered the loss of primary forests, recognized worldwide as carbon sinks. Finally, biological processes contribute the least on the basis that according to the Intergovernmental Panel on Climate Change (IPCC), biogenic CO_2 emissions (from bioenergy sources) are not included in the GHGs categories, as emissions are considered in the forestry and agricultural sector [51]. However, CO_2 emissions from industrial and agricultural activities acidify the ocean due to the absorption of gases from the atmosphere [52].

iii) Economic analysis

The lowest hydrogen production costs are found in the petrochemical and thermochemical pathways. The petrochemical pathways contributed 1.27 - 3.70 USD/kg, whereas thermochemical was 1.34 – 3.27 USD/kg. These results are similar to studies reporting 2.27 USD/kg for SMR and 2.57 – 2.77 USD/kg for biomass gasification [53]. Thermochemical cycles and conversion of fossil fuels to hydrogen are the most commercially competitive processes due to low feedstock costs and high production scales. Additionally, several technologies in these pathways present developments that facilitate the use of existing infrastructure, reducing operating and transport costs. The electrolytic and biological pathways cost was 5.95 – 6.95 USD/kg. Using renewable energy sources could increase production costs in electrolysis from 3.0 USD/kg to 10-25 USD/kg [54]. However, the high costs associated with the electricity and reagent demand in biological processes and low yields do not allow these pathways to be competitive in the market. Although the electrolytic process has industrial applications, the companies that use this technology are related to small scale, assuming high capital investment.

iv) Analysis of energy and exergy efficiencies

Figure 2.2 shows the energy and exergy efficiencies for each hydrogen production pathway. The petrochemical pathways present the highest energy efficiencies since they are the technologies present at the industrial scale and have multiple optimization processes. Followed by petrochemical, thermochemical processes are the most efficient, and the last pathway is electrolytic and biological. In recent years, efforts in electrolytic processes have focused on increasing energy efficiency by modifying the process by adding electrolytes with greater electron transport capacity, using membranes that directly separate the produced gases or solid oxides as catalysts [30]. These derivations of the electrolytic process seek to increase the yield by improving the energy efficiency and, therefore, electricity utilization in the process.

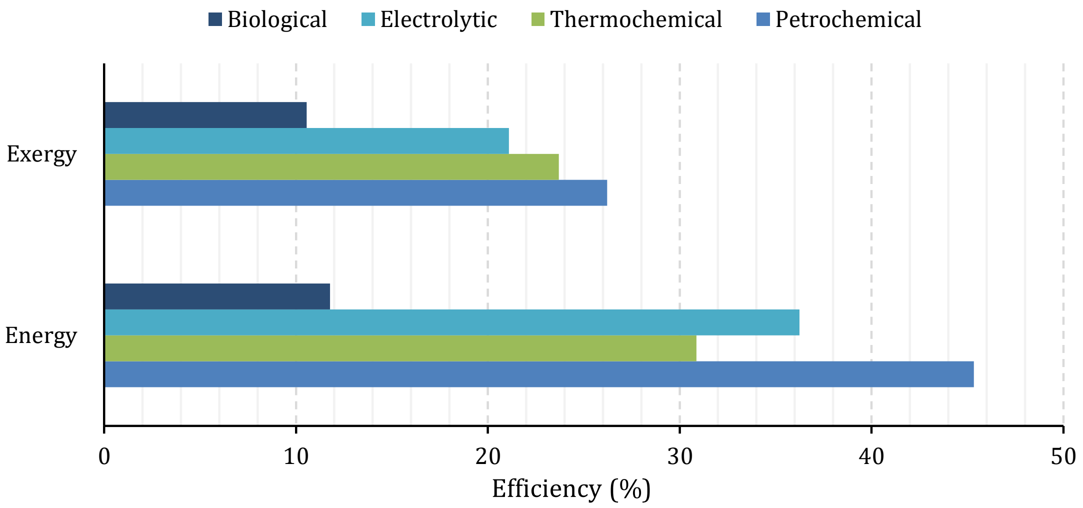

Figure 2.2. Energy and exergy efficiencies of selected hydrogen production pathways, based on heuristic analysis.

v) Key aspects for development

The main development aspects for each hydrogen production pathway are summarized in **Table 2.5**. Considering the current state of the production pathways, it is possible to ensure that hydrogen production by petrochemical processes is the most economical option. Additionally, the petrochemical and thermochemical pathways are the most efficient and have the highest production volumes, even considering the high production costs. Electrochemical and biological pathways present lower industrial development, lower efficiencies, and lower production volumes. For this reason, the TRL associated with these pathways is less than 5 for the biological pathways and less than 7 for the electrolytic pathways, given that alkaline electrolysis is developed in some specific sectors. However, using non-conventional pathways is necessary to ensure energy supplies and mitigate the impacts produced by conventional energy sources. Therefore, optimizing operation and maintenance costs, reducing investment costs, and improving process yield must be the critical points to be assumed by the new hydrogen production pathways.

Table 2.5. Key aspects of the development of selected hydrogen production pathways.

Petrochemical	Thermochemical	Electrolytic	Biological
High CapEx	Cost-effective reactor	High CapEx	Cost-effective reactor
High OpEx	High OpEx	High OpEx	Low OpEx
Raw material availability	Abundant and cheap feedstock	Cost of feedstock preparation	Feedstock pretreatment
Existing infrastructure	Existing infrastructure	Existing infrastructure	No existing infrastructure
High efficiency	High efficiency	Low system efficiency	Low system efficiency
High volume, low cost, flexible system design	High volume, low cost, flexible system design	Low volume production	Low volume production
Low purity product	Low purity product	High purity product	Medium purity product

High temperature Operation with operational risks	High temperature Operation with operational risks	Low temperature	Low temperature Operation with operational risks
TRL > 7	TRL > 6	TRL 4-7	TRL 4-5

CapEx: Capital expenditure, OpEx: Operating expenses

The partial results of the heuristic analysis of the hydrogen production pathways suggest that until the emerging processes improve their production levels and energy efficiency, they cannot find more commercial progress than the conventional processes. Therefore, improving these yields through catalysts or other alternatives is important, while conventional processes solve the problems associated with gas emissions.

b. Hydrogen production technologies

Table 2.6 summarizes the results of the heuristic analysis of hydrogen production technologies. In general, in the design indicators, petrochemical and thermochemical processes are benefits over technologies based on biological and electrolysis processes due to their technological readiness. Given the high environmental impact of petrochemical processes, including new operational stages for gas capture allows 13.2 tons CO_2/tons H_2 [32], promoting the commercial development of this technology. Similarly, it is important to highlight the scale of processing within the design processes. While alkaline electrolysis can produce 10 tons H_2/day, conventional technologies such as SMR produce up to eight times this value annually [31]. Limitations in production scale put energy security at risk, encouraging industries to continue using conventional processes instead of investigating emerging processes. The most relevant sub-indicators were temperature and pressure demand. Although the operating conditions are less severe in electrolysis and fermentation, the low production flow accompanied by low energy efficiency is a disadvantage compared to thermochemical and petrochemical processes. Thus, the interest in introducing these technologies on a commercial scale should not only be justified under lower pollution rates, but they are also technologies that can contribute to continuous energy production.

Table 2.6. Results of the heuristic analysis performed on hydrogen production technologies.

Pathways	Technologies	Indicators		Global score
		Design (0.45)	Operating conditions (0.55)	
Petrochemicals	Steam methane reforming	0.928	0.754	**0.83**
	Partial oxidation	0.844	0.793	0.82
	Autothermal Reforming	0.928	0.721	0.81
Thermochemical	Gasification	0.853	0.741	**0.79**
	Pyrolysis and co-pyrolysis	0.853	0.71	0.77
	Aqueous Phase Reforming	0.597	0.78	0.70
Electrolytic	Alkaline electrolyzers	0.691	0.719	**0.71**

	Photoelectrolysis	0.594	0.617	0.61
	Solid oxide electrolyzers	0.166	0.702	0.46
Biological	Dark fermentation	0.607	0.580	**0.59**
	Direct or indirect Biophotolysis	0.519	0.480	0.50
	Photofermentation	0.432	0.503	0.47

An overall score was calculated to comprehensively compare the technical, economic, and environmental impacts of the transformation pathways and technologies, as shown in **Table 2.7**. These values elucidate which factors impact the production pathways most. For example, in the petrochemical pathways, the indicator with the greatest impact was CO_2 production. In contrast, for thermochemical processes, the impact is associated with the GWP and AP indicators. Finally, low economic viability was the indicator with the greatest impact on the biological and electrochemical pathways.

The score obtained by each transformation technology shows that the processes with the highest energy efficiency and lowest production costs continue to be those derived from fossil fuels. However, emerging technologies such as alkaline electrolysis and biomass gasification may present improvements for larger markets. Finally, hydrogen production through biological processes requires further research and development due to the lowest yield as a consequence of the multiple difficulties related to the management and control of microorganisms.

Table 2.7. Comprehensive heuristic analysis of hydrogen production pathways and technologies.

Pathways	Score considering Eq (1.3) * / Heuristic analysis to pathways				Global score pathways	Technologies	Global score technologies
	Environmental impact	Ratio of CO_2 emission	Economic analysis	Analysis of energy and exergy efficiencies			
Petrochemicals	0.01	0.01	1.00	1.00	**0.50**	Steam methane reforming	**0.83**
						Partial oxidation	0.82
						Autothermal Reforming	0.81
Thermochemical	0.41	0.56	0.68	0.78	0.47	Gasification	**0.79**
						Pyrolysis and co-pyrolysis	0.77
						Aqueous Phase Reforming	0.70
Electrolytic	0.57	0.63	0.22	0.46	0.44	Alkaline electrolyzers	**0.71**
						Photoelectrolysis	0.61
						Solid oxide electrolyzers	0.46
Biological	1.00	1.00	0.01	0.01	0.45	Dark fermentation	**0.59**
						Direct or indirect Biophotolysis	0.50
						Photofermentation	0.47

* Values close to 1 indicate lower environmental impact, lower CO_2 production, lower economic investment, and better energy and energy efficiency

c. Integration of hydrogen production pathways and technologies

Among the hydrogen production technologies, there are different technological advances. The most commercially developed technologies at high TRL and a late stage of i+D offer the highest efficiency and production cost advantages. Technologies in early i+D stages, such as electrolytic technologies, offer lower environmental impacts. An important factor in analyzing is the availability of technologies to carry out high-scale processes. Hydrogen production technologies that allow large-scale production are those with the lowest investment in the initial i+D phase, such as thermochemical and petrochemical pathways where the gas downstream of the main reaction is subject to opportunities for improvement. Exhausted synthesis gas can be used for generation and cogeneration processes, producing usable undercurrents of electricity.

The main objective of any hydrogen process is to produce high volumes at a low cost, with high efficiency and minimal environmental impact. To achieve this purpose, research should focus on improving the production pathway and technology bottlenecks that do not allow further technology use. In addition, such research should focus on reducing conventional process environmental impact and improving non-conventional process yields. Thus, the advantages are leveraged while working on the disadvantages of each production pathway (see **Table 2.8**). Working in partnership would allow hydrogen to find multiple and diverse technologies that would allow its expansion into different industry sectors.

Table 2.8. Advantages and disadvantages of the selected hydrogen production pathway.

Pathway	Advantages	Disadvantages
Petrochemicals	Most developed industrial process	High levels of pollutant gas emissions
	Some technologies do not require the use of catalysts.	Air/oxygen requirement
Thermochemical	Low production costs	Complex handling process
	Recoverable by-products such as bio-oil and biochar	Separation and purification of the gas stream
	Abundant and cheap feedstock.	Tar and ash production
Electrolytic	Low production costs	Varying H_2 content due to seasonal availability and feedstock impurities.
	Abundant raw materials (water)	Separation of H_2 and O_2
	Carbon independent pathway	Low conversion efficiencies
Biological	The only products are H_2 and O_2	Low volumetric production rate
	high capital costs.	Removal of by-products such as Fatty acids
	Low emissions of polluting gases	Low levels of hydrogen production
	Requirement of large reactor volume	High costs associated with the microorganisms used

d. Raw materials for hydrogen production

The results of the heuristic analysis for the raw materials are presented in **Table 2.9**. Based on the AC indicator, the crop that generated the greatest number of residues was cassava. Therefore, the demand for raw material necessary to satisfy the flow of raw material was lower; the opposite was the case with corn, where corn stover represents only 11.8% of the total plant, and therefore, it was the crop with the greatest demand for raw material. Regarding productivity, the crop with the highest yield was cassava, with 16.88 tons/ha, and the lowest was corn stover, with 2.94 tons/ha, which means that a greater number of hectares is required, and its score is low in this indicator.

Table 2.9. Results of a heuristic analysis of raw materials.

Indicators	Importance	Corn stover	Cassava stalk	Rice straw
AC	0.10	0.00	0.50	0.03
TI	0.30	0.50	0.65	0.77
RC	0.15	0.36	0.75	0.00
RU	0.15	0.45	0.30	0.45
SR	0.10	0.00	0.50	0.28
CC	0.20	0.83	0.68	0.00
Global score		2.63	2.13	**3.38**

The TI indicator that evaluated the level of feedstock conversion into hydrogen under different processes showed that for petrochemical processes, the feedstock with the best yields for biomethane production was cassava stalk with 600 L/kg TS [42], which exceeded by more than 50% the yield of corn stover and rice straw. Moreover, in the thermochemical and biological processes, the raw materials with the best-reported yields were corn stover and rice straw, respectively.

For the RC indicator, the location of the biorefinery had to be considered as the first parameter. For this purpose, the city of Sincelejo was proposed because of its large industrial park and the centralization of operations. Additionally, a large part of the commercialization of the crops considered in this study is centralized in Sincelejo. Therefore, the development of the raw material value chain is promoted to expand its participation at the national level; (i) with the economic analysis, the valorization of the residues of these crops is promoted, increasing the value of the productive chain and encouraging the generation of employment in a city with an unemployment rate of 12.6% [55], and (ii) establishing the biorefinery in the same study region minimizes the costs of the raw material and its transportation. Thus, the municipalities with the highest corn, cassava, and rice production levels were Buenavista, Since, and Majagual, respectively, located at distances between 35 km and 94 km, which generates differences in the cost of raw material transportation, giving a greater advantage to cassava because it is in Since, the city closest to Sincelejo.

During the analysis of the RU indicator, it was found that in recent years, several studies have been developed for the use of corn stover as fuel in thermochemical processes and the development of new materials; however, the current use of this residue is as animal feed, and in agriculture, it is used as organic. Likewise, cassava stalks are particularly important, as they are the medium used for vegetative or asexual multiplication of the species, and rice straw is used as part of the diet of ruminants. Thus, each residue has low-scale applications and low levels of technological complexity.

Economically, the department is the country's leading producer of yams, cassava, rice, corn, cotton, sorghum, and tobacco in agriculture. However, these agricultural activities need more technification, and much of the production is centered on small producers, which triggers a high demand for labor in the region's crops. For this reason, the SR indicator considered the number of day laborers needed for agricultural production of the different crops, and based on different reports, it was found that the crop with the highest demand for workers per hectare was cassava, followed by corn and finally rice. However, since this demand is per hectare and the number of hectares required for each crop is different for the same amount of raw material, it was found that the crop with the highest demand for workers was corn due to its low ton/ha yield.

The last indicator considered the characterization of the raw material. Two sub-indicators were established: (i) the amount of sugar present in the raw material in cellulose, hemicellulose, or starch, and (ii) the calorific value of the raw material. For the first sub-indicator, the raw material with the highest content of usable sugars was cassava stalk, followed by corn stover. For the second sub-indicator, the raw material with the highest calorific value was corn stover, followed by cassava stalk. Therefore, these raw materials can be used in thermochemical processes, as reported by Lesme Jaén et al. [35], and in anaerobic digestion processes, as proposed by Ismail et al. [47]. Finally, developing this heuristic analysis, mainly the TI and CC indicators, allowed the establishment of technology and feedstock schemes with higher performance. Therefore, the following schemes are proposed to be validated at the experimental level and scaled to the simulation level considering the Colombian context: Scheme **1)** SMR with cassava stalk, Scheme **2)** Gasification with corn stover, Scheme **3)** Alkaline electrolysis and Scheme **4)** Dark fermentation with rice straw.

2.3. Conclusions

Once the heuristic analysis of the hydrogen production pathways has been developed, it can be inferred that despite the efforts made by multiple companies, petrochemical processes continue to lead the economic viability and the highest levels of hydrogen production because they have multiple advantages such as high mass yields of the process, high energy efficiency, and low investment costs due to the established infrastructure already in place. Then, with the analysis of technologies derived from the transformation pathways, it was possible to establish that the technologies with the highest level of commercial and research development were (i) steam methane reforming, (ii) biomass gasification, (iii) alkaline electrolysis and (iv) dark fermentation. These technologies received the highest scores since the first ones have high yields and the second ones have a low level of economic investment. Finally, once the heuristic analysis of the potential raw materials at the national level for hydrogen production was developed, it was established that the cassava stalk presented the best performance for producing biomethane usable in petrochemical technology. The second was corn stubble, reporting high yields in producing synthesis gas derived from biomass combustion. Finally, rice straw evidenced the highest content of sugars available for hydrogen-producing microorganisms. Thus, considering the results of the heuristic analysis, it was possible to establish the processing schemes that will be evaluated at the experimental level and scaled up with simulation schemes.

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Chapter 03: Comparative analysis of renewable technologies for hydrogen production using primary crop residues.

Abstract

Hydrogen is a versatile energy carrier that is produced from a variety of feedstocks and technologies. Although steam methane reforming (SMR) is the main conventional process, it is a commercial technology with a high environmental impact. In recent years, hydrogen production has focused on electrolytic pathways or biomass valorization using thermochemical and biochemical pathways. Therefore, this work experimentally evaluated anaerobic digestion for biomethane production in steam reforming (SBMR), gasification of lignocellulosic biomass, and water electrolysis with photovoltaic energy as non-conventional technologies. The results indicate that conventional technologies, such as SMR, present higher mass and energy yields and that non-conventional technologies, such as biomass gasification, need to improve the thermal and energy efficiency of the process. Finally, electrolysis needs more research to increase the hydrogen flow rate produced since it was the scheme with the lowest mass and energy yields. However, although non-conventional technologies do not yet present competitive yields with conventional technologies, they are susceptible to improvement and present an early opportunity to satisfy energy needs in a sustainable market in the future.

Keywords: *Hydrogen, biomethane, gasification, electrolysis, tecno-energetic assessment*

3.1. Introduction

The accelerated growth of the world economy and the constant increase in population associated with a high level of urban development has generated an accelerated demand for energy in all sectors [1]. However, the main trend in the industry has been focused on exploiting fossil resources, even when statistics indicate their depletion, complicating and increasing the cost of their extraction at a geographical scale [2]. The increasing consumption of non-renewable fuels due to the growing industrial development has also lead environmental consequences, causing a massive increase in the greenhouse gases (GHGs) emissions [3]. Therefore, the trend in the energy sector has focused on decarbonization processes through renewable energy resources (REs) [4]. REs are consolidated as promising technologies in the transition development towards a cleaner and more sustainable energy system, which does not imply imminent risks to the resources of future generations [5].

The use of REs technologies presents multiple challenges because the resources are variable and intermittent. Therefore, technical adaptations are mandatory in all industrial sectors to balance the demand and variability in energy supply [6]. Additionally, the inclusion of REs in current energy systems also raises the need to innovate in low and high-scale energy storage systems to overcome the logistical and supply bottlenecks derived from the primary source of renewable energies [7]. The proposed storage systems should support the separation of production and consumption systems, allowing the energy generated to be usable on different time scales (including time, date, and seasonal changes) [8]. The idea of energy storage in an energy carrier is based on the versatility and multiple advantages of these systems [9]. Hydrogen, as an energy carrier, does not generate particulate matter, sulfur, or nitrogen oxides and does not generate tropospheric ozone. Therefore, hydrogen-based energy storage systems (HydESS) are becoming of interest as a cost-effective solution for storage, transport, and use of REs at different scales [10]. Consequently, the interest in developing a hydrogen-focused value chain becomes relevant and aims to guide the industrial sector towards an energy-integrated and carbon-neutral society.

Some governments indicate that a hydrogen-dependent economy is still debatable, and more research is needed for its development [11]. The main difficulties limiting the implementation of hydrogen are due to the risk associated with its use, as it is a more energy-dense fuel, which increases the complexity of safety systems. In addition, although hydrogen can be produced from a wide range of technologies and feedstocks, petrochemical pathways are currently the most developed. Most of the world's hydrogen is generated from fossil fuels (coal and natural gas), and approximately 50% of the production comes from steam methane reforming (SMR) and other light hydrocarbons. These processes are characterized by a high range of CO_2 emissions (10-14 kg CO_2/kg H_2) and other pollutant gases such as sulfur oxides and nitrous oxides [12]. Thus, ensuring that the processes were environmentally friendly was not one of the factors considered for the initial hydrogen production. The total annual consumption of hydrogen in the world is 400 to 500 billion Nm^3, representing 3% of the world's energy consumption [13]. Only a fraction of this hydrogen is currently used for energy purposes, and most of it is used as a chemical feedstock in the petrochemical, food, electronics, and metallurgical industries [14].

Given the increasing concern about GHGs levels and global temperature increase, REs are becoming crucial to achieving low CO_2 emissions, especially REs derived from biomass utilization that can generate a gas capture of up to 21.7 kg CO_2/kg H_2, which considerably mitigates the environmental impact [15]. Different studies have considered the production of hydrogen derived from residual biomass, taking advantage of intrinsic characteristics of this feedstock, such as sugar content and calorific value. These organic materials are abundant, available in many places, economical, and highly biodegradable [16]. Between 1998 and 2001, about 700 million tons of agricultural and forestry residues were generated in Western Europe. In France, a study showed that between 1995 and 2006, total annual residue production had increased to about 849 million tons, of which agricultural and forestry residues accounted for about 43%, i.e., 374 million tons [17]. Likewise, in Germany, the second largest agricultural country in Europe, agricultural residues accounted for more than 175 million tons per year in 2000, including 25 million tons per year of agricultural biomass [18]. Agriculture is one of the most important economic activities in the world; however, after satisfying the demand for food, agricultural residues, generate a considerable volume of residues that can be used in other energetic processes [19].

The world's major crops are coffee, rice, cassava, cotton, sugar cane, corn, and soybeans. Among the various crops produced, cassava is an energetic and large-scale food crop developed in tropical and subtropical countries. The world's leading producers of this crop are Thailand (31,161,000 tons), Brazil (21,082,867 tons), Indonesia (20,744,674 tons), and Ghana (17,798,217 tons) [20]. This crop is developed as a food base for many regions worldwide since the root is an edible tuber that provides large quantities of starch. However, residues such as leaves, stalks, and peels are discarded in the field after harvest, generating an environmental liability [21]. Therefore, in recent years, different processing alternatives have been developed for these residues, given their high potential for energy generation through thermochemical and biochemical processes [22]. Among the technologies available for hydrogen production from biomass are the thermochemical pathways such as gasification or pyrolysis processes. Thermochemical processes involve combustion of the biomass, so there are carbon capture and sequestration (CCS) systems that reduce the environmental impact of these technologies up to 3.54 kg CO_2/ kg H_2 [23]. On the other hand, the electrolytic pathway allows hydrogen generation by breaking down water molecules using an energy current. Currently this technology is the second most widely used commercially and these processes consider less GHGs release, and that impact is associated with the primary energy source. Based on the above, this work aims to compare with experimental tests based on the first steps to produce platforms for hydrogen production. It means a necessary data collection based on other experimental work already published in the literature. Therefore, this approach allows the validation of multiple proofs of concept without any optimization, considering the operating conditions published and validated in many previously reported works. Thus, this paper considers the comparative analysis of experimental tests and simulation schemes of the main hydrogen production pathways, considering non-renewable technologies such as (i) steam methane reforming since it is the most commercially applicable process and renewable technologies such as (ii) steam reforming, with biomethane of anaerobic digestion, (iii) biomass gasification, and (iv) alkaline electrolysis. The renewable schemes based on biomass used cassava stalk as feedstock and all scenarios were compared based on techno-energetic analysis.

3.2. Methodology

3.2.1. Feedstock characterization

The cassava stalk was received from a crop located in Montes de Maria, a rural area of Sincelejo, Sucre, Colombia (9°17′58″N 75°23′45″O). The cassava stalk was characterized following the methodology reported by Cruz et al. [24]. First, some of the moisture was removed with a convective dryer and milled to 0.420 mm with a rotary knife mill (SR200 Gusseisen, Redsch GmbH, Germany). Cassava stalk composition was estimated by considering the content of extractives, fats, carbohydrates (cellulose and hemicellulose), lignin and ash. The extractives were determined based on the technical report of the National Renewable Energy Laboratory - NREL/TP-510-42619, and the liquors were analyzed by the 3,5 dinitrosalicylic acid (DNS) method. Carbohydrates were determined by the acetic acid chlorination method. Lignin and ash were determined following the methods described by NREL/TP-510-42618 and ASTME (1755)-01 2015, respectively. Additionally, proximal analysis was performed to estimate the content of total solids (TS), volatile solids (VS), volatile matter (VM) and fixed carbon (FC). MV was determined following ASTM E872-82 and SV and ST using ASTM E1756-08. Finally, FC was determined by difference.

3.2.2. Experimental procedure for hydrogen production

A. Steam biomethane reforming (SBMR)

Biomethane production was produced from anaerobic digestion assays. Dried and milled cassava stalk was used as substrate following the standard method VDI 4630 [25]. The experiments were carried out in 100 mL glass flasks (90 mL working volume), where the substrate, the inoculum, and solutions of micro and macronutrients were added [26]. The medium was bubbled with nitrogen for 5 min and then hermetically closed to ensure an anaerobic atmosphere [27]. The VS ratio between substrate and inoculum was set at 0.4 and the digestion was performed at 37°C. The biogas productivity was measured by volumetric displacement, while the gas composition using a portable gas analyzer (Gasboard - 3100P). The inoculum was obtained from an anaerobic reactor of a company producing soluble coffee (Buencafe Liofilizado de Colombia), located in Chinchiná, Caldas (4°58′50″N 75°36′27″W). Once the biogas was obtained, it must be improved by increasing its concentration by removing CO_2, which increases its calorific value. For this purpose, the yields reported by Cozma et al. in [28] were considered, where a high-pressure water scrubbing technology (HPWS) was proposed since it is a well-known technology with high levels of efficiency and allows the simultaneous removal of CO_2 and H_2S. Then, when the biogas was transformed into biomethane after the cleaning process, the biomethane was taken to a reforming process where the methodology and yields reported by Alrashed et al. [29] were considered.

B. Gasification (GF)

Biomass gasification was carried out using a pilot-scale downdraft gasifier air-powered integrated with a generator and a combustion engine (10 kW - GEK Gasifier, Power Pallet, California, USA). The process started by loading the gasifier hopper with 10 kg of cassava stalk with a size of 2-3 cm and a moisture content of 13%. The feedstock was then fed into the reactor through a worm screw controlled by a level sensor. Biomass combustion started in the equipment's lower zone (combustion and reduction zone) with a blowtorch and approximately 500 mL of gasoline until it reached 80 °C. After reaching this temperature, the reactor was isolated to avoid leaks and pressure issues. As a result, the gasifier temperature increased between 680 °C and 917 °C, with a total reaction time of 1 h (including start-up, biomass thermal decomposition, syngas production, and downtime). The syngas produced was passed through a cyclone to separate ash and unreacted solid material as a final step. The tars were removed with a wood filter, and the volumetric compositions of the gases generated during the experimental test (H_2, CO, CO_2, and CH_4) were recorded using a portable gas analyzer (GASBOARD 3100p, Wuhan, China). Finally, after the syngas were obtained, an additional purification step was required using hollow fiber membranes, widely used in many gas separation industries. Therefore, the methodology and performances reported by Feng et al. [30] in hydrogen purification were considered. However, before flowing the separation system, the gas must undergo a pretreatment to reach the appropriate pressure conditions inside the membrane and improve the separation. This treatment consists of removing steam traces with chillers and increasing gas pressure up to 35-70 MPa to minimize energy losses after membrane separation [31].

C. Electrolysis (EL)

Experimental alkaline electrolysis tests were performed following the methodology described by Shen et al. [32]. The electrodes were composed of metal oxides with a size of 70 mm and were immersed into 1 L of electrolyte solution (5% NaOH). A tube with a length of 120 mm connected the electrodes and temporarily stored the gases produced. The electrical current was measured with a UNI-T UT60A RS 232C digital multimeter and the amperage with a 400A 600VDC 600VAC KT200 Kewtech digital clamp ammeter. The gas composition produced at both electrodes was measured using the portable gas analyzer (GASBOARD 3100p, Wuhan, China). The energy that fed the electrolysis system was provided from a solar panel module corresponding to a 555W MBB Half-Cell JAM72S30 530-555/MR from JASOLAR company. The system's electrical parameters and operating specifications are shown in **Table 3.1**. The experimental tests were conducted on a day when the solar radiation was 850 W/m^2 at an average module temperature of 22 °C, a wind speed of 1.61 m/s [33].

Table 3.1. Technical properties of the used solar panel module.

Properties	Symbol	Unit	Value
Rated maximum power	P_{max}	W	540.00
Open circuit voltage	V_{OC}	V	49.60
Short circuit current	I_{SC}	A	13.86
Active voltage	V_m	V	41.64
Active current	I_m	A	12.97
Module efficiency		%	20.90
Fill factor	FF	%	78.56
Area covered by each panel		m^2	2.58
Number of cells			144

3.2.3. Simulation procedure

3.2.3.1. Scenarios description

Four scenarios were proposed to evaluate hydrogen production by petrochemical, thermochemical and electrolytic processes. The first and second scenarios involve steam methane reforming, in the first case with commercial methane, and in the second scenario with biomethane from anaerobic digestion of cassava stalk. The third scenario involves biomass gasification, and finally, the fourth scenario includes alkaline electrolysis.

Mass and energy balances were obtained using Aspen Plus v.9.0 software (Aspen Technology, Inc, USA). Hydrogen production with methane from petrochemical or biotechnological sources was developed considering a pseudo-homogeneous model described by Alrashed et al. [34]. Thermochemical processes were developed using equilibrium models, calcination, and decarbonization reactions, following the kinetics described by Nikulshina et al. [35]. The activity coefficients of the liquid phase were calculated with the Grayson-Streed thermodynamic model and the Redlich-Kwong equation to describe the vapor phase. Likewise, for the simulation of the electrolytic processes, the non-random two-liquid (NRTL) model was used to describe the liquid phase and the Hayden O'Connell equation for the vapor phase [36]. These models were established based on reports by López et al. [37]. All scenarios considered a feedstock flow rate of 25 tons/day and experimental data up to the generation of the main platform (biogas or syngas). For the simulation of the purification and gas separation processes to obtain 99% hydrogen, the yields previously reported by other authors were used.

A. Steam methane/biomethane reforming (SBMR)

For the steam biomethane reforming, the dried and milled feedstock was introduced into an anaerobic digester with inoculum and nutrients at 37°C. The biogas was carried to a cleaning stage where CO_2 and traces of other components were removed with absorption towers, using a high-pressure water scrubbing technology (HPWS). Gas absorption by HPWS was performed in an absorber due to the larger contact surface and efficient mass and heat transfer offered by this technology. In this way, biomethane contents 96.6% can be achieved in countercurrent at 10 bar pressure and 20 C temperature. Then, the biomethane or commercial methane was heated to 450 ˚C at 23 bar to be introduced into a reformer with a steam/biomethane ratio of 3 – 3.5. The crude syngas in the reformer leaved at 900 ˚C and 22 bar with an approximate H_2/CO ratio of 4.5-4.9. Then, the syngas was cooled and sent to a water gas shift (WGS) reactor to increase the hydrogen content, where CO reacts with steam and were converted to H_2 and CO_2 at 300 ˚C. The WGS reaction was exothermic, so the gas produced must be cooled before being sent to a flash separator, separated from the unreacted water. Finally, the hydrogen-enriched stream was sent to a pressure swing adsorption (PSA) unit to recover and purify the H_2, while the other separated gases are recycled back into the process [38].

B. Gasification (GF)

Hydrogen production by gasification process has three sections: (i) biomass conditioning, (ii) syngas production, and (iii) hydrogen separation and purification. In the pretreatment, the moisture and the particle size were reduced to 13% and 0.4 cm, respectively. Particle size and especially moisture content are key parameters in the modeling of gasification systems. Some authors have studied the influence of moisture content on thermochemical processes and have concluded that high moisture content increases hydrogen production but decreases the calorific value of the syngas due to the extra energy consumption to evaporate water [39]. Therefore, the pretreatment conditions were selected considering multiple authors' reports suggesting particle sizes between 0.4 and 0.5 cm and a moisture content of no more than 20% [40]. Then, biomass gasification in a downdraft gasifier was performed considering three reactors. In the first reactor, biomass pyrolysis occurs, decomposing it into H, C, O, and ash. Then, in the second reactor, all the components of the pyrolysis zone were consumed in a combustion stage. Gasses such as CO_2, CO, H_2, and heat were produced due to combustion with air, controlling that an equivalence ratio of 0.3 was maintained. Finally, in the reduction stage, the components were taken to a cyclone to separate the ash from the syngas. For hydrogen purification, hollow fiber membranes were proposed since they allow the separation of gaseous mixtures with recoveries higher than 85% on a molar basis and purity levels higher than 70% [41].

C. Electrolysis (EL)

The cell stack was the most important equipment in alkaline electrolysis. The modeling and simulation of the stack were based on a model previously described by Sánchez et al. [42]. This model considers the electrical power input to the stack and some technical data of the system (number of cells, operating temperature and pressure, reaction time, and active area of the electrodes). These parameters predicted the flow and purity of gases generated. In the simulation, water was introduced into a cell stack together with an electrolyte (NaOH), which was continuously fed with an electric current, causing the decomposition of water into oxygen (anode) and hydrogen (cathode). Next, the biphasic stream (gases and unreacted solution) was sent to a separation process. First the liquid solution was removed with liquid-gas separators, and then the gas stream was separated with membranes, producing hydrogen- and oxygen -enriched streams.

3.2.3.2. Techno-energetic assessment

The simulation schemes were analyzed considering the mass and energy balances provided by the Aspen Plus simulation fed with the experimental data. For this purpose, mass and energy indicators described in **Table 3.2** were used. Mass indicators include product yield (Y_H), process mass intensity (PMI), and mass loss index (MLI). The Y_H identifies the hydrogen produced from one kg of feedstock. The PMI determines the amount of feedstock used in the transformation processes and is described as the ratio between the input flows (feedstock and reagents) and the hydrogen flow produced. The MLI identifies the flow of waste produced per kg of product generated. The energy analysis considers the specific energy consumption (SEC) and the self-generation index (SGI). The SEC allows calculating the process's energy needs regarding work and heat and the SGI allows evaluating the on-site energy production potential regarding hydrogen [43].

Table 3.2. Mass and energy index used to compare the proposed scenarios.

Index	Equation	Unit	Eq.
Mass			
Product yield	$Y_P = \frac{\sum \dot{m}_{Product,i}}{\dot{m}_{feedstock}}$	kg hydrogen/ton of raw materials	(1)
Mass intensity of the process	$PMI = \frac{\sum_{i=1}^{N} \dot{m}^{in}}{\sum \dot{m}_{Product,i}}$	kg reagents and raw materials/kg hydrogen	(2)
Mass loss index	$MLI = \frac{\sum_{i=1}^{N} \dot{m}^{in} - \sum \dot{m}_{Product,i}}{\sum \dot{m}_{Product,i}}$	kg waste streams/ kg hydrogen	(3)
Energy			
Specific energy consumption	$SEC = \frac{\dot{Q} + \dot{W}}{\dot{m}_{feedstock}}$	kW/kg raw materials	(4)
Self-generation	$SGI = \frac{(\dot{m}_{Product,i} LHV_{Product,i})}{\dot{Q} + \dot{W}}$	N.A.	(5)

N.A: Not applicable

3.3. Results

3.3.1. Characterization of feedstock

Table 3.3 shows the results of the chemical and proximal composition analysis of cassava stalks. The feedstock presents a high content of extractives similar to other crop residues, such as thick stalk, where some authors report 27.76% [44]. In terms of carbohydrate content, cellulose is the component with the highest presence, coinciding with other studies (40.73% cellulose and 12.14% hemicellulose) where the variation of this composition could be the harvesting time [44]. These contents suggest that the cassava stalk is a potential source of usable sugars in anaerobic digestion processes. In addition, the biomass has a high volatile matter content (>85%), which implies that it is a suitable residue for thermochemical processes. A higher volatile matter content increases the reactivity of lignocellulosic materials, accelerating the combustion process, increasing the flame's adiabatic temperature, and promoting high ignition rates, phenomena reported by other studies [45]. Regarding the proximal analysis, the ash content is similar to Cruz et al. who report a content of 4.3% [45]. The ash content of cassava stalk is significantly lower than that of other agricultural residues such as rice husks (18%) and coffee husks (7.4%) [46]. Low ash content is desirable in gasification's since issues associated with fouling, deposition, sintering, and agglomeration are avoided. These problems are usually solved using fractionation and ash-leaching processes in the reactor [47].

Table 3.3. Chemical characterization and proximate analysis of cassava stalks.

Item					
Chemical characterization (% dry basis)		SD	Proximal analysis		SD
Initial moisture	17.5		Volatile matter	87.058	± 0.15

Extractives in water	18.93	± 3.43	Fixed carbon	9.245	
Sugars (g/L)	0.91	± 0.70	Total solids	89.278	± 0.04
Extractives in ethanol	18.43	± 7.00	Volatile solids	4.479	± 1.77
Sugars (g/L)	0.25	± 1.67	Ash	3.696	± 3.82
Total extractives	22.35		VM/FC	9.416	
Cellulose	36.68	± 0.54			
Hemicellulose	16.26	± 3.03			
Insoluble acid lignin	23.42	± 9.09			
Soluble acid lignin	1.29	± 0.45			

SD Standard deviation

3.3.2. Experimental hydrogen production

A. Biomethane

The potential for biomethane production from cassava stalk as agricultural residue was evaluated considering the biochemical methane potential (BMP) assay, as shown in **Figure 3.1.** The anaerobic digestion process involves a combination of multiple processes, such as hydrolysis, acidogenesis, acetogenesis, and methanogenesis, to produce biomethane and volatile fatty acids in the medium. The maximum biogas yield was 3.57 L/g TVS, similar to those reported by Sivamani et al., with yields of 3.2 L/ g SV [48]. However, these values are lower than other residues, such as avocado peel, where yields of 8.5 L/g SV are reached [49]. The C/N ratio during biogas tests should be between 25 and 30 to obtain optimum yields. In the case of the cassava stalk, the C/N ratio was 54.41, generating an excess of nitrogen that can lead to an accumulation of ammonia, inhibiting biomethane-producing microorganisms [44]. In addition, some authors have reported that the low ash content of cassava limits biomethane production levels. Acidification problems and consequent process instability are major concerns in biogas production plants. However, the use of ash as an additive generates a high buffering capacity that increases the efficiency of the process and significantly reduces the need for commercial alkaline reagents for pH regulation [50] Therefore, the addition of ash improves the anaerobic digestion, allowing the production of 5.22 L/g SV in 45 days of testing [48]. Finally, in **Figure 3.1**, the hydrogen sulfide content produced daily can also be seen. Bücher or diesel engines can only operate at a maximum of 600 ppm H_2S [51]. Therefore, biogas production never exceeds this concentration for cassava stalk, suggesting that using a biological filter before biogas combustion is unnecessary for hydrogen generation. Finally, after the biogas was obtained, considering a production rate of 3.57 L/g TVS it is possible to establish a yield of 0.19 kg biogas/kg feedstock. However, after gas purification, with yields ranging between 80% and 95%, it is possible to obtain flows of 0.16 kg biomethane/kg feedstock.

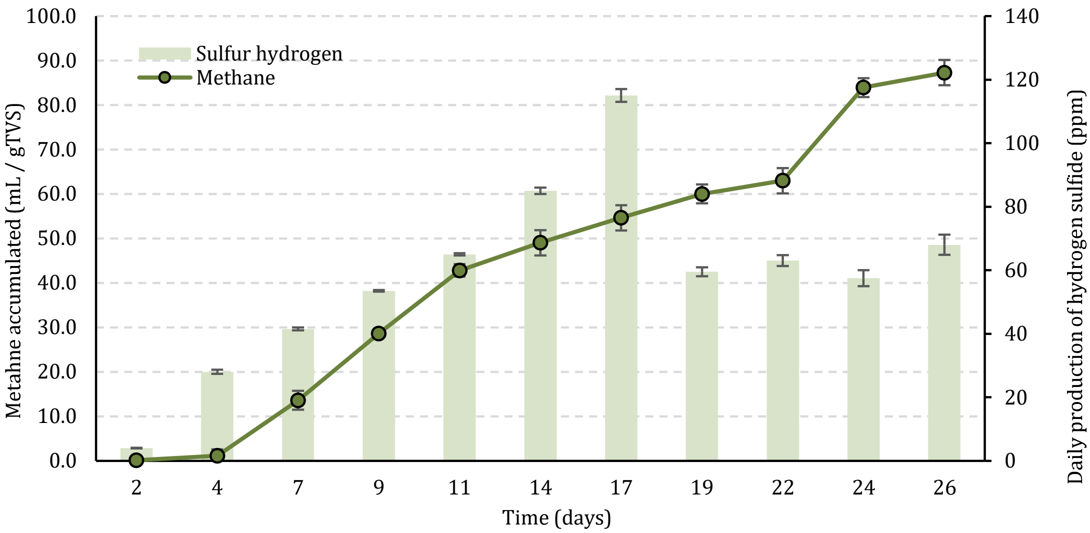


Figure 3.1. Biogas and hydrogen sulfide (H_2S) production from cassava stalk.

B. Gasification

The temperature has a fundamental role in the decomposition of the lignocellulosic material during gasification. In general, high temperatures and VM/FC ratios between 2-3 promote syngas production, especially methane and hydrogen fractions. Therefore, the temperature inside the gasifier was monitored, and it was observed that in the different reactor zones such as pyrolysis, combustion, and reduction, the temperatures were recorded at 680°C, 917°C, and 260°C respectively. These values suggest that the gasification was carried out in a normal temperature range, based on different reports, where maximum temperature was reported at 1160°C [52]. The average composition of the syngas was 6.90% CO, 9.60% CO_2, 1.30% CH_4, 9.24% H_2, and 2.44% O_2 (see **Figure 3.2)**. The potential of the synthesis gas for the production of high value-added compounds such as methanol was determined as the H_2/CO ratio; however, for these purposes the ratio should be between one and two and the gasification of the cassava stalk presented ratios of 2.4. It should be noted that during the gasification process, the airflow was controlled, and an equivalence ratio of 0.3 was established to improve the hydrogen yield and achieve values close to 14% in H_2, as reported by other authors [52]. The calorific value of the syngas was 7.04 MJ/m^3, higher than other reports for gasification's from cassava stalk or rice husk (4.2-5.8 MJ/m^3) or sugarcane bagasse with values of 5.3-5.93 MJ/m^3 [53]. These values show that, compared to other types of biomasses, cassava stalks have superior HHV; however, these values cannot compete with syngas derived from wood biomass combustion. Moreover, the generation of hydrogen and methane as main value-added products is less than 20%, which implies a low utilization of the raw material. Therefore, some authors have reported the improvement of yields through co-digestion processes with other raw materials such as wood that allow reaching higher temperatures and therefore a higher volume of hydrogen [54]. After the synthesis gas was produced, it is possible to establish production flows of 0.0378 kg hydrogen/kg feedstock and considering that the membrane can reach separation efficiencies of 88.78% hydrogen, 7.5% hydrogen sulfide and 3.72% CO, a flow of 0.033 kg hydrogen/kg feedstock with purities close to 99% was obtained.

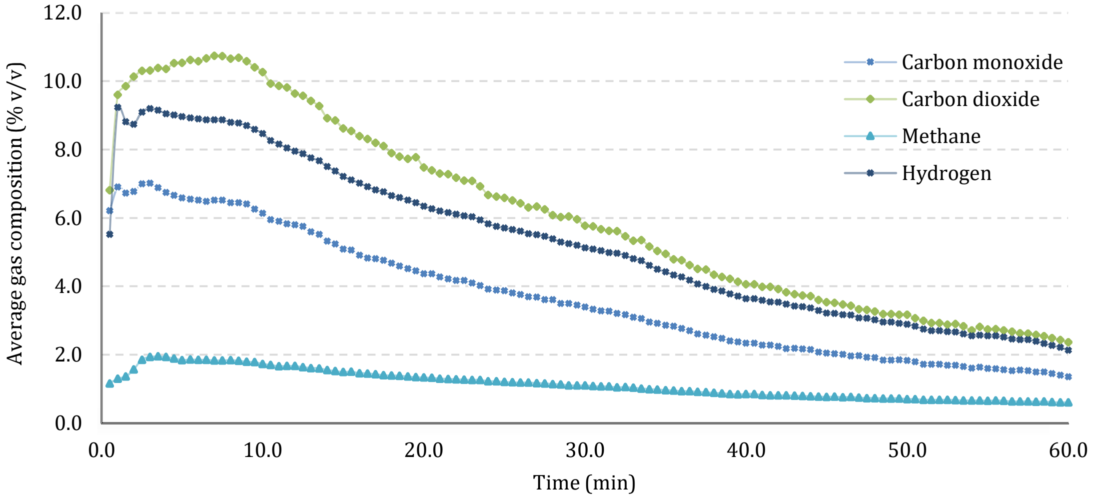


Figure 3.2. Syngas composition of cassava stalk gasification.

C. Electrolysis

The hydrogen production from alkaline electrolysis was performed considering the variation in the concentration of the electrolyte (NaOH) and the fluctuations in the energy provided by the solar panel (Direct - energy from the panel and Indirect - energy provided by the batteries in times of absence of light). The voltage and amperage ranged from 9-10V and 0.12-0.15A during all tests due to the solar panels' fluctuations in the energy supplied. **Figure 3.3** shows the volumes of hydrogen as a function of time for different NaOH concentrations. As the voltage and amperage, the electrolyte concentration strongly affects the hydrogen volume, going from 0.19 mL/min (10 g/L NaOH) to 0.96 mL/min (50 g/L NaOH). Thus, it is evident that the production is higher as the concentration increases because increasing the amount of ions present in the solution increases the electrical conductivity and consequently promotes the reaction. This observation agrees with the results obtained by Guy and coauthors, where graphite tubes were used as cathode, and the maximum yield was observed at the highest NaOH concentrations [55]. After the hydrogen gas was produced and the respective mass balances were carried out, it can be established that alkaline electrolysis can achieve yields of 0.013 kg hydrogen/kg feedstock.

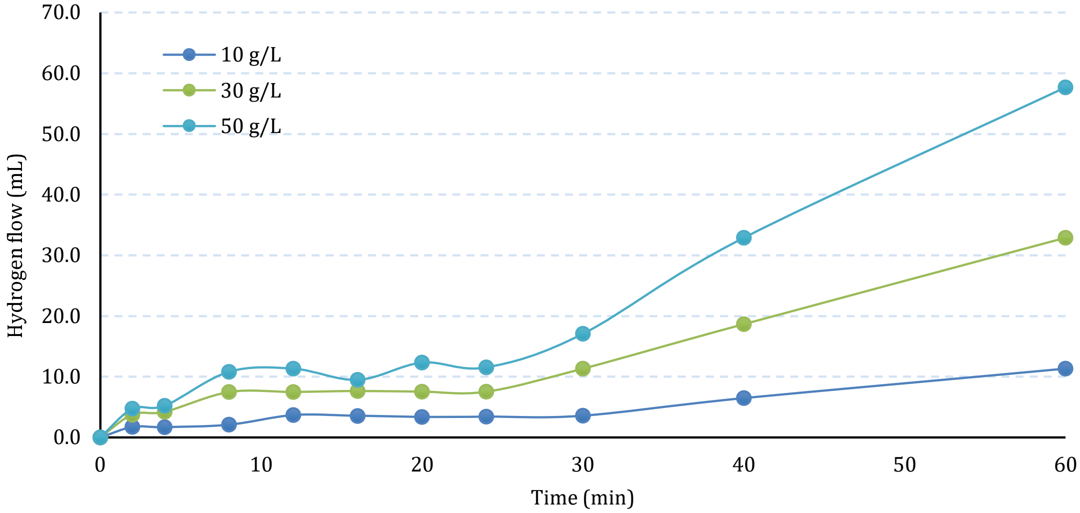
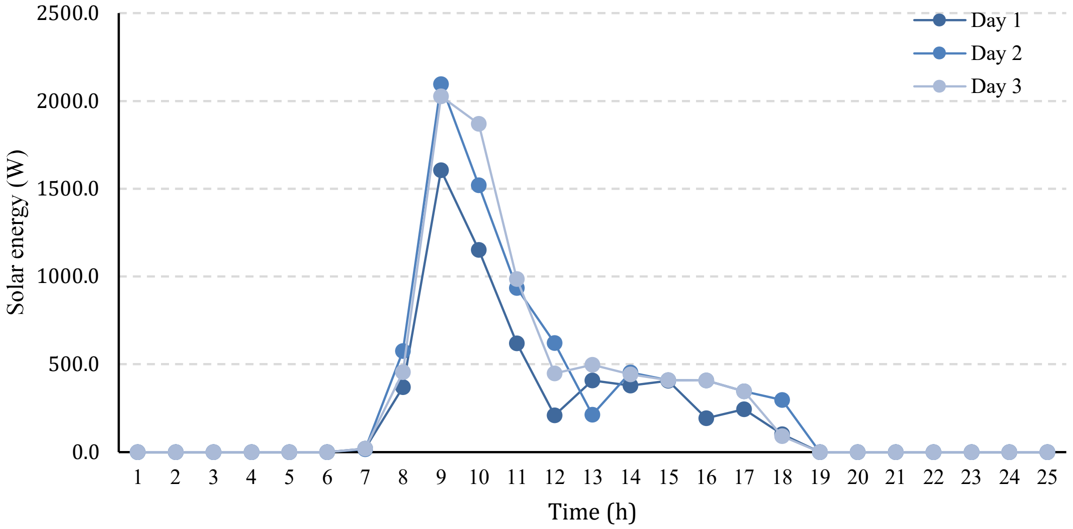
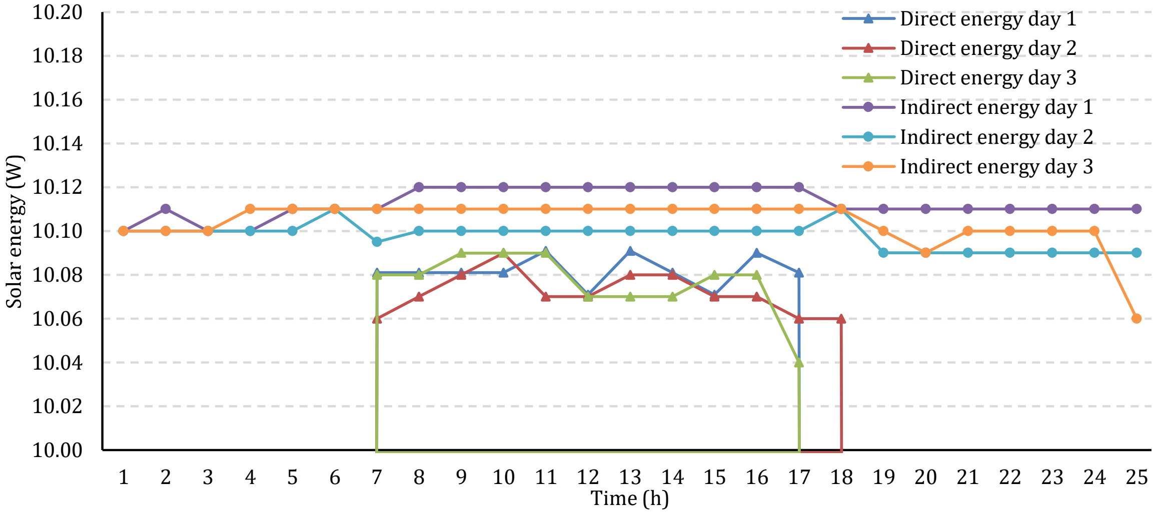


Figure 3.3. Hydrogen flow as a function of time at different electrolyte concentrations (NaOH).

Fluctuations in power input to the system also affect process performance. Therefore, the fluctuation of the power level of the solar panel was analyzed when power was acquired directly (solar peak hour) and indirectly (batteries powered by the solar panel). **Figure 3.4** shows how the energy produced by the solar photovoltaic modules is not constant, and this variation is due to changes in solar irradiance throughout the day. The measurements were taken on different days during the month of June with an average temperature of 22°C-23°C. The climates of the intertropical zone are very stable and show little variation over the years. All climatic types in this zone are isothermal, i.e., with little variation in temperature throughout the year, so they are not considered divergent measurements. Since the amount of hydrogen produced is directly proportional to the current supplied to the electrodes, the rate of hydrogen production is affected by the variation in the energy rate. These variations stem from external phenomena in the solar panel, such as power losses in the inverters and transformers, losses ranging from 3-10% of the energy produced. Additionally, wiring can also impact energy variations of 1% to 2%, and finally, there is the phenomenon of disparity. The disparity is found in solar cells, where one cell can capture solar radiation better than others despite being built with technological rigor. This is a common phenomenon in solar panels, generating variations of approximately 5% of the energy [56]. In contrast, the indirect energy provided by the batteries can be considered more "stable" because the batteries regulate the energy, avoiding over-power peaks or low-intensity currents. These phenomena have been previously reported by other authors [57].



A) Solar energy production



B) Energy supplied by the solar panels (i) Direct: peak solar time and (ii) Indirect: energy from the batteries in the absence of sunlight

Figure 3.4. Variations in A) Solar energy production and B) Energy supplied by the solar panels (i) directly: peak solar time and (ii) indirectly: energy from the batteries in the absence of sunlight.

3.3.3. Techno-energetic assessment

The techno-energetic assessment for hydrogen production is summarized in **Table 3.4**. Within the mass indicators, the scheme with the highest hydrogen yield was the SMR since this technology presents the highest feedstock utilization and does not require processes before the transformation, such as biomass pretreatment. A higher yield also generates a lower PMI index, which implies a higher use of the input streams, where feedstock and reagents were included. The second best-performing scheme was SBMR, followed by GF. However, considering the PMI and MLI indices, in the SBMR the raw materials were better utilized while in the GF higher residual flows were generated (exhausted syngas, after hydrogen extraction). Finally, the scheme with the lowest yield was the EL since the hydrogen flow generated is low, and the amount of waste generated is high (water with electrolyte that did not react). One way to improve process performance and generate lower waste streams is water recirculation; some authors report that recirculation of 90 % of the unreacted water can increase net benefits by up to 250% [58].

Table 3.4. Techno-energetic analysis for hydrogen production schemes.

Index	Unit	SMR	SBMR	GF	EL
Mass					
Product yield (Y_H)	kg Hydrogen/ kg RM	0.412	0.036	0.034	0.006
Process mass intensity (PMI)	kg IS/ kg P	3.26	6.45	23.38	24.69
Mass loss index (MLI)	kg WS/ kg P	2.26	5.45	22.38	23.69
Energy					
Specific energy consumption (SEC)	kW/ kg RM	0.95	0.81	4.62	0.38
Self-generation (SGI)	N.A	14.46	1.50	0.24	0.53

RM: Raw materials, IS: Inlet streams, P: Products, WS: Waste streams.

The GF scheme had the highest energy consumption (SEC), because it is the process with the highest temperature, where biomass combustion ranges between 900-1000°C [59]. The endothermic nature of the reaction causes excessive energy consumption during the process and becomes an important constraint when evaluating the thermal efficiency of the process. Followed by GF, the second process with the highest energy consumption was SMR and SMBR due to using two reactors to carry out methane or biomethane reforming and WGS. This equipment demands high-pressure steam to obtain the reaction temperatures. Additionally, using multiple heat exchangers that condition the streams for the separation stages where the membrane temperature ranges between 30°C and 50°C implies energy for cooling. Also, in the EL process, energy consumption is relatively low, and is associated with the use of membranes for gas separation and the energy supplied to the electrolysis stack.

The SGI indicator shows that the process with the highest mass yield (Y_H) also had the highest energy produced in situ as hydrogen. In this case, SMR has multiple advantages over non-conventional processes derived from biomass utilization, considering that commercial methane has a higher purity than biomethane produced by anaerobic digestion. The high efficiency of reforming processes is because this process is carried out at high pressures and temperatures, which promotes the combustion of methane. As a result, a significant volume of syngas is produced. In addition, the reformed gas is cooled and fed into a WGS exchange reactor to maximize hydrogen production, which significantly increases the yield of the process.

Finally, the energy analysis included the Net Energy Value (NEV) analysis, which is established as the difference between the energy of the products (hydrogen) and the energy demanded by the process in terms of utilities. In this way, the processes that involve more energy produced in the form of hydrogen are optimal at the energy level. On the contrary, the processes that demand greater energy in the form of utilities are processes with negative NEV. For the considered schemes, only petrochemical processes such as SBMR and biomethane processes such as SMR showed positive values of 13349.7 kWh and 438.04 kWh, respectively, which implies an integral use of energy in the process. Contrary, the thermochemical and electrolytic processes showed low energy utilization with negative NEV values of -3765.36 kWh and -185.56 kWh, respectively. The process with the lowest energy utilization was GF due to the multiple demands of utilities in the form of steam to reach combustion temperatures and cooling water to recondition the streams. In addition, it was necessary to increase the membrane pressure in the separation processes, which entails using compressors, equipment known because about 10 % to 30 % of the compressed air reaches the point of final use. At the same time, the rest is lost in the form of thermal energy and, to a lesser extent, through leakage and inefficient use [60]. Finally, electrolytic processes have low reaction yields, generating large energy losses. Thus, both processes must include energy recovery systems to reduce utility demand and improve the NEV.

3.4. Conclusions

Production systems using hydrogen as an energy carrier or feedstock are essential to find logical pathways towards a medium to long term energy transition. Furthermore, it must be ensured that the hydrogen produced is cheap, safe, clean, and efficient in order to promote the establishment of carbon-neutral societies. Therefore, the objective of this study was to compare and evaluate, using experimental tests and simulation schemes, the main technologies for hydrogen production, considering conventional (SMR) and non-conventional (SBMR, GF, and EL) technologies. The analysis considered technical and energetic indicators to establish the critical challenges faced by the technology and, thus, to establish possible solutions that allow the implementation of new hydrogen-based energy systems.

According to the results, conventional technologies such as SMR show the best mass efficiencies and the lowest energy consumption. However, when the methane becomes a biotechnological source, the production yield decreases considerably because cassava stalks anaerobic digestion shows lower yields than other agricultural residues. On the other hand, the GF processes presented the highest PMI and MLI index, which implies a lower utilization of feedstocks and a high production of waste flows. One way to improve these indicators is to use the exhaust syngas from the GF in cogeneration processes. Likewise, one way to improve feedstock utilization in the EL is to propose recirculation schemes that allow utilization of up to 90% of the solution that is not reacted. These changes can promote the energy and mass efficiency of the process. However, it is necessary to continue researching the SBMR, GF, and EL processes to improve the hydrogen production flows by adding catalysts, finding electrolytes with higher yields, or generating valuable by-products in the processes. Until these issues are solved, hydrogen production will continue to be strongly dependent on conventional processes since they are the most energy, mass, and economically productive.

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Chapter 04: Comparative analysis of biological and electrolytic processes for hydrogen production.

Abstract

Fossil fuels are facing imminent depletion due to the accelerated energy consumption worldwide, leading to the necessity of alternative fuels such as hydrogen. In this study, hydrogen production was experimentally evaluated considering two alternative technologies: alkaline electrolysis and dark fermentation based on rice straw processing with T. *thermosaccharolyticum* W16. Electrolysis was performed using a 5% NaOH solution and solar photovoltaic energy. In the biological processes, the rice straw was first pretreated with 2% NaOH for delignification, and the sugar-enriched solid was then hydrolyzed with Cellic CTec2 for sugar hydrolysate production (29.3 g/L glucose and 7.51 g/L xylose). The experimental data were used to scale up the processes through simulation computational tools, obtaining yields of 11 g H_2/kg and 6 g H_2/kg feedstock for alkaline electrolysis and dark fermentation, respectively. The electrolysis scheme showed higher economic feasibility, with a production cost of 4.98 USD/kg and a profit of 26.4%. In contrast, dark fermentation had high operating costs of 4.7 M-USD/year and high capital costs of 6.68 M-USD, which raised the cost of hydrogen to 6.98 USD/kg. These results suggest that both processes require further research to increase the net benefits and decrease the cost of hydrogen production.

Keywords: *Hydrogen, dark fermentation, electrolysis, photovoltaic energy, tecno-energetic and economic assessment*

4.1. Introduction

Most of the world's energy needs are supplied by fossil fuels, which will lead to an imminent depletion [1]. The accelerated and excessive use of fossil resources has also caused an increase in global temperature due to the emissions of polluting gases, soot, ash, tars, and other organic compounds [2]. According to a report published by the International Energy Agency (IEA) in 2020, the primary use of fossil fuels was more than 12 billion tons of oil, equivalent to 81% of the total energy worldwide [3]. Among the main resources are coal and natural gas for electricity production, while gasoline supplies the demands of the transportation sector. Therefore, global attention has focused on the search for energy alternatives with lower environmental impact and high flexibility levels. The development of this objective raises the need for renewable fuels and energy systems with low carbon intensity since the energy and transportation sectors contribute the largest amount of GHGs [4].

The IEA has recognized the role of hydrogen in advancing industry and society towards renewable fuels [5]. However, the challenge of its widespread use as an energy carrier requires adopting appropriate strategies for effective and safe production with less environmental impact [6]. These aspects are evaluated from a sustainable perspective. Thus, identifying deficiencies in production schemes is key to making improvements and optimizations to develop a hydrogen-centered economy [7]. In recent years, significant efforts have been made to understand and evaluate hydrogen production schemes; however, many studies have focused on thermochemical and fossil fuel-derived processes and have yet to consider other production pathways, such as biological or electrolytic schemes. High mass yields and high pollutant by-products characterize thermochemical and petrochemical processes. In contrast, hydrogen from renewable resources such as biomass or water could reduce the environmental impact while using highly available feedstocks [8].

Sustainable hydrogen can be obtained by different technologies, including biological processes using algae and bacteria in bioreactors, where the CO_2 produced by biomass metabolism is considered carbon neutral, as it is part of the natural carbon cycle [9]. Suitable substrates for hydrogen production by dark fermentation include carbohydrate-rich crops or food industry residues [10]. Among the most prominent agricultural residues is rice straw, produced after plant cutting during harvesting and constitutes approximately 50% of the gross weight of the rice paddy. Global rice production peaked in 2022 at 516 million tons of rice, and the current trend indicates that rice production will continue to increase over the years due to accelerated population growth [11]. Meanwhile, the raw material in electrolytic processes is water, a highly available and renewable resource. Electrolysis is an electrochemical process where electrical currents act as a driving force for chemical reactions such as water decomposition into valuable gaseous hydrogen and oxygen [12]. Thus, hydrogen produced by electrolysis derived from renewable energies (i.e., solar and wind energy), being a sustainable, simple, and environmentally friendly process. In addition, electrolytic processes have the advantage of producing hydrogen with high purity levels. However, one of the main challenges of electrolysis is to increase energy efficiency to expand its applications on a large scale.

Hydrogen production through biomass fermentation or alkaline electrolysis schemes are established as promising schemes to decrease the environmental impact associated with conventional schemes such as thermochemical and petrochemical pathways. However, these processes have been evaluated in stand-alone schemes, and only some studies report techno-energetic and economic comparisons of alternative hydrogen generation schemes. Based on this, this work evaluated with experimental test the hydrogen production by (i) dark fermentation, considering an alkaline pretreatment and enzymatic hydrolysis of rice straw for subsequent hydrogen production using a Thermoanaerobacter *thermosaccharolyticum* W16 and (ii) alkaline electrolysis of water, with solar energy. Additionally, the processes were scaled in simulation schemes to be evaluated considering a techno-energetic and economic assessment, in order to establish the economic feasibility of renewable technologies and their opportunity of application as an alternative to conventional processes.

4.2. Methodology

4.2.1. Experimental procedure

4.2.1.1. Dark fermentation

a) Raw materials and reagents

Rice straw was obtained from a crop located in Montes de María, a rural area of Sincelejo, Sucre, Colombia (9°17′58″N 75°23′45″O). Rice straw was characterized following the methodology reported by Hsu et al. [13]. First, the moisture was adjusted to 10%, and the biomass size was reduced to 0.42 cm using a rotary knife mill (SR200 Gusseisen, Redsch GmbH, Germany). Rice straw composition was estimated by considering carbohydrates, lignin, extractives, and ash content. Carbohydrates were determined by the acetic acid chlorination method to establish the cellulose and hemicellulose content. Lignin and ash were determined following the methods described by the National Renewable Energy Laboratory NREL/TP-510-42618 and ASTM (1755)-01, 2015, respectively. Finally, extractives were determined based on the technical report NREL/TP-510-42619, and liquors were analyzed by the 3,5 dinitrosalicylic acid (DNS) method. The reagents used for the experimental assays were NH_4Cl (Loba Chemie, India), K_2HPO_4 (Loba Chemie, India), KH_2PO_4 (Scharlau, Australia), $MgCl_2.6H_2O$ (Loba Chemie, India), NaCl (Loba Chemie, India), KCl (Scharlau, Australia), cysteine-HCl (Alfa Aesar, United States of America), yeast extract (Scharlau, Australia), tryptone (Condalab, Spain) and NaOH (Panreac, Spain).

b) Microorganisms and culture media

The strain, T. *thermosaccharolyticum* W16, was a glucose-xylose fermenting strain provided by Vortex company (Bogota, Colombia). The strain was grown at 60°C and in a modified medium (MB) based on the methodology reported by Ren et al. [14]. The composition of the MB in g L^{-1} was 1.0 NH_4Cl, 3.0 K_2HPO_4, 1.5 KH_2PO_4, 0.5 $MgCl_2.6H_2O$, 1.0 NaCl, 0.2 KCl, 0.5 cysteine-HCl, 2.0 yeast extract, 2.0 tryptone, 10 glucose, 1 mL L^{-1} of trace element and vitamin solutions. The trace elements and vitamins were prepared considering the methodology reported by Balch et al. [15], and the strain was used as inoculum when it reached its exponential growth phase.

c) Pretreatment and enzymatic hydrolysis

The pretreatment and enzymatic hydrolysis of rice straw were carried out following the methodology reported by Ren et al. [14]. The rice straw was pretreated with 2% NaOH in a liquid-solid ratio of 1:10 (w/v) at 80°C for 2 h. The cellulose-rich solid was collected, washed with distilled water until neutral pH, and dried at 105°C until constant weight. Then, a batch of enzymatic hydrolysis was performed in 250 mL flasks. The working volume was 100 mL of a mixture of 0.05 M citrate buffer (pH 4.8) and solid substrate in a 1:10 (w/w) ratio. The enzyme used was Cellic CTec2 (Sigma Aldrich, USA) with a ratio of 0.3 mL/g substrate based on the reports of Castillo García et al. [16]. The sample was incubated with stirring at 150 rpm and 50 °C for 72 h. Periodically, samples were taken from the reaction mixture for sugar analysis. After the time elapsed, the enzymatic hydrolysis was stopped with a thermal process, and the hydrolysate was vacuum filtered and stored at 4 °C.

d) Batch fermentation

Hydrogen production with strain T. *thermosaccharolyticum* W16 was performed in amber flasks of 100 mL (50 mL of working volume) using the hydrolysates from the previous steps. The hydrolysates were modified based on the components of the MB medium, except for carbon sources (glucose), all other nutrients in the medium were kept constant. The exponential growth phase inoculum was added at a concentration of 2% v/v, and the solution was gassed with nitrogen for 10 min before hermetic sealing to ensure an anaerobic atmosphere. All experiments were performed at 60 °C for 36 hours, stirring at 150 rpm, initial pH of 7.0 (adjusted with 2 mM NaOH), and an initial sugar concentration of 10 g/L. Pure glucose was used as a blank. Samples of produced gas were collected through a gas syringe before composition quantification using a portable gas analyzer (GASBOARD 3100p, Wuhan, China).

e) Analytical methods

The content of cellulose, hemicellulose, and lignin in the raw material, before and after pretreatments, was calculated considering the chemical characterization methodology previously reported. The initial and final sugar composition of the enzymatic hydrolysate and the sugar consumption during dark fermentation were quantified using an Agilent model 1260 high-performance liquid chromatography (HPLC) system (Agilent Technologies, Santa Clara, CA, USA) with an ICSep ICE-COREGEL 87H3 column (Concise Separations, San Jose, CA, USA). The column oven temperature was set at 65 °C. A 5 mM solution of H_2SO_4 was used as the mobile phase, and an operating flow rate of 0.6 mL/minute, using a refractive index detector at 35 °C.

4.2.1.2. Electrolysis

a) Raw materials and reagents

The water used during the experimental tests was distilled water, which was subjected to a prior distillation process to extract contaminants and prevent corrosion of the electrodes. This process was carried out using a ViLab distiller (Medellin, Colombia). Additionally, reagents with NaOH (Panreac, Spain) were used as electrolytes in the solution.

b) Alkaline electrolysis

Experimental alkaline electrolysis tests were performed following the methodology described by Shen et al. [17]. Initially, a 5% NaOH solution was prepared, where electrodes composed of metal oxides with a size of 80 mm were introduced. The system's power source was a 555W MBB Half-ell JAM72S30 530-555/MR half-cell solar panel module from JASOLAR. During the test, a tube with a length of 100 mm connected the electrodes and temporarily stored the gases produced. The experimental tests were conducted daily when the solar radiation was 850 W/m^2 at an average module temperature of 22 °C. The volumetric composition of the gases generated during the experimental tests was recorded using a portable gas analyzer (GASBOARD 3100p, Wuhan, China). The electrical current was measured with a UNI-T UT60A

RS 232C digital multimeter and the amperage with a 400A 600VDC 600VAC KT200 Kewtech digital clamp ammeter.

4.2.2. Simulation methodology

4.2.2.1. Scenarios

The scale-up and simulation of the hydrogen production schemes used experimental data from the tests, which fed the schemes established in the Aspen Plus v9.0 software. The first scenario considered the dark fermentation of rice straw, with previous stages such as pretreatment and enzymatic hydrolysis. Additionally, the production of volatile fatty acids in the fermentation stage was modeled considering the yields reported by Sekoai et al. [18]. The hydrogen and volatile fatty acid separation step was established with the yields reported in the literature [19]. In the second scenario, the alkaline electrolysis of water was considering the yields obtained in the experimental tests. In the separation stage, yields reported in the literature using membranes were considered [20]. Both scenarios used a raw material flow rate of 25 tons/day.

A. Dark fermentation

Three processing stages were considered in the simulation of the biological processes: (i) raw material pretreatment, (ii) dark fermentation, and (iii) hydrogen separation and purification, as shown in **Figure 4.1**. First, the raw material was dried, and the particle size of the raw material was reduced. Then, an alkaline pretreatment was performed to increase the availability of sugars for subsequent enzymatic hydrolysis. The alkaline pretreatment was carried out with 2% NaOH at a temperature of 80°C for 2 h and enzymatic hydrolysis was carried out with Cellic CTec2 for 72 hours and obtained a liquid stream enriched in glucose and a solid fraction with high hemicellulose content. Then, in the second stage, dark fermentation of the hydrolysates with strain T. *thermosaccharolyticum W16* was carried out in a bioreactor at 60°C with a pH of 6.5-7 for 36 hours. Simulations of the first two stages considering the operating conditions and mass ratios used in the experimental tests. Finally, in the separation stage, the gas stream was purified using pressure swing adsorption (PSA) to obtain hydrogen, and CO_2 was captured with a vacuum swing adsorption (VSA) unit with recoveries of 90.8% [19]. Finally, during the simulation, the valorization of the volatile fatty acids (VFAs) produced during the fermentation of the biomass was considered. For the simulation of this productive stage, the yields reported by Sekoai et al. [18] were used, and the separation stage was developed following the methodology described by García-Velásquez et al. [21].

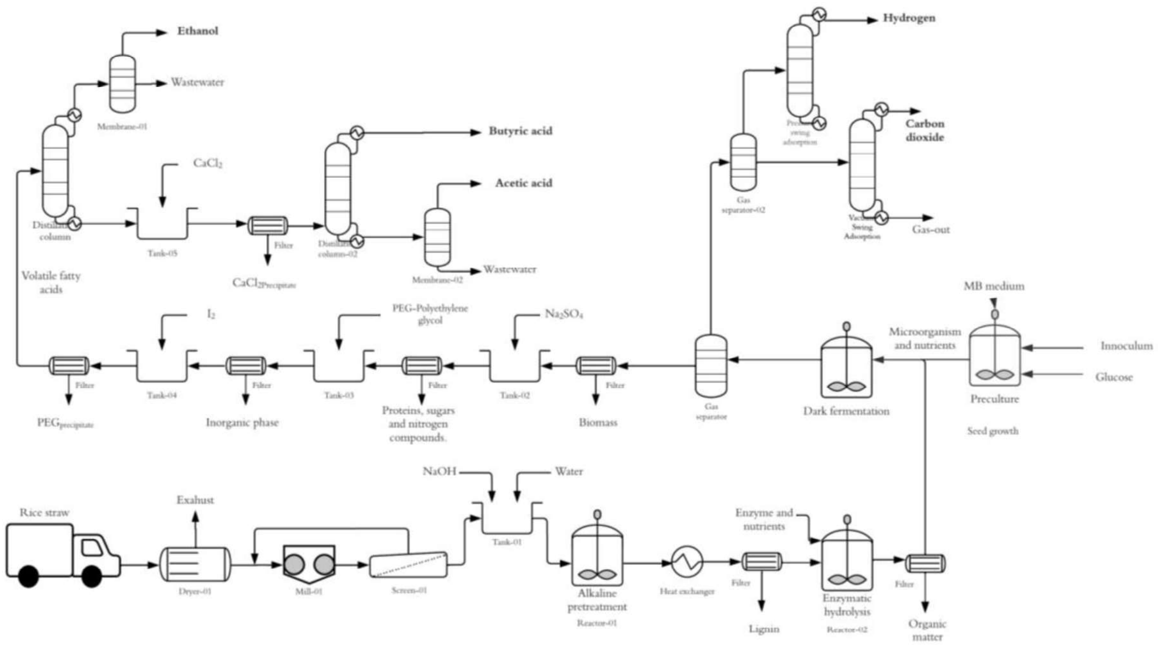

Figure 4.1. Dark fermentation flow diagram.

B. Alkaline electrolysis

An electrochemical model previously reported by Sanchez et al. [22] was used for the electrolytic process. First, an electrolyte solution of NaOH was produced and introduced into the electrolysis stack and continuously fed with electric current from the solar panels. The most commonly used electrolyte for alkaline electrolysis is sodium hydroxide (NaOH) in aqueous solution. This electrolyte has a high concentration of hydrogen ions, which facilitates the decomposition of water into hydrogen and oxygen following equations (1-3) [23]. Then, the generated gases were fed individually to a separation process, where first, the electrolyte solution was removed with liquid-gas separators. Finally, the gases were concentrated with membranes (see **Figure 4.2**) based on yields reported by Brauns et al. [20]. The non-random two-liquid thermodynamic (NRTL) model was used for the liquid phase, and the Hayden O'Connell equation was used for the vapor phase [24].

$$\mathrm{H_2O} \rightarrow \mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \qquad \text{Eq. (1)}$$

Cathode

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H_2} \qquad \text{Eq. (2)}$$

Anode

$$2\mathrm{OH}^- \rightarrow \frac{1}{2}\mathrm{O_2} + \mathrm{H_2O} + 2e^- \qquad \text{Eq. (3)}$$

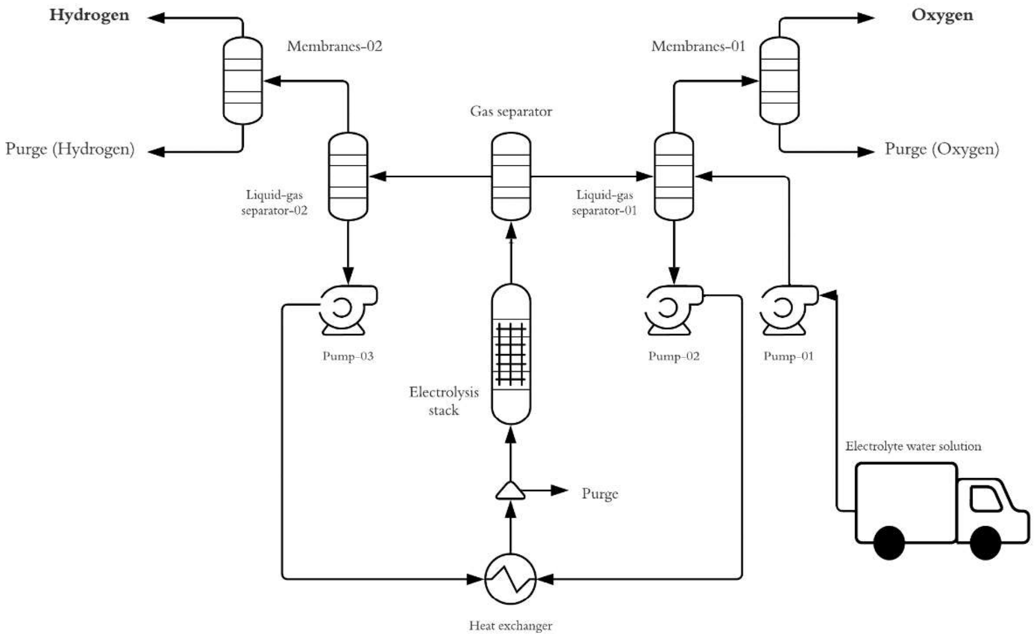

Figure 4.2. Alkaline electrolysis flow diagram.

4.2.2.2. Techno-energetic and economic assessment

The proposed schemes for alternative hydrogen production were analyzed considering a techno-energetic and economic assessment. For this purpose, the mass and energy balances provided by the simulation schemes were used. The techno-energetic evaluation was carried out using the indicators presented in **Table 4.1**, where product yield ($Y_{Hydrogen}$), mass loss index (MLI), and process mass intensity (PMI) refer to mass indicators and specific energy consumption (SEC) was the energy indicator [25]. Mass indicators determine the mass used during the process and quantify the waste generated for kg of product. Likewise, the energy indicator determines the energy consumed (SEC) in utilities and hydrogen, respectively.

Table 4.1. Mass and energy index used to compare the proposed scenarios.

Indicators	Equation	Unit	Eq.
Mass	$Y_{Hydrogen} = \frac{\sum \dot{m}_{Product,i}}{\dot{m}_{Feedstock}}$	kg hydrogen/ton of raw material	(4)
	$MLI = \frac{\sum_{i=1}^{N} \dot{m}^{in} - \sum \dot{m}_{Product,i}}{\sum \dot{m}_{Product,i}}$	kg waste streams/ kg hydrogen	(5)
	$PMI = \frac{\sum_{i=1}^{N} \dot{m}^{in}}{\sum \dot{m}_{Product,i}}$	kg raw material and reagents/ kg hydrogen	(6)
Energy	$SEC = \frac{\dot{Q} + \dot{W}}{\dot{m}_{feedstock}}$	kW/kg of raw material	(7)

The economic assessment considered the socio-economic context of Colombia and an annual working time of 8,000 hours. Data provided by the central bank were used, where the interest rate was set at 9.34 % and the tax rate at 35 % (see **Table 4.2**). Similarly, the annual minimum wage in 2023 was used to establish the labor cost of operators and supervisors in the schemes. The costs associated with utilities (i.e., electricity or steam), depreciation, maintenance, administrative, and general plant expenses were obtained from the economic assessment performed in the Aspen Process Economic Analyzer v9.0 software and considering the proposed evaluations reported by Peters et al. [26]. Finally, the economic profitability of the schemes was determined with the net present value (NPV) for 20 years, operating expenses (OpEx), capital expenditures (CapEx), and net profits. In addition, the production cost of hydrogen as the main product and the by-products derived from each scheme were determined.

Table 4.2. Parameters used during the economic evaluation of hydrogen production schemes.

Component	Value	Units	Economic parameters		
Rice straw	0.022	USD/kg	Shifts	3	Shifts/day
Water	0.326	USD/m^3	Working time	8	Hours/day
Hydrogen	3.35	USD/kg	Operator wage	328.31	USD/month
Oxygen	1.67	USD/kg	Supervisor wage	656.62	USD/month
Butyric acid	2.00	USD/kg	Electricity	0.055	USD/kWh
Acetic acid	0.53	USD/kg	High P. Steam (105 bar)	8.15	USD/ton
Ethanol	2.00	USD/kg	Middle P. Steam (30 bar)	8.07	USD/ton
			Low P. Steam (3 bar)	7.89	USD/ton

4.3. Results

4.3.1. Experimental results

4.3.1.1. Dark fermentation

a) Pretreatment and enzymatic hydrolysis

The chemical composition of rice straw changed during alkaline pretreatment, and it is presented in **Table 4.3**. The chemical characterization of the initial raw material agrees with other studies, where a cellulose composition of 40.3%, hemicellulose of 15.3%, and lignin of 12.7% were reported [27]. It should be noted that the chemical composition of rice straw varies according to its origin, variety, and harvesting time. However, most literature reports agree that rice straw contains a significant amount of sugars that can be utilized by hydrogen-producing microorganisms. After pretreatment, a 45% increase in cellulose concentration and a decrease in hemicellulose and lignin content can be observed. The main objective of an alkali pretreatment is to hydrolyze lignin with alkaline agents at high temperatures due to its amorphous and cross-linked structure. However, such removal also allows the hydrolysis of a fraction of the hemicellulose in the lignocellulosic matrix [28]. Thus, the pretreatment proves efficient as it increases the amount of cellulose, decreases lignin by 42%, and removes up to 50% of the hemicellulose from the initial biomass.

Table 4.3. Chemical composition of original and pretreated rice straw.

Item (% wt. dry basis)	Raw material	SD	Raw material pretreated (2%v/v NaOH)	SD
Total extractives	18.368		16.502	
Cellulose	42.725	± 0.93	61.366	± 0.54
Hemicellulose	10.082	± 4.05	4.467	± 3.03
Insoluble acid lignin	20.019	± 4.10	14.296	± 1.09
Soluble acid lignin	0.594	± 1.28	2.042	± 0.45
Ash	8.210	± 0.07	0.979	± 0.82
Solid recovery yield (%)			43.98 ± 7.35	

SD Standard deviation

During the enzymatic hydrolysis of rice straw with Cellic CTec2, it was observed that the concentration of monosaccharides changed over time, with the first 15 h being the most productive (see **Figure 4.3**). Thus, glucose, xylose, and arabinose concentration increased in the first hours to 29.13 g/L, 7.51 g/L, and 1.19 g/L, respectively. The accessibility of cellulose and hemicellulose to enzymatic attack is related to the type of substrate, enzyme used, feed rate, and agitation speed. Thus, some authors suggested that effective stirring with optimal particle size reduction increases the efficiency of the hydrolysates [29]. The Cellic CTec2 enzyme was developed specifically for the hydrolysis of lignocellulosic materials and, therefore, has significant advantages over other existing enzymes, such as lower enzyme requirements for hydrolysis, lower cost, and greater stability against inhibitors [30]. Additionally, this enzyme presents the advantage that it is not necessary to enrich the enzyme solution with exogenous b-glucosidases, as in the case of Celluclast 1.5L FG, which for many years was considered for the enzymatic hydrolysis of cellulose [31].

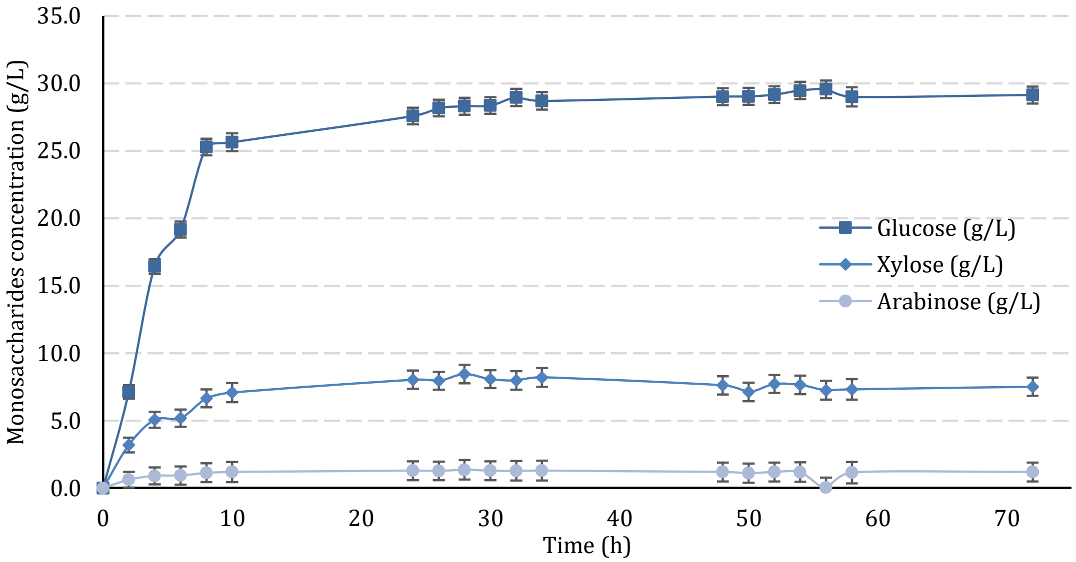

Figure 4.3. Variation of monosaccharide concentration during enzymatic hydrolysis.

Finally, **Figure 4.4** shows the sugar balance corresponding to the raw material pretreatment stage. Initially, the raw material starts with approximately 15.84 g of sugars in cellulose and hemicellulose. Then, once the first pretreatment corresponding to delignification with alkaline agents was carried out, the fraction of sugars recovered in the solid corresponded to 8.687 g, while in the liquid fraction was retained at 7.151 g in the form of C_5 sugars such as xylose and arabinose, and C_6 sugars such as glucose, galactose, and mannose, which implies a loss of 0.006 g in the process. Then, the solid fraction resulting from the alkaline pretreatment continues to an enzymatic hydrolysis stage, where the liquid fraction enriched in sugars retains 6.55 g of sugars. In comparison, the residual solid fraction leaves with 1.17 g, which implies a loss of 0.96 g. Thus, of the initial sugars (15.84 g), approximately 6 % was lost during the pretreatment stages, and 52 % was retained in the black liquor from the alkaline pretreatment (85.9 %) and the remaining solid from the enzymatic hydrolysis (14.1 %). Thus, the pretreatment stages facilitate the access of the microorganisms to the sugar sources. Still, they also involve the loss of more than half of the sugars available in the raw material.

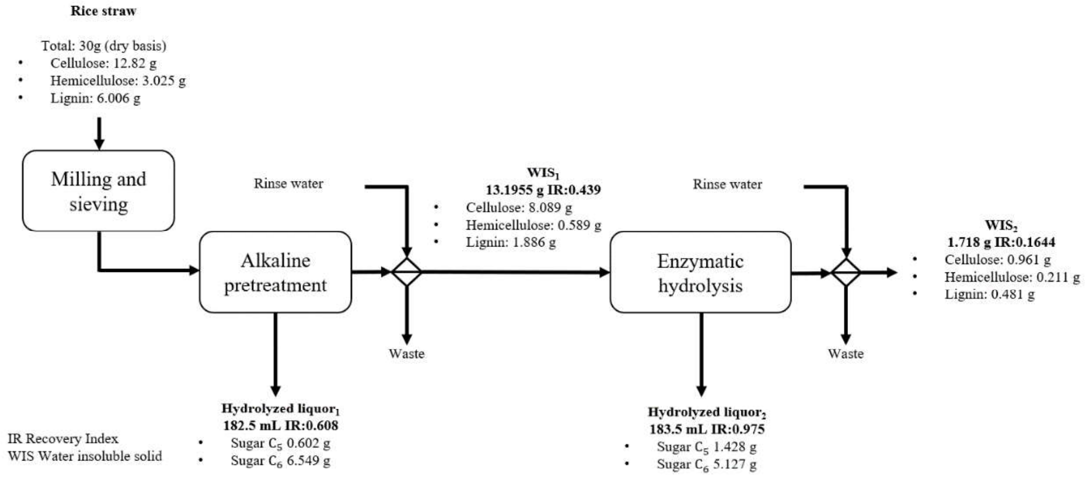

Figure 4.4. Sugar balance in the alkaline pretreatment and enzymatic hydrolysis stages for rice straw.

b) Batch dark fermentation

The culture of strain T. *thermosaccharolyticum* W16 showed a high growth on rice straw hydrolysates containing glucose and xylose as the main source of reducing sugars. It was possible to achieve an optical density similar to the synthetic MB initially prepared to promote the growth of the microorganism. The hydrogen generation presents in the hydrolysates and the blank (glucose) occurred simultaneously, as seen in **Figure 4.5**. The greatest microbial growth occurred during the first five hours of the fermentation test, where hydrogen production was lower and greater turbidity was generated in the liquid media. However, between 10 h and 25 h, the highest gas production rate occurred, mainly H_2 and CO_2. The measurements recorded in both media allowed inferring that the gas produced by the microorganisms had concentrations that varied between 90 % and 94 % for H_2 and between 5 % and 8 % for CO_2. The high concentration of H_2 in the medium allows inferring that although the volumes recorded are not higher than 5 mL, the gas produced was enriched in hydrogen, favoring the purity of the gas. This trend is also reported by Ren et al., where a maximum hydrogen concentration of 112 mM/L was recorded at 36 h of fermentation [14], which is lower than the 131 mM/L produced by rice straw hydrolysate, or the 188 mM/L produced in pure glucose medium.

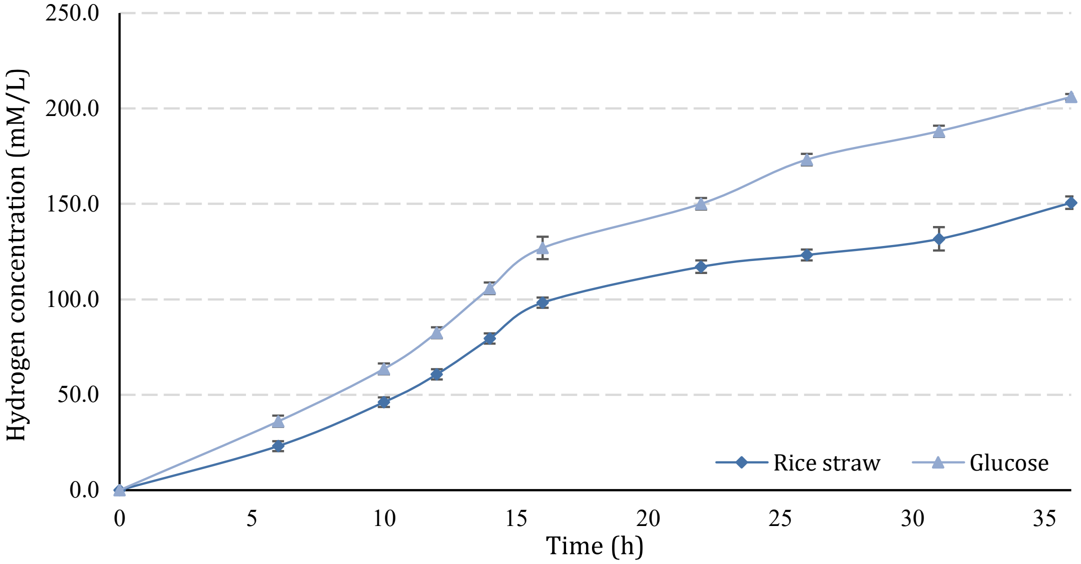

Figure 4.5. Hydrogen production by T. *thermosaccharolyticum* W16 using rice straw hydrolysate and glucose.

The hydrolysates presented the same compounds of the MB (pure glucose), except for the source of sugars that came from an alkaline pretreatment, followed by enzymatic hydrolysis, so that in their composition, there were also components produced in these stages, such as furfural, xylitol, formic acid, and acetic acid, as degradation products. Additionally, sugars such as glucose, xylose, arabinose, and mannose, among others, are produced both as monomers and oligomers [32]. Therefore, **Figure 4.5** shows that hydrogen production was higher in the medium containing pure glucose compared to the medium made from the hydrolysates. This trend is due to the microorganism T. *thermosaccharolyticum* W16 being inhibited by furfural and HMF by-products recorded during delignification. With alkali pretreatment, a production of 0.03 g/L furfural was recorded, which affected hydrogen generation in the hydrolyzed medium. Similar studies have reported a 17.9% reduction in hydrogen production when the medium had concentrations of 0.60 g/L furfural with dilute acid pretreatments for corn stover [33]. Moreover, some reports inform that these furan derivatives act as potent inhibitors of many soluble enzymes involved in glycolysis, causing a presence of greater than 2 g/L furfural in corn stover hydrolysates to show no microbial growth [34]. In this study, the furfural in the hydrolysate reduced hydrogen production by 30 % compared to the pure glucose medium. Additionally, sodium acetate, recorded at 3.46 g/L for rice straw hydrolysates, affected hydrogen production yield. For example, some reports studied the effect of acetate on T. *thermosaccharolyticum* W16 strain and found that when the sodium acetate concentration ranges between 4 and 5 g/L, it could stimulate hydrogen production, increasing yields up to 9

% [35]. Therefore, it is concluded that the presence of sodium acetate in the hydrolysates could have increased the hydrogen production (131 mM/L) compared to that reported by other studies where hydrogen yields range between 110 and 120 mM/L [14]. Finally, considering the yields obtained in the experimental tests, a yield of 0.01506 g of hydrogen/g of glucose and 6.24 g of hydrogen/kg of raw material can be established.

4.3.1.2. Electrolysis

The experimental tests for hydrogen production by alkaline electrolysis considered (i) the influence of the electrolyte concentration on hydrogen production, (ii) the variation in the voltage supplied to the electrolysis stack based on direct energy (energy in solar peak hour) or indirect energy (absence of sunlight). Thus, measuring the amount of hydrogen produced over time was possible, as shown in **Figure 4.6**. In the stacks, the gas production yield is strongly associated with the supplied electric potential and the concentration of the electrolyte, so it is evident that the hydrogen goes from producing 0.2 mL/min (10 g/L NaOH) to 0.96 mL/min (50 g/L NaOH). Thus, it is observed that hydrogen production is higher as the electrolyte concentration increases due to the increment of ions and electrical conductivity in the solution, which causes higher gas generation. Other studies also observed this trend at higher KOH concentrations [36]. After the hydrogen gas was produced and the respective mass balances were carried out, it can be established that alkaline electrolysis can achieve yields of 13.02 g hydrogen/kg raw material.

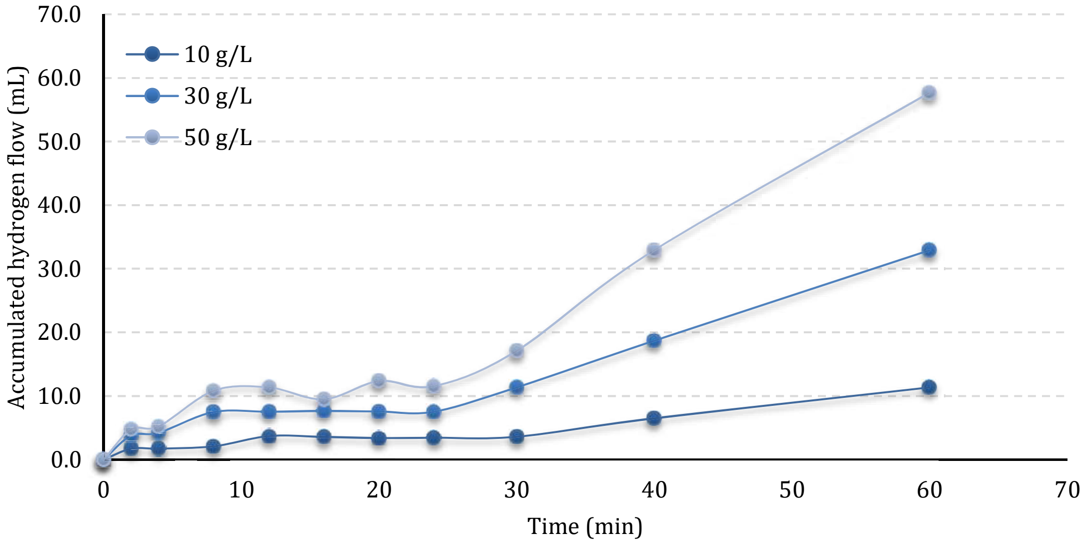

Figure 4.6. Hydrogen production at different electrolyte concentrations (NaOH).

Similar to electrolyte concentration, fluctuations in the input power flow to the system also severely affect the yield of the generated gases. Therefore, the variation in the energy flow input to the electrolysis system (see **Figure 4.7**) was evaluated involving two scenarios. In the first scenario, direct energy comes from the solar panel during the peak solar hour. In the second scenario, the energy supplied by the batteries that were fed during the day by the solar panel is also called indirect energy.

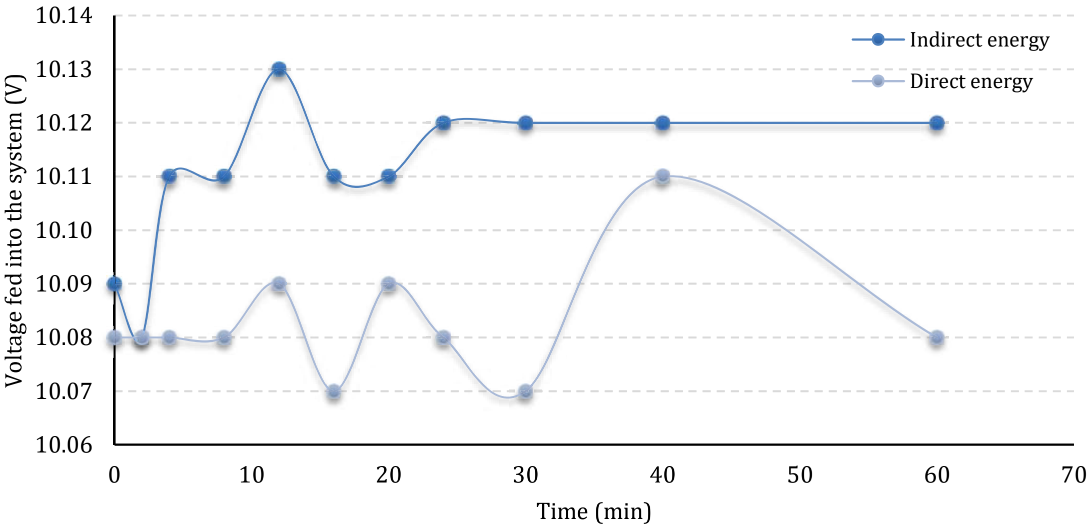

Figure 4.7. Variation in voltage supplying the electrolysis system

Figure 4.7 shows that the energy supplied by the electrolysis cell was not constant, especially in the case of direct energy, where greater variations were evident. Since the volume of hydrogen was proportional to the current supplied to the electrodes, the rate of hydrogen production was affected by the variation of the energy current. These variations result from energy transformations that occur throughout the electrical system. Thus, the energy provided by the solar panel module also shows fluctuations for each scenario, with a higher variation in the energy obtained directly. These variations are derived from external phenomena in the solar panel, such as energy losses in the inverters and transformers, losses due to wiring, or the disparity phenomenon, which can cause losses of up to 40 % of the energy received by the system [37]. Some authors suggest that the worldwide installed capacity of solar photovoltaic (PV) systems will increase in the coming years, from 486 GWp in 2018 to 10 TWp in 2030 [38]. However, as the development of solar panels increases, fluctuations due to climate variability and system losses will have a greater impact on power grids, causing negative effects on the stability of the power grid by affecting its voltage and grid frequency [39]. Therefore, one of the recent solutions is the installation of batteries that store and regulate the energy before distribution. As seen in **Figure 4.7**, the indirect energy scenario presents smaller variations, and therefore, the energy can be considered more "stable," and some authors have focused on improving these storage systems [40]. For this purpose, some studies recommend using different types of batteries. For example, supercapacitor storage can only be applied to very small photovoltaic-PV systems, Zn-Br batteries to medium-sized PV systems, flywheel energy storage (FES), Pb-acid batteries, Ni-Cd batteries, and lithium-ion batterie (LIB) can be applied to small and medium-scale PV systems, while applied compressed air energy storage (CAES) and pumped hydro storage (PHS) systems are used for large scale [41].

4.3.1.3. Techno-energetic and economic assessment

The techno-energetic assessment for hydrogen production with electrolysis and dark fermentation is summarized in **Table 4.4**. Among the mass indicators, the yield hydrogen production was evaluated, where electrolysis presented the best performance compared to fermentation. In biological processes, the hydrogen produced depends on sugars available in the medium; however, this concentration decreases as the process contemplates more production stages. Therefore, if an overall yield (including all products generated in each scheme) was considered, electrolysis and fermentation have yields of 0.099 and 0.281 kg of products/kg of raw material. Therefore, if an overall yield (including all products generated in each scheme) was considered**,** a total product yield of 0.099 and 0.281 kg of products/kg of raw material for electrolysis and fermentation was obtained if contemplate the addition of oxygen in electrolysis as well as VFAs in fermentation. However, considering the MLI indicator, which establishes the amount of waste generated per kg of product, it can be seen that the biological production, by increasing its product portfolio, also increases the waste generated, such as Na_2SO_4, iodine, and $CaCl_2$ precipitates, used during the purification stage of the VFAs. Thus, expanding the product portfolio in a scheme can involve higher mass yields but incur higher reagent consumption and, thus, higher waste generation. This phenomenon is also observed in the results of the PMI indicator. The PMI allows the consumption of raw materials and reagents per kg of product generated to be analyzed. Thus, the demand for input streams is significantly lower for hydrogen generation with electrolytic technologies than for biological processes.

Table 4.4. Techno-energetic analysis for hydrogen production schemes.

Indicators		Unit	Scenarios	
			Electrolysis	Dark fermentation
Mass	$Y_{Hydrogen}$	kg Hydrogen/ton of Raw material	11.0	6.0
	MLI	kg Waste streams/ kg Hydrogen	13.86	49.58
	PMI	kg Feedstock and reagents/ kg Hydrogen	12.86	48.58
Energy	SEC	kW/kg of Raw material	1.04	0.83

The results of the mass analysis of the schemes are due to the nature of the process. In electrolysis, the main raw material is decomposed in the presence of electricity, but in dark fermentation, it is necessary to condition the rice straw to isolate the sugars and use them in a bioreactor. In biological processes, yields are subject to operating conditions and the nature of the microorganism, showing inhibition from the hydrogen of VFAs [42]. Some authors suggest continuously extracting gases and metabolites to avoid stressing the microorganisms. For example, the strain *Thermoanaerobacter* strain AK68 is inhibited with relatively modest substrate loads (>20 mM) since it only manages to degrade half of the sugars, leading to hydrogen accumulation, a drop in pH, and low productivity of the microorganism [43]. After rice straw pretreatment, degradation by-products such as sodium acetate, furfural, HMF, and phenolic compounds, typical in an alkaline degradation, can be produced. Sodium acetate can stimulate the bacteria growth and hydrogen production at concentrations below 6 g/L. However, furfural, HMF, and phenolic compounds are characterized as inhibitors of hydrogen production, decreasing the process yield by up to 54.1% [33]. Thus, an exhaustive degradation product control is mandatory to improve the fermentation performance. In the energy analysis, SEC relates the energy demand of the process (heat and work) per kg of raw material. In this case, fermentation was the scheme with the best performance since electrolysis generates a high consumption of electricity, which increases the energy required to transform the raw material.

Finally, the results shown in **Table 4.5** were obtained in the economic assessment. In the CapEx, biological processes are more expensive due to the required equipment. Large or highly complex equipment such as bioreactors and distillation towers account for about 43 % of the CapEx. Dark fermentation also requires multiple heat exchangers to condition the streams in sensitive processes such as enzymatic hydrolysis or fermentation, representing up to 8 % of the CapEx. In electrolysis processes, the electrolysis stack accounts for 24 % of CapEx, followed by the membranes used to separate the gases, which can account for about 58 % of CapEx because they are susceptible to pressure and temperature changes and can easily become dirty, incurring higher maintenance costs. In addition, considering that the alkaline electrolysis scheme used energy coming from solar panels, the inclusion of this equipment in the CapEx increased its value by 20 %, which suggests that panels are a very relevant parameter at an economic level since they significantly affect the initial investment of a production scheme.

Table 4.5. Economic assessment for hydrogen production.

Item	Scenarios	
	Electrolysis	Dark fermentation
CapEx (M-USD)	1.88	6.68
OpEx (M-USD/year)	1.56	4.70
MPSEF* (kg/h)	151.04	190.13
Production cost (USD/kg)		
Hydrogen	4.98	6.96
Oxygen	1.22	
Ethanol 90%		1.75
Acetic acid 99%		0.32
Butyric acid 98%		1.74
Profit (%)	15.76	12.80
Gross income (M-USD/year)	0.49	0.69

*Minimum processing scale for economic feasibility

In the OpEx for biological processes, the cost of raw materials and capital depreciation contribute about 55 %. These results are due to the demand for multiple reagents to separate and purify VFAs. If these by-products were not considered, operating costs could decrease by up to 25 %. Still, net income would decrease by 16% since butyric acid and ethanol are products of high commercial interest. Similarly, the development of enzymatic hydrolysis has been considered a fundamental stage in reducing operating costs and water consumption and increasing the concentration of sugars in the fermentation broth. Preliminary studies indicate that increasing glucose concentration in the substrate can considerably reduce the cost of distillation after fermentation [44]. In electrolytic processes, the OpEx is strongly influenced by raw materials, especially the cost of water and utilities. Utilities account for about 46 % of the OpEx, with electricity making the largest contribution at 67 %. These phenomena have been previously reported by other authors, where variations in the cost and demand of electricity strongly influence the hydrogen cost [45]. For example, the electricity of a proton exchange membrane electrolyzers (PEM) is 22 % higher than alkaline-based technology, implying a 21 % increase in the cost of hydrogen produced [45]. Another important aspect of great relevance in electrolysis processes is water recirculation and the maintenance and operation of solar panels. The inclusion of solar panels increases operating costs by 14.7 %. Thus, since the yields are low compared to other technologies, the level of unreacted water in the process is more than 60 %. Therefore, some authors suggest that water recirculation can generate significant decreases in OpEx. In this study, the recirculation of unreacted water was considered, which decreased the operating costs by more than 21 %.

Given the feasibility of the process, a scale analysis was carried out to determine the minimum processing scale for economic feasibility (MPSEF). In this study, dark fermentation is the process with the highest MPSEF due to the lower mass yield generated. However, a minimum flow rate of 190.13 kg/h can generate serious supply problems if this technology is implemented in areas where rice production is not representative, or the residue is engaged in other industries. For example, some authors have reported using rice straw to produce ethanol, energy, and non-wood fibers, which generates competition for acquiring agricultural residue [11].

Finally, one of the most relevant indicators is the hydrogen production cost, which presented high values in both scenarios. This cost for petrochemical and thermochemical pathways is between 1.6 and 2.9 USD/kg H_2, which implies that electrolysis and biological processes require optimization processes to compete with these values. Optimization processes for electrolysis schemes must consider the variation in the electricity cost (electricity from a national grid or solar panels) and the return of unused water. In biological processes, increasing hydrogen production and separation schemes are critical for optimization [46]. However, the values obtained in the present work are similar to other studies, where the cost can vary between 5.78 and 23.27 USD/kg H_2 for biological and electrolytic processes [47]. Similarly, the price of ethanol, acetic acid, and butyric acid was consistent with other reports of 0.40-2.15 USD/kg ethanol [48], 0.35 USD/kg acetic acid [49], and 1.3-3.5 USD/kg butyric acid [50], Finally, **Figure 4.8** shows the net present value for both schemes. In general, the electrolytic processes involve lower CapEx and OpEx than the biological processes, which generates higher profit margins and higher net income. Thus, expanding the product portfolio can generate higher profits but also requires higher utility consumption, equipment acquisition, and not necessarily higher economic viability.

However, two scenarios were evaluated in the electrolysis schemes. Considering the strong influence of solar panels on the CapEx and OpEx, the NPV analysis was performed considering the inclusion of this equipment or the use of electricity from a national grid. Solar panels decrease the economic viability of the process since they influence the most relevant costs and become extra machinery. Some authors suggest that the possibility of including electrolysis schemes accompanied by solar panel (PV) or wind energy schemes should be accompanied by economic bonuses or government subsidies to promote renewable technologies. This would allow the development of sustainable production schemes without severely affecting the profitability of the process [51].

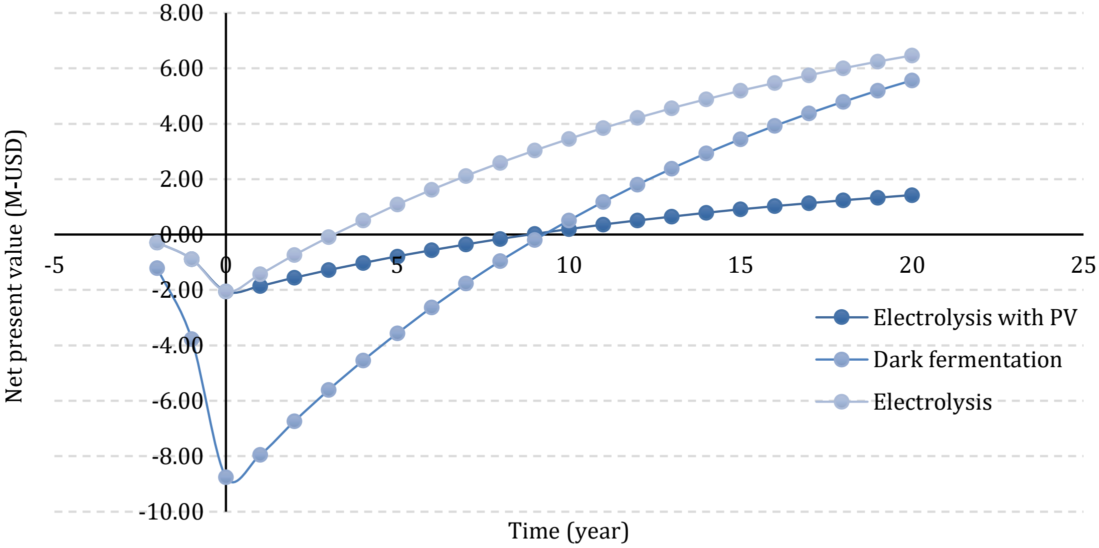

Figure 4.8. The net present value for the analyzed hydrogen production scenarios.

4.4. Conclusions

In recent years, due to the imminent depletion of fossil resources and the environmental impact derived from their use, collective efforts have focused on developing technologies for alternative energy carriers, such as hydrogen. Therefore, the objective of this study was to evaluate, experimentally and through simulation tools, the production of hydrogen through alkaline electrolysis and dark fermentation of rice straw. The results obtained in the experimental test suggest that in electrolytic processes, the volume of hydrogen produced depends on the primary energy source, in this case, solar energy. The fluctuations in direct energy must be solved with the use of batteries. In the biological processes, rice straw achieved concentrations of 29.3 g/L of glucose and 7.51 g/L of xylose after alkali pretreatment and enzymatic hydrolysis with Cellic CTec2. The experimental data were used to scale up the processes by simulation schemes where yields of 11 g H_2/kg and 6 g H_2/kg were obtained for electrolysis and dark fermentation, respectively. In the techno-energetic assessment, the electrolysis processes presented better performance and better utilization of the raw material, with the lowest CapEx (1.88 M.USD) and OpEx (1.56 M-USD/year), which generated a production cost of 4.98 USD/kg. However, during the analysis of the electrolysis schemes, it was found that the addition of electricity from solar panels increases the CapEx by 20 % and the OpEx by 14.7 %, decreasing the economic profitability of the process, reducing the profit from 26.4 % with energy from the national grid to 15.76 % with solar energy. In contrast, adding new operating units to expand the product portfolio increased the CapEx and OpEx in the biological processes, generating a production cost of 6.96 USD/kg. These results suggest that both processes require further research to increase net profits and decrease operating costs since the production costs are higher than those of conventional technologies such as steam methane reforming or coal gasification.

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Chapter 05: Sustainability of hydrogen production towards a neutral carbon society.

Abstract

Hydrogen could be produced from several feedstocks and technologies, making it an important partner in the energy transition to carbon-neutral societies. Hydrogen production can be based on renewable raw materials, such as agricultural residues, which are highly available and economical. However, there is no comprehensive analysis of all available hydrogen production technologies. Therefore, this work focused on developing a comparative analysis of the sustainability of the main hydrogen production technologies. Techno-energetic, economic, environmental, and social indicators were used to calculate a comprehensive sustainability index (S_{Id}). Steam biomethane reforming (SBMR) and electrolysis (EL) were the schemes with the highest S_{Id} based on the techno-energetic and environmental dimensions, respectively. However, the S_{Id} decreased substantially when the economic dimension was considered because SBMR presented high capital and operating costs and EL had low technical performance. On the other hand, thermochemical and biological technologies require further research to decrease the environmental burden and improve the mass yield of the process. Therefore, each production scheme involves different disadvantages that must be resolved to increase the opportunities for hydrogen development.

Keywords: *Hydrogen, sustainability index, life cycle assessment, economic assessment, carbon-neutral societies*

5.1. Introduction

The development of the world economy has always been strongly dependent on large energy reserves, especially fossil fuels, used as a primary energy source for industry, transport, and heat [1]. However, these energy reserves have been consumed disproportional to their production rate, leading to their imminent depletion. Additionally, the excessive use of fossil resources has triggered since the mid-20th century an anthropogenic concentration of greenhouse gases (GHGs) responsible for the increase in global temperature [2]. Therefore, the depletion of fossil fuels, the uncertainty of energy supply security, the strong connection between energy demand and economic growth, climate change, and the need to reduce CO_2 emissions have become humanity's main issues [3]. Accordingly, the world is facing a change of energy scenario, guided by a strong interest in renewable energies and the decarbonization of the global energy system [4]. Thus, some authors suggest that carbon-neutral energy production must exceed 10 TW to meet energy demand and to keep acceptable CO_2 levels in the atmosphere [5]. This goal requires shifting energy production, conversion, storage, and distribution technologies toward clean and sustainable development policies [6].

Environmental and economic concerns have led to great interest in alternative energy sources such as solar, wind, and geothermal energy [7]. However, all these technologies are variable and require energy carriers that allow seasonal storage and safe energy distribution. Therefore, hydrogen is anticipated to play an important role in the future of the energy sector [8]. Hydrogen is a clean fuel with no toxic emissions and can be produced from several technologies, using raw materials such as agricultural residues or forest biomass, as well as water in electrolytic systems. Additionally, the energy yield of hydrogen is 122 MJ/kg, being 2.75 times more than hydrocarbon fuels [9]. However, the high energy density also requires a suitable storage and transportation system [10]. Despite the many difficulties of a hydrogen-based value chain, the future energy perspective imposes hydrogen as a partner in the transport and manufacturing sectors. This phenomenon is evidenced by the large number of countries developing roadmaps, in many cases with specific numerical targets, for advancing hydrogen production technologies [11].

Currently in the case of hydrogen, three important technological bottlenecks must be overcome to rationally perceive an energy system based on renewable resources (i) reducing the cost of efficient and sustainable hydrogen production and supply, (ii) developing new storage systems for stationary and mobile applications, and (iii) establishing global policies aimed at developing clean energy systems that promote the inclusion of these resources in the global energy matrix [11]. Regarding the first bottlenecks, hydrogen can be produced from different raw materials and production technologies, with the predominant petrochemical pathway. Nowadays, more than 95 % of the hydrogen produced is derived from non-renewable resources, and hydrogen production with electrolysis or biomass-based systems accounts for only 1 % - 4 % [12]. Since conventional hydrogen production systems have high environmental impacts due to high CO_2 emissions, hydrogen produced from renewable sources such as biomass, solar energy, and electrolysis is ideal to replace conventional technologies [13]. Nevertheless, the environmental perspective alone cannot be considered for substituting an overall energy system. For example, although electrolytic processes report the lowest pollution rates due to zero emissions, the overall energy efficiency is very low [14]. Similarly, thermochemical processes present high production yields but low thermal efficiencies and high environmental impact associated with the production of secondary gases [15]. Conventional processes such as steam methane reforming are characterized by high environmental emissions and fermentation processes in biological pathways have the lowest yields in the market [16]. Therefore, processes should be evaluated from multiple perspectives, including their social impact. This work compared the main hydrogen production technologies based on renewable energy sources, such as electrolysis and biomass utilization by thermochemical and biochemical pathways. Additionally, steam methane reforming was evaluated considering methane of biotechnological source. Each technology was evaluated using simulation schemes, considering as raw material, agricultural residues of the main crops worldwide and a sustainability analysis was carried out considering the techno-energetic, economic, environmental, and social dimensions.

5.2. Methodology

5.2.1. Raw material characterization

The main agricultural residues worldwide were considered as raw materials. Among the largest crops worldwide are (i) cassava, an energy food with a production of more than 303 million tons in 2020 [17]; (ii) corn, with 1,216.9 million tons in 2022; and (iii) rice, with 212 million metric tons in 2021 [18]. However, after satisfying food demand, agricultural residues such as cassava stalks, corn stover, and rice straw represent between 11.8 % and 20.0 % by weight of the product, generating a considerable residue volume that can be used in energy processes. Cassava stalk, corn stover, and rice straw were selected and used in the experimental test. The agricultural residues were received from a crop located in Montes de María, a rural area of Sincelejo, Sucre in the north of Colombia (9°17′58″N 75°23′45″O). The residues were characterized following the methodology reported by Poveda-Giraldo [19]. Initially, some moisture was removed with a convective dryer and ground to 0.420 mm with a rotary knife mill. The composition of the residues was estimated by considering the content of extractives, carbohydrates (cellulose and hemicellulose), lignin, and ash. Extractives were determined based on the technical report of the National Renewable Energy Laboratory - NREL/TP-510-42619 and liquors were analyzed by the 3,5 dinitrosalicylic acid (DNS) method. Carbohydrates were determined by the acetic acid chlorination method. Lignin and ash were determined following the methods described by NREL/TP-510-42618 and ASTME (1755)-01 2015, respectively. Additionally, proximal analyses were performed to estimate total solids (TS), volatile solids (VS), volatile matter (VM), and fixed carbon (FC) content. MV was determined following ASTM E872-82 and SV and ST using ASTM E1756-08, and, finally, FC was determined by difference.

5.2.2. Process simulation: Hydrogen production with renewable technologies

The biorefinery schemes for hydrogen production were developed considering the socioeconomic context of Colombia and four scenarios were considered. The first scenario included hydrogen production from biomethane produced by anaerobic digestion of cassava stalk (steam biomethane reforming -SBMR) following the methodology reported by Ismail et al. [20]. The second scenario involved the thermochemical processing of corn stover (gasification), considering the methodology reported by Garcia et al. [21]. The third scenario included hydrogen production from the electrolytic process considering the reports of Sánchez et al. [22], and finally, the fourth scenario involved biological hydrogen production from rice straw, considering the study by Ren et al. [23]. Mass and energy balances were obtained using Aspen Plus v.9.0 software (Aspen Technology, Inc, USA) considering a feedstock flow rate of 25 tons/day and the experimental data from previous works. The assignment of feedstocks for each simulation scheme was developed considering the highest yield of each feedstock for hydrogen production considering the proposed technologies. Thus, cassava stalk presented better yields towards biogas [24], corn stover presented better thermochemical yields [25], and rice straw presented higher content of usable sugars in fermentation [26]. The process flow diagrams are reported in the Supplementary Material-Appendix A (see **FigA1 – FigA4**).

A. Steam biomethane reforming - SBMR

Hydrogen production from steam reforming of biomethane (SBMR) was developed using equilibrium models previously described by Abd et al [27]. First, the particle size and moisture content of the feedstock were reduced. Next, the biomass was fed into an anaerobic digester and mixed with sludge and nutrients at 37°C. Steam and biomethane were then mixed at a Steam/Biomethane ratio of 3, to be heated to 450 ˚C and 23 bar in a reformer. The syngas produced has an approximate H_2/CO ratio of 4.5 and outputs at 900 ˚C and 22 bar. The syngas was then cooled and sent to a water gas shift (WGS) reactor to increase the hydrogen content, where CO reacts with steam and increases the production of H_2 and CO_2 at 300 ˚C. The WGS reaction was exothermic, so the produced gas had to be cooled before being sent to a flash separator, where the remaining water was removed. In the last stage the pressure swing adsorption (PSA) unit was used to purify hydrogen from the reactor outlet stream.

B. Gasification – GF

For the thermochemical processes, the Grayson-Streed thermodynamic model and the Redlich-Kwong equation were calculated to describe the vapor phase, considering the data reported by Son et al. [28]. The simulation was carried out with biomass pretreatment, gasification, and hydrogen separation and purification. In the pretreatment stage, the particle size and the moisture content of the raw material were reduced to 2.5 cm and 10%, respectively. Then, the biomass was decomposed into H, C, O, and ash in a pyrolysis reactor and sent to a combustion chamber where CO_2, CO, H_2 and heat were produced. Finally, the carbon was reduced in the reduction stage, and a cyclone separated the ash from the syngas. For hydrogen separation and purification, the use of PSA columns was proposed. The exhaust syngas (after H_2 extraction) obtained at high temperatures and pressures, which can be used for electricity generation according to the principle of the Brayton cycle. The gas stream was mixed with fresh air and then compressed to 10 bars at 1000-1200°C [29]. The gases were heated in the combustion chamber, and the products were expanded in the turbine to the pressure required by the internal combustion engines.

C. Electrolysis -EL

For the simulation of the electrolytic processes, the non-random two-liquid model (NRTL) was used to describe the liquid phase and the Hayden O'Connell equation the vapor phase. An electrochemical model was also considered for the simulation [30]. The model includes different technical aspects to predict the electrochemical system, generate the polarization curve, establish the stack potential as a function of current density, and, therefore, calculate the hydrogen and oxygen production rate. For simulation purposes, water was introduced into a electrolytic reactor together with an electrolyte (KOH) at 75°C and 7 bar, and an electric current was continuously fed, causing the decomposition of water into oxygen (anode) and hydrogen (cathode). Once the gases are generated, an internal membrane in the reactor separates them so that they can be purified. The unreacted liquid solution was first removed with liquid-gas separators, and then the hydrogen- and oxygen-enriched stream was separated by membranes.

D. Dark Fermentation -DF

Finally, for fermentative processes, the studies previously reported by Ren et al. were considered [31]. The hydrogen production involves three stages: (i) raw material pretreatment, (ii) dark fermentation, and (iii) hydrogen separation and purification. First, the raw material was conditioned with an alkaline pretreatment to isolate the lignin in the liquid fraction at 80°C for 2 h with NaOH 2% v/v. Then, enzymatic hydrolysis was carried out to obtain a liquid stream enriched in glucose and a solid fraction with high hemicellulose content. For enzymatic hydrolysis, the Cellic CTec2 enzyme was used at 50°C for 15 h. Next, in the fermentation stage, the glucose-rich stream was fed with T. *thermosaccharolyticum* W16 strain in a fermenter at 60°C with a pH of 6.5-7 for 36 h. Finally, the gas stream (H_2 and CO_2) was purified using a PSA system and CO_2 was extracted with a vacuum displacement adsorption unit (VSA) with recoveries of 90.8% [32]. The process yields were derived from previous experimental work, and the separation of volatile fatty acids (VFAs) was developed following the methodology described by Garcia-Velasquez, et al. [33].

5.2.3. Techno-energetic analysis

The schemes were analyzed considering the mass and energy balances derived from the Aspen simulation. Comparative indicators were used to establish the potential of each coupling of each technology with its respective feedstock in hydrogen production (SBMR with cassava stalk, GF with corn stover and DF with rice straw). The mass indicators included product yield (Y_H), process mass intensity (PMI), and mass loss index (MLI). The PMI was calculated as the ratio of the input streams, including reactants, to the amount of products generated. Then, the MLI indicator relates the waste stream to the product streams. The specific energy consumption (SEC) calculated from the heat and energy requirements in the process and the flow of raw materials were considered for the energy indicators. Additionally, the self-generation index (SGI) was calculated to determine the potential for on-site energy production in the form of hydrogen. The mass and energy indicators were calculated using the equations reported by Garcia-Vallejo et al. [34].

5.2.4. Economic analysis

The economic assessment was carried out considering the economic indexes of Colombia and the data provided by the central bank to set the interest rate at 9.34% and the tax rate at 35%. Likewise, the national minimum wage was also used to calculate the labor costs for operators and supervisors. The costs associated with utilities (i.e., electricity or steam), maintenance, labor, administrative, and general plant expenses were obtained from the economic evaluation performed in the Aspen Process Economic Analyzer v9.0 software. **Table 5.1** shows some of the economic parameters considered during the analysis. The economic profitability of the different scenarios proposed was evaluated considering the net present value (NPV) over the 20-year life of the project, operating expenses (OpEx), capital expenditure (CapEx), and gross income. Finally, the production cost of hydrogen as the main product and the by-products derived from each scheme were determined.

Table 5.1. Raw materials, utilities, and economic parameters.

Component	Value	Units	Economic parameters		
Cassava stalk	0.020	USD/kg	Operating time	8000	Hours/year
Corn stover	0.019	USD/kg	Shifts	3	Shifts/day
Rice straw	0.022	USD/ton	Working time	8	Hours/day
Water	0.326	USD/m^3	Project lifetime	20	Years
Electricity	0.055	USD/kWh	Depreciation method	Linear	
High P. Steam (105 bar)	8.15	USD/ton	Salvage value	15	%
Middle P. Steam (30 bar)	8.07	USD/ton	Operator wage	328.31	USD/month
Low P. Steam (3 bar)	7.89	USD/ton	Supervisor wage	656.62	USD/month

5.2.5. Environmental analysis

The environmental analysis was carried out using the life cycle assessment (eLCA) approach and following the methodology proposed by ISO 14040. Four stages were defined for this assessment, including the definition of the objective and scope, the establishment of the inventory, the environmental impact assessment, and the interpretation of the results. The analysis was performed with SimaPro v9.1 software (Pré Sustainability, Netherlands) and the Ecoinvent v9.0 database and included quantitative estimates with midpoint indicators using the ReCiPe Midpoint (H) V1.05/World (2010) method.

The objective of the eLCA was to determine the environmental impact of the proposed schemes for hydrogen production, considering a gate-to-gate approach. The functional unit selected for the evaluations was 1 kg of hydrogen, and the environmental life cycle inventory (eLCI) was developed considering the mass and energy balances provided by the Aspen Plus simulations.

5.2.6. Social analysis

The social analysis was developed considering the social life cycle assessment (sLCA) based on the Product social life cycle assessment (PSILCA) database developed by GreenDelta [35]. Similar to the eLCA, the sLCA consists of three stages in which the objective and scope were defined, the social life cycle inventory (sLCI) was established, the social impact assessment was calculated and, finally, the results were interpreted. First, the objective of the social analysis aims to determine the social impact of each hydrogen production scheme to identify the bottlenecks and the risk involved in its implementation in a society such as Colombia. Therefore, the sLCA was developed under the same approach as the eLCA, from gate to gate, and the necessary information for developing the sLCA inventory was derived from simulation results and government reports.

The sLCA was developed as a stakeholder-based indicator analysis of the complete production, processing, and marketing process. Thus, in the PSILCA database, workers, value chain actors, society, and the local community can be identified as stakeholders throughout the life cycle of a process. However, the sLCA used for the analysis of hydrogen production schemes did not involve stakeholders from value chain actors and society due to the lack of information from primary sources on indicators such as illiteracy, health expenditure, risk of conflicts, and violations of mandatory health and safety standards, among others. Therefore, the sLCA was performed considering the analysis of workers and local community stakeholders. For the worker stakeholders, the indicators of minimum wage (M_W) and working hours per employer (H_W) of the subcategories of fair wage and working time were considered. On the other hand, for the local community stakeholder, the subcategories of access to material sources were considered, which included the indicators level of industrial water use (concerning total extraction - LW_H and concerning renewable water resources - LW_R), biomass extraction (concerning cultivation area - E_B) and extraction of fossil fuels (E_F). Likewise, the indicators of employment generation (J_G) and CO_2 eq footprint (P_{CO_2}) were considered for the local employment and greenhouse gas footprint subcategories. The equations for calculating each of the sLCA indicators are reported in Supplementary Material-Appendix A (see **Table A1**).

The social life cycle inventory (sLCI) considered for industrial processes, one supervisor and two operators are needed per processing stage, working 8 hours per shift, with three shifts per day [36]. The indicators for the subcategories of access to material sources focus on the use of industrial and renewable water available in Colombia and the national energy demand related to coal. The energy demand contrasts the energy required in schemes such as low, medium, and high-pressure steam with the energy capacity of coal as a fuel source in steam boilers. For water and energy use, the AQUASTAT database of the Food and Agriculture Organization of the United Nations (FAO) in 2020 [37] and the reports of the Ministry of Energy for the coal flow produced in 2019 [38] were used. Additionally, the eLCA results were used to compare the carbon footprint with the total national CO_2 generation related to industrial activities in Colombia. Finally, the sLCA results were analyzed using risk scale described in the PSILCA database. However, the risk scale was contextualized for Colombia based on available statistical information, and each indicator was compared to a risk score, and a risk value was assigned. The risk scale and score are also reported in **Table A2** in the Supplementary Material - Appendix A.

5.2.7. Sustainability analysis

A sustainability index (S_{Id}) was used to evaluate the four dimensions: techno-energetic, economic, environmental, and social assessments [39]. Each of these dimensions would determine the development of a production process in terms of product flows, profit margins, and the environmental and social repercussions that its implementation would imply. Thus, the S_{Id} was calculated from the results of the simulation process and each of the assessments performed (techno-energetic, economic, eLCA, and sLCA). Each dimension provides different indicators, which were evaluated and normalized following equation (5.1) (see **Table A3** in the Supplementary Material - Appendix A). After normalizing the values, an overall value was obtained for each dimension. (D_j where *j* represents each dimension evaluated) due to an equivalent distribution of weights, based on equation (5.2), where α_i proportional to the level of relevance of each indicator, being *i* each indicator evaluated (for this analysis, all indicators were equivalent in weight).

$$\mathrm{Rank}_{\mathrm{Scheme_i}} = \frac{\mathrm{Route_i} - \mathrm{Worst}}{\mathrm{Best} - \mathrm{Worst}} \qquad \text{Eq. (5.1)}$$

$$\mathrm{D_j} = \sum \alpha_i (\mathrm{Indicator_i})_\mathrm{j} \qquad \text{Eq. (5.2)}$$

Finally, a statistical distribution was considered to vary the significance range of each dimension between 10% and 70% (w_j). It was possible to analyze the impact of each dimension against a significance range and how this might affect the S_{Id} (see equation (5.3), where *n* is each scheme). For example, schemes presenting an $S_{Id} \geq 70\%$ were considered highly sustainable, moderately sustainable $40\% \leq S_{Id} \leq 70\%$, and with a low sustainability index of $40\% \leq S_{Id}$. The statistical distribution of the significance range w_j used for the S_{Id} analysis was reported in Supplementary Material-Appendix A.

$$\mathrm{S_{Id_n}} = (\mathrm{w_1} \sum \mathrm{D_{Techno-energetic}} + \mathrm{w_2} \sum \mathrm{D_{Economic}} + \mathrm{w_3} \sum \mathrm{D_{Environmental}} + \mathrm{w_4} \sum \mathrm{D_{Social}})\mathrm{x}100 \qquad \text{Eq. (5.3)}$$

5.3. Results

5.3.1. Raw material characterization

The results of the chemical characterization were summarized in **Table 5.2**. The cassava stalk and the rice straw present high contents of extractives and are similar to other residues, such as avocado seed and peel, known for their high content of phenolic compounds [40]. In terms of carbohydrates, all agricultural residues, especially corn stover and rice straw, presented high cellulose and hemicellulose contents, with results similar to those reported by Kumar et al. at 58 % for corn stover [41] and 61.6 % for rice straw [42]. These results allow to infer that the residue was a significant source of available sugars in the anaerobic digestion and dark fermentation processes. Additionally, corn stover and cassava stalk have a high MV content with values above 85 %, appropriate for thermochemical processes. At higher MV, lignocellulosic materials increase their reactivity, accelerating the combustion process. Finally, the proximal analysis indicated that the ash content was 1.6 % and 3.6 % for corn stover and cassava stalk, respectively, values lower than those reported for other residues, such as coffee peels, which present contents close to 8 % and contrary, rice straw had a high ash content, similar to rice husk at 18 % [43]. A high ash content can generate technical problems in the equipment due to deposition, sintering, and agglomeration.

Table 5.2. Chemical characterization of residues crop.

Item	Corn stover	SD	Cassava stalk	SD	Rice straw	SD

Chemical characterization (%w/w dry basis)						
Total extractives	10.208		22.350		20.048	
Cellulose	45.258	5.33	36.678	0.54	46.634	0.93
Hemicellulose	15.522	8.60	16.263	3.03	11.005	4.05
Insoluble acid lignin	27.571	4.15	23.420	9.09	21.851	4.10
Soluble acid lignin	1.441	0.16	1.290	0.45	0.463	1.28
Ash	1.600	8.84	3.696	3.82	14.079	0.07
Proximate analysis						
Volatile matter	87.225	0.18	87.058	0.15	77.270	0.38
Fixed carbon	11.175		9.245		8.651	
Total solids	93.490	0.18	89.278	0.04	90.375	0.03
Volatile solids	1.841	2.05	4.479	1.77	15.436	0.55
VM/FC	7.806		9.416		8.932	

SD Standard deviation

5.3.2. Techno-energetic assessment

The results of the techno-energetic assessment are summarized in **Table 5.3**. These indicators show the performance of the different processes based on the transformation of raw materials into hydrogen and other by-products. By analyzing the PMI and MLI indicators, the SBMR scenario maximizes the feedstock use because the production of H_2 coupled with the CO_2 transformation into value-added by-products. On the contrary, in the GF scenario, the residual gas stream after H_2 extraction was used in a combustion chamber for electricity production and then released, affecting the MLI indicators. The yields obtained are similar to those reported by other authors, obtaining between 20-40 g H_2/kg raw materials for SBMR and yields of 25-40 g H_2/kg raw material for GF [44]. For the EL and DF processes, the yields range between 4-12 g/kg raw materials [45]. Additionally, an increase of the MLI can be observed across scenarios, where the DF implies higher consumption of reagents needed for hydrogen production. Among the input streams with the highest demand is water with a share of more than 63 % of the total input streams, followed by feedstock with a share of 11 %. The excessive water consumption is due to the pretreatment stages that include alkaline hydrolysis and enzymatic hydrolysis, both with high liquid: solid ratios. The GF and SBMR schemes involve fewer reagents, in SBMR the reagents are sludge for anaerobic digestion and water for reforming and in GF only air needs to be introduced into the system.

Table 5.3. Results of techno-energetic assessment.

Index	Unit	SBMR-CS	GF-CR	EL-W	DF-RS
Mass					
Product yield	g Hydrogen/ kg RM	36.60	38.10	6.10	6.30
Process mass intensity	kg In/ kg P	6.453	21.21	24.69	49.58
Mass loss rate	kg WS/ kg P	5.453	20.21	23.69	48.58
Energetics					
Specific energy consumption	kW/ kg RM	0.81	1.71	0.38	0.83
Self-generation (Hydrogen)	N.A	5.39	0.97	1.92	0.90

RM: Raw materials, P: Products, WS: Waste streams, In: Inlet streams

CS: Cassava stalk, CR: Corn stover, W: Water, RS: Rice straw

The EL and DR scenarios have lower energy consumptions. The efficiency of the EL processes was measured by the energy consumed in relation to the hydrogen produced. Therefore, the lower the energy consumed by the generator, the higher the efficiency of the process. A theoretical electrolysis stack would consume about 39.4 kWh/kg H_2; however, the best-performing electrolyzers have been found to consume between 50-65 kWh/kg H_2 [46]. In the EL simulation, 52 kWh/kg H_2 was obtained, which implies a higher consumption based on the theoretical value. The industry has two main technologies: alkaline electrolysis and proton exchange membrane (PEM) electrolyzers. Alkaline electrolyzers are cheaper but less efficient, and PEMs are more expensive. However, they can operate at higher current densities and thus be economically feasible if hydrogen production is large enough to offset investment and operating costs. Finally, the DF scenario was characterized by a decrease in performance throughout the separation and purification stages due to physicochemical limitations of the operating units or process inefficiencies.

Regarding the energy indicators, the process with the highest on-site energy production was the SBMR and the GF due to their high mass yields. However, the GF had the highest energy consumption due to the high temperatures required for biomass combustion and electricity generation. In contrast, EL and DF processes have lower electrical consumptions to process 1 kg of raw material, which may represent an economic advantage. **Table 5.4** illustrates the demand for utilities in the production schemes; after performing the energy integration in the Aspen Energy Analyzer software, the production of hydrogen by GF is the process with the highest demand for utilities, specifically the cooling water needed to condition the streams leaving the gasifier and the combustion chamber. Following the GF, DF process has a high utility demand because of the multiple processing steps involved (pretreatment, hydrolysis, fermentation, gas separation, and VFAs separation). The SBMR process, similar to GF, requires lowering the temperature of the streams from the reaction stage for hydrogen separation and purification. The process with the lowest demand for utilities was EL because it has the lowest number of operating units, and its energy demand is associated with electricity consumption and low-pressure steam. In the thermochemical scheme, the production of electricity was considered to cover up to 16 % of the electricity demand of the process. Unfortunately, biological, and thermochemical processes are processes that demand large amounts of water and energy, which is one of the main bottlenecks in the design process and makes it necessary to include energy recovery stages such as heat exchange systems.

Table 5.4. Utilities demanded in the hydrogen production process.

Utility	Schemes			
(kg/kg Raw material)	SBMR-CS	GF-CR	EL-W	DF-RS
LP- Steam	-	-	5.21	0.52
MP-Steam	-	-	-	0.30
HP-Steam	2.23		-	-
Cooling water	39.44	82.06		67.23

Electricity (kWh/kg Raw material)	0.22	0.07	0.06	0.12

Finally, the energy analysis also considered the Net energy value (NEV) calculation as the difference between the energy of the products (hydrogen) and the energy demanded by the process in terms of utilities. Thus, the only process considered a positive NEV was the SBMR since the product flow allows to compensate at the energy level for the demand for utilities in the process, contrary to what happens in the GF, EL, and DF. For these processes, the values are negative, which implies an extra energy consumption in the form of steam or cooling water that cannot be compensated by the hydrogen produced. The scheme with the lowest extra energy demand was the EL with -668.02 MJ/h, followed by the DF with -2676.9 MJ/h, and finally, the system with the highest extra energy demand was the GF with -13112-4 MJ/h, which agrees with the utility analysis (**Table 5.4**) indicating that it is the scheme with the highest utility demand, increasing the operating costs and decreasing the overall efficiency of the process.

5.3.3. Economic assessment

The economic assessment analyzed the investment costs (CapEx), operating costs (OpEx), net present value (NPV), and the cost of hydrogen production. **Table 5.5** summarizes some evaluated indicators showing that the DF scheme is the most expensive for CapEx and OpEx, followed by SBMR, GF, and EL. The high investment costs in fermentation are due to the demand for multiple operating units required for raw material pretreatment, biomass fermentation, and the separation stage. In the separation stage, multiple membranes and distillation columns were used to separate the gas (H_2 and CO_2) and the liquids (VFAs), producing acetic acid, butyric acid, and ethanol. Thus, CapEx can be distributed with a share of 24.8 %, 33.3 % and 41.9 %, for the pretreatment, fermentation, and separation stages, respectively. Thus, the separation stage represents an economically critical stage, which increases the cost of hydrogen production. Likewise, operating costs are increased based on the demand for nutrients needed in fermentation and compounds such as Na_2SO_4 needed for protein precipitation, unreacted sugars, and nitrogen compounds in the liquid streams. Additionally, during the VFAs purification stage, it is necessary to add I_2 and $CaCl_2$ to obtain 90 % ethanol, 91 % acetic acid, and 99 % butyric acid. The inclusion of the VFAs separation stage increases the separation costs by more than 60%, however, the valorization of these acids is crucial to achieve economic profitability in the process. If the acids were not valorized, the economic profitability would decrease by 72 %.

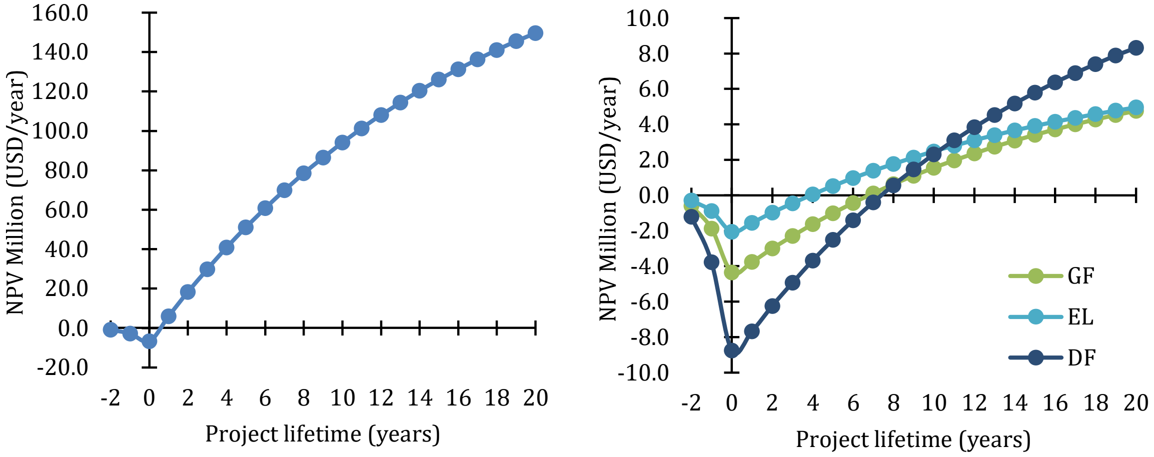
For the SBMR scheme, CapEx is due to the reactor volume for anaerobic digestion, biomethane reforming, and the WGS reaction and this equipment represents more than 41 % of the investment costs. On the OpEx, utilities, maintenance, and depreciation costs account for more than 50 %. However, it is the most profitable scheme in the gross income, with about 17.6 M-USD/year. Following the SBMR process, the process with the highest expenses, especially CapEx, is the GF, where the gasifier and the combustion chamber consume about 23 % and 20 % of the investment costs, respectively. Additionally, at GF, the use of membranes to separate gas streams implies a high maintenance expense since this equipment is sensitive to changes in temperature, pressure, or obstruction by dirt. Finally, the EL scenario presented the lowest OpEx costs associated mainly with raw material and utilities (especially electricity) and was the scenario with the lowest CapEx cost; since this scenario only requires the use of an electrolysis stack and gas separation membranes, it is the process with the lowest number of operating units and therefore with the lowest investment demand.

Table 5.5. Operating and investment costs in economic assessment.

Item	Scenarios			
	SBMR-CS	GF-CR	EL-W	DF-RS
OpEx (M-USD/year)	2.63	1.67	1.34	4.70
				%
Raw materials cost	6.8	10.0	46.8	41.9
Utilities cost	13.4	8.6	5.0	3.8
Maintenance cost	13.5	13.7	8.0	9.8
Labor cost	7.1	7.5	4.6	3.3
Fixed & General Costs	9.5	9.7	5.7	6.6
Plant Overhead	10.8	11.1	6.7	6.9
Capital Depreciation	31.2	31.5	18.5	22.6
Other operating costs**	7.7	7.9	4.7	5.1
CapEx (M-USD)	5.15	3.31	1.57	6.68
MPSEF* (kg/h)	21.1	164.6	156.2	190.1
Production cost (USD/kg H_2)	1.18	4.82	6.77	6.96
Gross income (M-USD/year)	17.61	0.42	0.52	0.69

*Minimum processing scale for economic feasibility ** Laboratory charges, insurance and taxes, and administrative cost. Base flow rate 25 tons/day

Generally, raw material and utility costs contributed the most to the total OpEx of all schemes. In addition, comparing scenarios, it can be concluded that installing multiple operating units that expand the product portfolio implies an increase in the OpEx. Finally, from the economic perspective, the scenario that presented the lowest production cost was the SBMR since it presents moderate investment and operating costs but high mass and energy yields. This was followed by the GF, which, although it implies high energy demands, presents mass yields similar to the SBMR. These results are similar to other authors, that report hydrogen production costs of 2.08-2.27 USD/kg H_2 for SMR [47] and costs of 3.25 USD/kg H_2 for biomass gasification [44]. Finally, the schemes with the highest production costs were EL and DF, which oscillated between 5.78-23.27 USD/kg H_2, decreasing the commercial competition of these schemes unless they relate to hybrid systems, or there are governmental aids that cover part of the operating costs (mainly in the decrease of electricity cost for EL and the optimization of the separation processes of the VFAs) [48].



A) SBMR B) GF, EL and DF

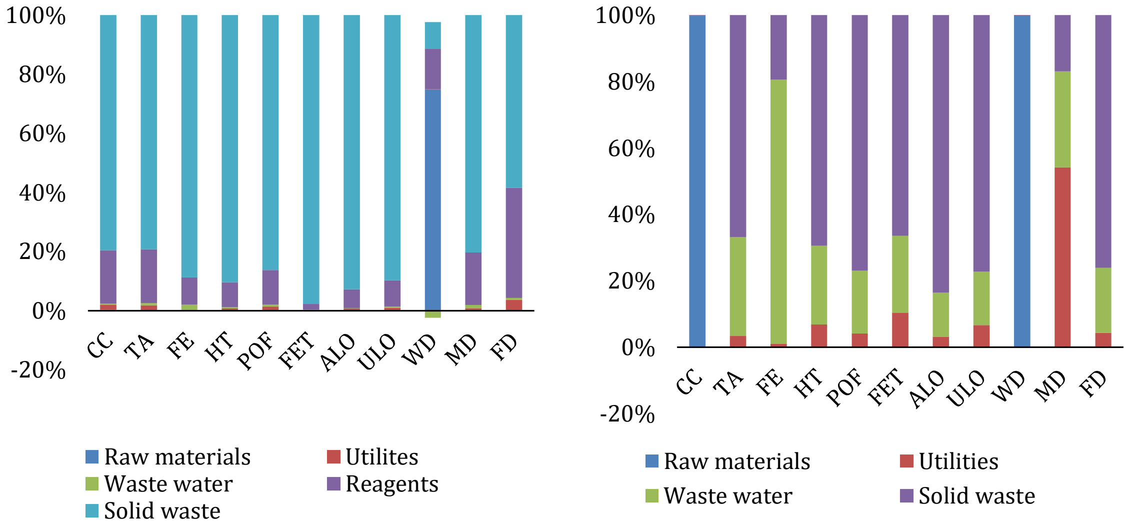
Figure 5.1. Net present value of the schemes under a flow rate of 25 tons/day.

Finally, the NPV analysis over the proposed 20-year lifetime indicates that all schemes are economically feasible (see **Figure 5.1**). However, the revenues vary considerably among the schemes, with the SBMR and the GF having the largest economic benefits. Therefore, a sensitivity analysis was performed by varying the raw material flow to determine the minimum processing scale for economic feasibility (MPSEF) reported in **Table 5.5**. This scale implies that the SBMR scheme can operate with less than 25 kg/h of raw material without economic losses, while the GF, EL and DF schemes need at least 150-250 kg/h. These analyses are important to consider when working with raw materials of agricultural source and coming from an established value chain. This value chain can be affected by multiple external factors such as climate, crop plagues, or agricultural taxes that can decrease its productive flow and, therefore, affect the raw material. However, the agricultural residues selected in this work have the advantage of globally distributed crops with high production levels.

5.3.4. Environmental life cycle assessment eLCA

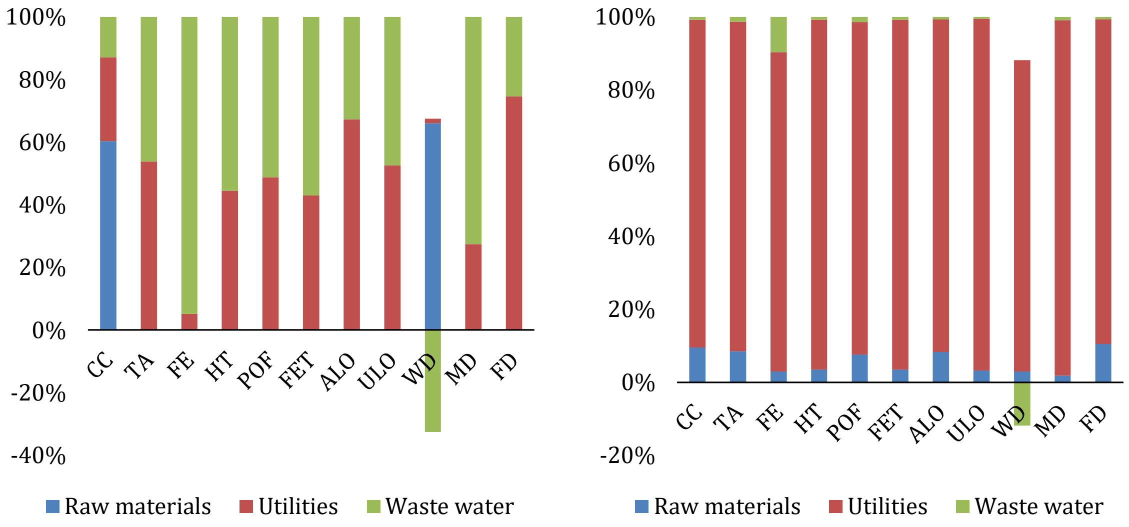
The environmental assessment of the schemes started with identifying mass and energy balances for each technology. Thus, the flows of raw materials, inputs, wastes, and products and their impact on the indicators were identified using the simulation data. The carbon footprint of the hydrogen production technologies were 1.34, 4.79, 0.90, and 5.2 kg CO_2 eq/ kg of hydrogen in the SBRM, GF, EL, and DF schemes, respectively. Similar results to that reported by Ozbilen et al. for GF processes where the carbon footprint varied between 1.9 and 11.5 kg CO_2 eq/ kg hydrogen, considering schemes without carbon sequestration. [49]. Other studies have reported environmental impacts of 0.83-1.25 kg CO_2/kg and 2.5-9.58 kg CO_2/kg for EL y DF technologies, respectively [50]. These values show that biological and thermochemical schemes have the highest environmental impact.

The categories that had the greatest impact on the hydrogen production schemes were climate change (CC), terrestrial acidification (TA), freshwater eutrophication (FE), human toxicity (HT), photochemical oxidant formation (POF), freshwater ecotoxicity (FET), agricultural land occupation (ALO), urban land occupation (ULO), water depletion (WD), metal depletion (MD) and fossil depletion (FD). **Figure 5.2a** shows the relative contribution of the different mass flows in the biological production of hydrogen. Thus, the waste streams had the greatest impact, and these results agree with the MLI and PMI mass index, which show that it was one of the schemes with the lowest use of raw materials and the highest generation of waste streams. Among the reagents used in the DF schemes was NaOH which causes multiple emissions to the soil, causing pH changes and emissions to the air with nitrous oxides [51]. Furthermore, I_2, Na_2SO_4 and $CaCl_2$ were also used in the production scheme. Thus, in recent years multiple studies have reported that the chemical reactions of ozone with iodine are the second cause of destruction of surface ozone in the atmosphere, Na_2SO_4 decomposes by heating, generating sulfur oxides and sodium oxides, toxic to aquatic organisms, and $CaCl_2$ in high concentrations, preventing plant growth and disrupting ecosystem balances [52].



a) DF

b) GF



c) SBMR

d) EL

Figure 5.2. Relative percentage contribution to the environmental impact of different impact categories for a) DF, b) GF, c) SBMR, and D) EL.

For the GF processes, **Figure 5.2b** shows that the environmental impact was associated mainly with the waste streams of syngas exhaust, post-H_2 extraction and post-utilization in the combustion chamber. The exhaust syngas was composed mainly of gases such as CO_2, CO and CH_4. Thus, these residues are responsible for the environmental impact in almost all indicators, except for CC and WD. The CC was affected in this scheme since CO_2 capture was not contemplated generating about 0.35 kg CO_2/ kg syngas exhausted, and the WD to the excessive consumption of cooling water necessary to condition the streams after gasification. Similarly, the release of pollutant gases affects other indicators such as HT, since CO_2 and CO are among the gases that most affect human beings, the TA since it favors the formation of carbon acids, the acidification of water sources (MD) or the formation of acid precipitation. The FD indicator is affected due to the consumption of carbon for steam generation used to increase the gasifier temperature.

For the SBMR scheme (see **Figure 5.2c**), the environmental impact was associated with using utilities, especially the HP-Steam and cooling water. Likewise, the water generated during the process, which derives from anaerobic digestion, has a strong impact on the EF and MD indicators where eutrophication is responsible for an excess input of inorganic nutrients (such as nitrogen and phosphorus) and metals in an aquatic ecosystem, producing an uncontrolled proliferation of phytoplanktonic algae and causing adverse effects on the affected water bodies [53]. Finally, in the EL scheme in **Figure 5.2d**, the environmental burden was mostly derived from utilities including the electricity, where the electricity was produced from hydroelectric plants (main electricity source in Colombia). Some authors report greater impacts from hydropower plants than from other electricity generation systems due to their impact on adjacent ecosystems [54]. According to the Catalan Institute of Climate Sciences (IC3), the environmental conditions created around hydroelectric reservoirs, especially in tropical climates, cause organic matter, when decomposing, produces CH_4 and other gases with high environmental impact, with a level of emissions similar to thermal power plants [55]. Based on this, it is recommended to consider the use of renewable energies such as photovoltaic or wind power systems to mitigate the impact generated by the production of electricity, allowing a better development of alkaline electrolysis.

Table 5.6. Environmental indicators with the greatest impact on hydrogen production schemes.

Indicator	Unit	SBMR-CS	GF-CR	EL-W	DF-RS
Climate change	kg CO_2 eq	1.345	4.798	0.904	5.209
Human toxicity	kg 1,4-DB eq	0.116	0.002	0.351	1.798
Agricultural land occupation	m^2a	0.026	0.001	0.050	0.627
Water depletion	m^3	0.022	0.823	0.005	0.101
Fossil depletion	kg oil eq	0.138	0.001	0.235	0.696

CS: Cassava stalk, CR: Corn stover, W: Water, RS: Rice straw

Finally, **Table 5.6** summarizes the indicators with the greatest environmental impact in the simulation schemes. Among these indicators, the CC due to the gases generated during the thermochemical and biological schemes is highlighted. Additionally, the HT indicator increases due to the impact of some substances on human health and the ALO due to the land occupation necessary to obtain these agricultural residues. Finally, WD and FD present significant impacts due to the demand for utilities that translate into water demand for cooling and carbon demand for generating useful steam in the heating systems.

5.3.5. Social analysis sLCA

The social assessment is summarized in **Table 5.7**, which also shows the risk score for each of the indicators evaluated. For the worker stakeholder, the M_W indicator showed that the minimum wage in Colombia was USD 292.82/month, a ratio of 0.82 with the average wage for Latin America, which does not represent a social risk. Likewise, the H_W indicator related to the number of working hours per week indicates that Colombia is in the average of Latin American countries. However, there are other countries, such as Panama, where the working hours per week are 34.1, or El Salvador, where they are between 43 and 44 h/week [56]. Thus, in the Fair Salary and Working Time subcategories, the proposed schemes for hydrogen production present a low risk. On the other hand, in the stakeholder of the local community, the number of jobs generated in the schemes varied according to the processing stages. It was calculated assuming that these were direct jobs for operators and supervisors. Thus, the schemes with the largest number of operating units, such as DF and SBMR, had the largest number of operators with ranges of 50-60 jobs generated, for each working day, which implies 10-12 workers with a supervisor per shift. Moreover, considering the working time in the different Latin American countries, where the average suggests a 15-day rest period per year, an additional number of direct employees were considered to replace the previous ones during vacation time. Regarding indicators LW_H and LW_R, it can be assured that the social impact is very low because the schemes do not represent excessive water consumption.

In contrast, the E_B for SBMR scheme represents a very high risk due to the consumption of agricultural areas necessary to supply the demand for cassava stalk as raw material in the process. However, considering the MPSEFs of the economic assessment, the flow of raw material can be reduced to balance the economic benefits and the social impact generated. Regarding the E_F indicator, the schemes showed a very low risk for all schemes when comparing utilities consumption with the annual energy production in Colombia derived from coal. Therefore, in the subcategory access to material resources, the only indicator that can present a risk to be considered is E_B. However, considering the raw material is a crop residue, there is no direct social impact due to the consumption or occupation of land used for food crops. Finally, for indicator P_{CO_2}, the carbon footprints of the schemes were contrasted with the annual carbon footprint in Colombia, derived from the industrial sector, resulting in a very low impact, as shown in **Table 5.7**.

Table 5.7. Results of Social assessment and risk score.

			Value					Risk score			
Stakeholder	Subcategory	Symbol	SBMR-CS	GF-CR	EL-W	DF-RS	Unit	SBMR-CS	GF-CR	EL-W	DF-RS
Workers	Fair salary	M_W	0.812					1			
	Working time	H_W	41.700				h/week	1			
Local community	Local employment	J_G	60	40	20	50	jobs/year	NA			
	Access to material resources	LW_H	0.202	3.996	0.005	0.416	%	0	0	0	0
		LW_R	0.016	0.324	0.000	0.034	%	0	0	0	0
		E_B	1688.0	294.0	NA	475.0	ton/km$_2$	4	1	NA	2
		E_F	9.35x10^{-11}	NA	1.92x10^{-11}	2.29x10^{-11}	%	0	NA	0	0
	GHG Footprints	P_{CO_2}	0.0408	0.1427	0.0265	0.1740	%	0	0	0	0

NA Not applicable

5.3.6. Sustainability assessment

The indicators used for the sustainability analysis are summarized in **Table A3** and **A4** of the Supplementary Material-Appendix A. For the techno-energetic dimension, the indicators of product yield, PMI, SEC, and SGI were considered. For the economic dimension, the OpEx, CapEx, gross income, and production cost. In the environmental dimension, CC, HT, and ALO were considered the most influential. Finally, for the social analysis, included local employment, extraction of biomass, level of industrial water use (withdrawal). All indicators were normalized and assigned a weight factor (equivalent for each dimension, e.g., in the environmental dimension CC, HT and ALO considered a share of 33% each). After being normalized, each indicator allowed the establishment of an overall value per dimension and for each scheme. Then, the level of importance of each dimension was varied to identify dynamics in the S_{Id} when one dimension was relevance compared to the others, thus obtaining the results shown in **Figure 5.3**.

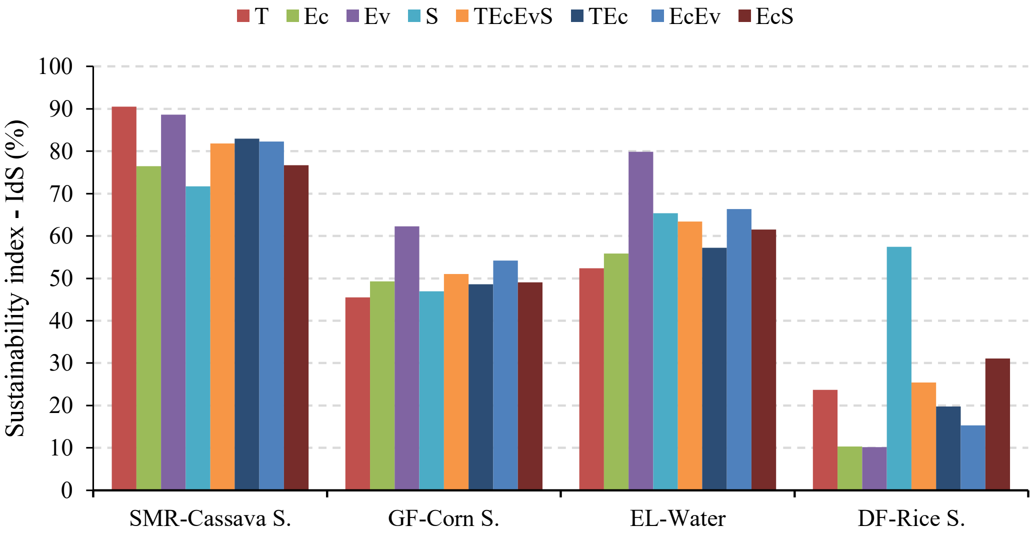


Figure 5.3. Sustainability index for different statistical distributions in hydrogen production schemes. SBMR-CS: steam biomethane reforming with cassava stalk, GF-CS corn stover gasification, EL-W alkaline electrolysis and DF-RS dark fermentation of rice straw.
T Technical, Ec Economic, Ev Environmental and S Social. TEcEvS Tecno, economic, environmental, and social, TEc Tecno-economic, EcEv Economic-environmental, and EcS Economic-social.

The GF and EL schemes presented very similar values, and the scheme with the lowest sustainability was DF. In the SBMR process, the S_{Id} reaches maximum levels (≥85 %) when considering the techno-energetic and environmental dimensions. However, the S_{Id} decreased when the economic dimension was considered since the indicators include CapEx and OpEx, which were high in the economic analysis. For the GF processes, the S_{Id} reaches average values between 50 % and 60 % when considering the economic and environmental dimensions because it has lower OpEx and production cost. At the environmental level, the HT and ALO impact categories were considered, which presented the lowest values for GF. HT is an index that reflects the potential damage of a unit of chemical compound released into the environment, considering the toxicity inherent to its potential dose. ALO refers to the use of land for agronomic biomass production. Thus, the gases derived from GF are GHGs that focus their impact on the ozone layer, affecting humans through global warming effects but indirectly and in ALO, the residues used in production schemes are developed worldwide crops that are part of the basic food chains in the world, which favors crop yields, reducing the occupation of agricultural land [57].

The EL processes presented S_{Id} close to 80% when the most important dimension was the environmental analysis since it was the process with the lowest carbon footprint and low impact on HT and ALO. Consequently, when the economic dimension was introduced, the EL continued to develop well due to the OpEx and CapEx being the lowest. However, when considering the techno-energetic and social dimensions, the S_{Id} decreases because this process has the lowest number of operators, water consumption, and mass yields. Finally, the DF process presented low performance in all dimensions. The dimension that most favors the S_{Id} of the DF process is the social dimension due to the complexity and extension of the production process, which makes it necessary to hire more workers. Generally, the sustainability analysis provides an assessment of the impact of each dimension on the different schemes. For this reason, the definition of the level of importance (w_j) is a key factor. It may vary depending on the study's context and objective and may even depend on the final application of hydrogen. However, each scheme is expected to find a logical development path in the future according to its advantages. It should be noted that the applications and the production will determine each scheme's viability. For example, some industries require high production scales at lower purity rates where SBMR and GF processes would have a chance. In contrast, other sectors require higher purity levels that only a scheme such as EL can achieve without incurring excessive separation costs. Likewise, it is expected that advances in biological research will allow these pathways to improve their technical indicators and decrease costs, allowing the technology to find market applications.

5.4. Conclusions

The multiple efforts deployed in research, with investment from governments and industries that intend to use hydrogen as a raw material or energy carrier, are essential to finding logical paths towards a carbon-neutral society in the medium and long term. Therefore, the hydrogen production processes must provide accessible, safe, efficient, and low environmental impact to promote the installation of a low-carbon energy matrix. Therefore, this study aimed to analyze different hydrogen production schemes, considering techno-energetic, economic, environmental, and social assessments. In this way, it was possible to identify the difficulties faced by each technology to encourage future research to focus on resolving these issues and thus facilitate the development of a hydrogen-based economy.

According to the results, the SBMR and GF schemes showed the best techno-energetic yields and the lowest production costs, which ranged between 2.0 and 6.0 USD/kg H_2. However, the thermochemical processes had a high environmental impact, with a carbon footprint of 4.79 kg CO_2 eq/ kg H_2, affecting the environmental dimension and decreasing the S_{Id}. In the case of SBMR, maximum levels (≥90 %) were reached if the techno energetic dimension was considered due to the high energy and mass efficiencies of the system. On the contrary, when the economic dimension was considered, the S_{Id} for SBMR decreased to 75 %, as it required higher CapEx and OpEx investment. Following the SBMR processes, the processes with the highest S_{Id} were the EL processes since they presented the lowest CapEx and OpEx costs with 1.54 M-USD and 1.57 M-USD/year, respectively and the lowest pollutant rates. Finally, the biological processes (DF) presented low techno-energetic performance, high operating costs, and high levels of environmental pollution. Consequently, the price of hydrogen for these processes was USD 6.96/kg H_2, which reduced their ability to enter the market. However, the improvement in VFA purification processes presents an opportunity to reduce both the CapEx and OpEx of the process, lowering the cost of hydrogen production. Therefore, each scheme presents critical points that must be studied and optimized to provide hydrogen with development pathways that allow its expansion in the shortest possible time.

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Chapter 06: Life cycle assessment of the cassava value chain in Colombia and the possible use of cassava residues as energy carriers.

Abstract

Cassava is a highly distributed crop in Colombia, and Sucre is a region that contributes more than 40 % of national production through an established value chain. Like other crops, cassava generates different usable residues, such as the cassava stalk, which can be valorized by producing energy carriers that meet the needs of the process. Therefore, this work aimed to evaluate the environmental impact of the cassava value chain for the Sucre region and to analyze the possibility of including residues processing stages to produce low (biomethane) and high complexity (hydrogen) energy carriers. The evaluation of the life cycle analysis considered the agronomic stage, including some links of the value chain (suppliers, producers, transformers, and market) and the production schemes of energy carriers, generating biomethane through anaerobic digestion and hydrogen through steam biomethane reforming. The inventory was developed considering reports from the National Cassava Federation (COLFEYUCA) for the Sucre region, and the mass and energy balances in the simulation schemes were obtained from the Aspen Plus v8.0 software. As the main results, the influence of the transformer stage in the value chain can be highlighted, contributing more than 90 % of the impact due to energy demands and waste generated. Additionally, when the production of energy carriers was included, biomethane and hydrogen can supply the energy needs of the biorefinery and between 72 % and 58 % of the energy demand of the transformation stage, respectively. In addition, it was established that the value chain without the valorization of the cassava residues produced 1.22 kg CO_2 eq/kg of cassava. In comparison, when including the valorization stages, the value chain generated 1.20 kg CO_2/kg of cassava, where the raw materials, especially the sludge for anaerobic digestion, presented the greatest contribution to the environmental impact in the biorefineries. Thus, it can be concluded that cassava crop residues and biomethane production are established as a processing alternative for generating usable energy within the links of the production chain, mitigating, in turn, the overall impact of the value chain.

6.1. Introduction

Energy resources have always been essential to satisfy human needs and thus improve the quality of life; however, energy production can also lead to critical environmental consequences [1]. To date, collective efforts between governments and industry have focused on resolving and overcoming the environmental consequences of energy production. In addition, the limitation of energy supply generated by the depletion of fossil resources demands innovation in developing new energy systems such as hydrogen and biomethane [2]. Currently, more than 80 % of the world's hydrogen production comes from steam methane reforming (SMR), a cost-effective technology that transforms natural gas and other hydrocarbons into syngas on a commercial scale, however, such transformation generates large amounts of CO_2 [3]. Some studies report that greenhouse gas (GHG) emissions in hydrogen production by SMR can reach up to 13.7 kg CO_2/kg net H_2 produced [4]. Thus, considering the hydrogen production capacity of U.S. refineries in 2022, which amounted to more than 10 million tons, CO_2 emissions are expected to amount to more than 100 million tons per year, which would generate large impacts in terms of global warming, atmospheric pollution, acid precipitation, stratospheric ozone depletion, the emission of radioactive substances and the destruction of forests [5].

Based on this, using raw materials and energy from renewable sources has been considered to reduce the environmental impact of petrochemical processes in hydrogen and biomethane production. For this purpose, some authors using biomethane to replace natural gas as a feedstock for processes such as SMR [2]. In addition, biomethane can be obtained from biogas. Biogas is a product derived from the anaerobic digestion of biomass through the action of microorganisms present in organic waste, such as sewage sludge and animal manure. Biogas mainly comprises methane, carbon dioxide, and minor species such as hydrogen sulfide and ammonia, among others, and can be used directly as fuel gas [6]. However, during biogas combustion, relatively low energy yields were obtained due to the moisture and CO_2 content, which reduces the calorific value of the biofuel [7]. For this reason, some studies suggest using biogas for hydrogen production since it offers several environmental and economic advantages. Biogas (i) is a renewable fuel that can reduce GHG emissions, (ii) is generated from a diverse source of feedstock, and (iii) contrary to direct combustion of biogas, moisture, and CO_2 present operational advantages in hydrogen production. Thus, using agricultural residues for biomethane or hydrogen generation by steam biomethane reforming (SBMR) can be established as an energy processing alternative [8].

Biorefineries are complex systems where agricultural residues are transformed to obtain a portfolio of high-value-added products and energy carriers sustainably and have been considered the next step towards establishing a bioeconomy [9]. For this reason, implementing biorefineries in a scheme promotes socioeconomic growth, as these facilities provide the opportunity to create new jobs, increase the flow of profits, and improve the purchasing power of people [10]. According to this scenario, regions in the process of social and agroeconomic reconstruction are postulated as an example of the potential of the bioeconomy. In Colombia, several regions have these characteristics, including the Sucre region. Sucre is characterized by the high availability of agricultural residues that require valorization alternatives to improve local conditions and establish an economic benefit based on its resources [11]. The Colombian government has promoted the development of different value chains where cassava stands out. Cassava (*Manihot esculenta Crantz*) is a very relevant crop in this area since it represents about 36% of regional crops, followed by rice with a 19 % share [12]. However, after supplying the needs of the food chains, multiple residues are generated, such as cassava stalks, which have no application and become an environmental problem due to their disposal.

Thus, the energy carriers such as biomethane and hydrogen production from the anaerobic digestion of agricultural residues such as cassava stalk can establish a sustainable system. However, significant efforts are still required to evaluate the production system from an environmental impact perspective. Currently, life cycle analysis (LCA) is a widely used method since it is a methodology that allows establishing the impact generated by each actor or subsystem involved in a production system. LCA is a methodology that represents a systematic set of procedures to collect and examine the inputs and outputs of materials and energy and the associated environmental impacts directly on a product or service throughout its life cycle [13]. LCA identifies and evaluates the interrelated stages of a product or service system, from natural resource extraction to final disposal, as defined by the Society of Environmental Toxicology and Chemistry (SETAC) and codified by ISO 14040 standards [14]. Therefore, LCA has become an important tool for decision-making on alternative fuels and has been widely used to assess the environmental performance of energy processes in recent years. Several studies on biomethane and hydrogen production from agricultural residues have been published, but most still need to include the analysis of the agronomic phase. Therefore, the main objective of this study was to perform the environmental assessment of the life cycle of the value chain of cassava in the Sucre region and the environmental impact that would be generated by the integration of the valorization of its agricultural residues considering (i) the production of biomethane and (ii) the production of hydrogen, as energy vectors of low and high complexity, respectively. The biomethane was produced from the anaerobic digestion of cassava stalk, and the analysis contemplated a "cradle to gate" approach. The paper was structured in three sections: (i) identification of the cassava value chain in the Sucre region of Colombia; (ii) description and analysis of biorefineries for biomethane and hydrogen production, considering experimental data; and (ii) life cycle assessment. Finally, the main results of the work were presented and discussed.

6.2. Methodology

The methodology was divided into three sections: (i) a description of the cassava value chain in the department of Sucre, Colombia; (ii) the valorization of cassava crop residues (cassava stalk) through biorefineries guided towards the production of biomethane and hydrogen through SBMR, considering carbon dioxide capture, and (iii) the environmental life cycle assessment (LCA). First, the value chain description focused on identifying the links, actors, activities, and flows present in the production chain. Next, the production of biomethane and hydrogen was detailed, considering two scenarios. Biogas was generated and upgraded in the first one by including a cleaning stage with high-pressure water scrubbing technology (HPWS). Then, hydrogen was generated from biomethane with a steam biomethane reforming, with CO_2 capture, considering purification technologies such as Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA). Finally, the third section describes the life cycle assessment methodology to identify the environmental impact generated by the value chain and the production schemes evaluated.

6.2.1. Cassava value chain

The Sincé region (9°14′41″N 75°08′45″W) in Sincelejo was considered the study area since it covers more than 21% of the cassava production of Sucre, Colombia [12]. The raw material considered was the cassava stalk, which represents about 1.14% of the crop residues, only surpassed by the weeds at 1.51 %. However, weeds were not considered a potential raw material for biomethane or hydrogen generation. The value chain begins with the input suppliers link, who provide the materials necessary for crop establishment, such as herbicides, fungicides, and fertilizers. The generation and establishment of nurseries were not considered since the crop did not require them. The second link includes the producers (mainly small producers) grouped into associations. Then, in the third link were the transformers. Two types of cassava are produced in Sucre: sweet cassava or cassava for direct consumption and bitter cassava, which is used mainly to produce sour starch. Sweet cassava is considered a direct energy food because when cooked, the peel comes off and softens easily. On the other hand, in bitter cassava, when cooked, the skin is harder, and the tuber acquires a bitter taste and yellow color. This study considers only the value chain of bitter cassava so as not to intervene in Colombia's primary food chain. The mass and energy balances developed in the area's rural "rallanderias" or starch processors were considered in the transformer stage. Finally, in the national market stage, the transportation from the rural rallanderias to the starch marketing companies such as Almidones de Sucre SAS, was considered. Subsequent links, such as the distribution, transformation, and commercialization of sour starch or derived products, were not considered due to the limited primary information available [15].

6.2.2. System description

The biorefinery schemes for biomethane and hydrogen production were developed considering the socioeconomic context of Colombia. For this purpose, two transformation scenarios were proposed that involved valorizing the cassava stalk as a residue of the cassava value chain in the Sucre region. Based on this, the scenarios considered biomethane production through anaerobic digestion and hydrogen production with steam reforming (SBMR). However, the first scenario only produces biomethane, while the second produces hydrogen with carbon capture. The production of biomethane derived from the anaerobic digestion of cassava stalk considered experimental data from previous work, and the mass and energy balances were obtained using Aspen Plus v.9.0 software (Aspen Technology, Inc, USA). All scenarios considered a raw material flow of 5 tons/day, considering that the Sucre region generated in 2020 a production of 89609.40 tons/year of bitter cassava, which generated a flow of 2577.59 tons/year of cassava stalk, which allows the use of 65 % of this flow, in order not to incur in supply problems [16].

Biomethane production was developed using experimental data and the anaerobic digestion models previously reported by Martínez-Ruano et al. [17]. First, the feedstock's particle size and moisture content were reduced to 0.4 cm and 12%. Then, the dried cassava stalk was fed into an anaerobic digester and mixed with sludge and nutrients at 37 °C. Once the biogas was obtained, it must be improved by increasing its concentration by removing CO_2, which increases its calorific value. For this purpose, the yields reported by Cozma et al. in [18] were considered, where a high-pressure water scrubbing technology (HPWS) was proposed since it is a well-known technology with high levels of efficiency and allows the simultaneous removal of CO_2 and H_2S. Similarly, for hydrogen production biomethane was also produced considering the described methodology. Below, the biomethane was mixed with water and heated to 450 °C and 23 bar. The gas stream was introduced into a reformer with a steam-to-biomethane ratio of 3 - 3.5. The synthesis gas produced outputs at 900 ˚C and 22 bar with an H_2/CO ratio of 4. Then, to increase the hydrogen content, the syngas was cooled and sent to a water gas shift (WGS) reactor, where the CO was converted to H_2 and CO_2 at 300°C. In the last separation stage, the pressure swing adsorption (PSA) unit was used to purify the hydrogen and vacuum swing adsorption (VSA) to obtain CO_2 (see **Figure 6.1**).

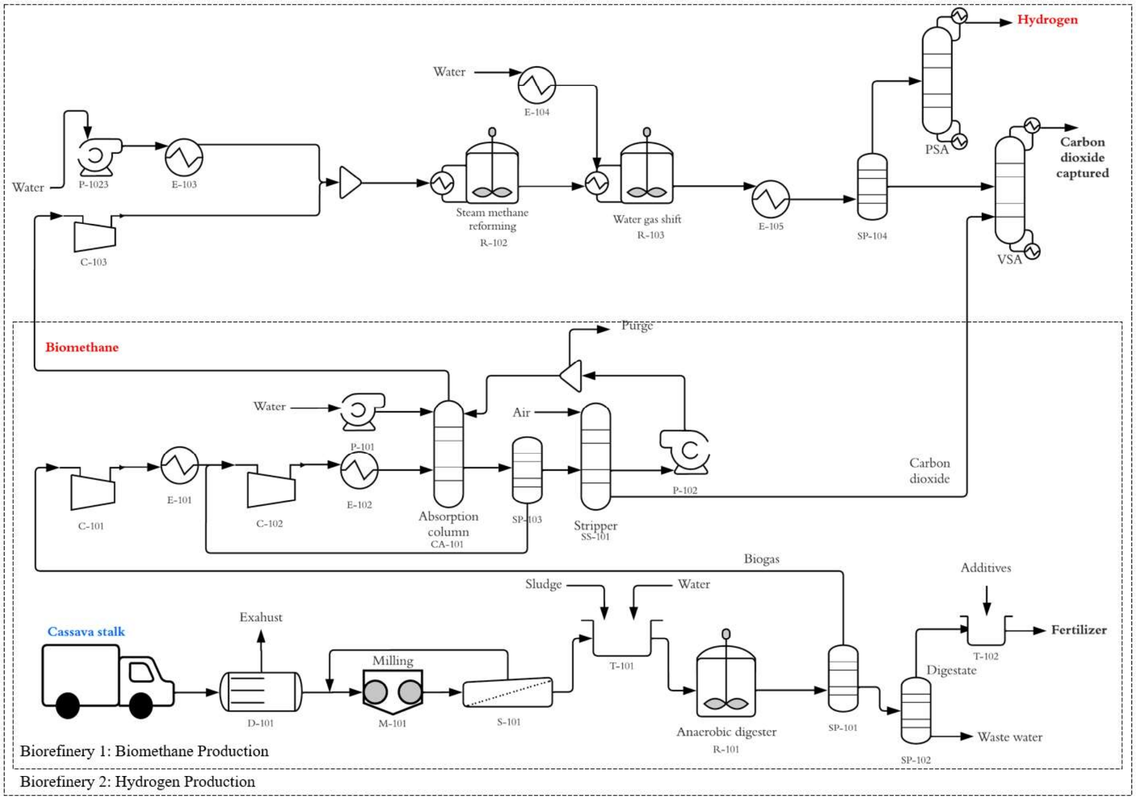


Figure 6.1. Biomethane and hydrogen production flowsheet.

6.2.3. Life cycle assessment (LCA)

The environmental analysis is considered a life cycle assessment (LCA) approach based on the methodology reported by the ISO 14040:2006 standard [14]. The methodology involved four steps: (i) definition of the objective and scope, (ii) definition of the life cycle inventory, (iii) impact assessment, and (iv) interpretation of the results. SimaPro v9.1 software (PRé Sustainability, The Netherlands) and the Ecoinvent v9.0 database were used for the LCA. The environmental analysis included quantitative estimates with midpoint indicators using the ReCiPe Midpoint (H) V1.05/World (2010) method. Additionally, soil organic carbon was determined to determine changes in the solid carbon stored in the crop soils.

a) Goal and scope definition

The objective of the LCA was to determine the environmental impact of the cassava value chain (VC) in Sucre and the valorization schemes. Also, to establish the bottlenecks it presents considering the following specific objectives: (i) determine the environmental impact of cassava crop in the department of Sucre and (ii) compare the environmental impact of the VC with the proposed valorization schemes based on the transformation of residues generated to produce energy carriers and identify the stages of the process with the greatest contribution to environmental impact.

b) System boundaries

The scope of the LCA was considered a geographical limit to the Sincé region (Sincelejo) to produce cassava and its processing for generating cassava stalks. As a temporal limit, information from primary sources from the second semester of 2022 and the first semester of 2023 was used to collect data on the cassava crop. The information was verified through secondary sources of open literature, such as regional reports and databases of the National Federation of Cassava (COLFEYUCA) in Colombia. The estimation of parameters such as soil organic carbon content (COS) was carried out using information from soil studies for the region, carried out in 2011 and 2022. Regarding the technological limit, a typification of the producers' link in the cassava value chain was done from a non-technified crop. Therefore, the LCA was carried out from a "cradle to gate" approach, involving the cassava VC and the processing of cassava stalk residue in low-scale biorefinery schemes.

c) The system studied and functional unit

The cassava VC includes four main links: (i) input suppliers, (ii) producers, (iii) transformers, and (iv) the market. This work does not consider the marketers or distribution link due to insufficient information on the distribution of sour starch in regional, national, and international markets. **Figure 6.2** shows the system's boundaries analyzed, the set of activities, and the processes involved and considered for this study. The functional unit (FU) was selected based on the productivity of cassava in the department of Sucre, to compare different links of the VC, and the valorization schemes analyzed. Then, 1 kg of cassava was selected as the FU and the analysis considering a mass allocation.

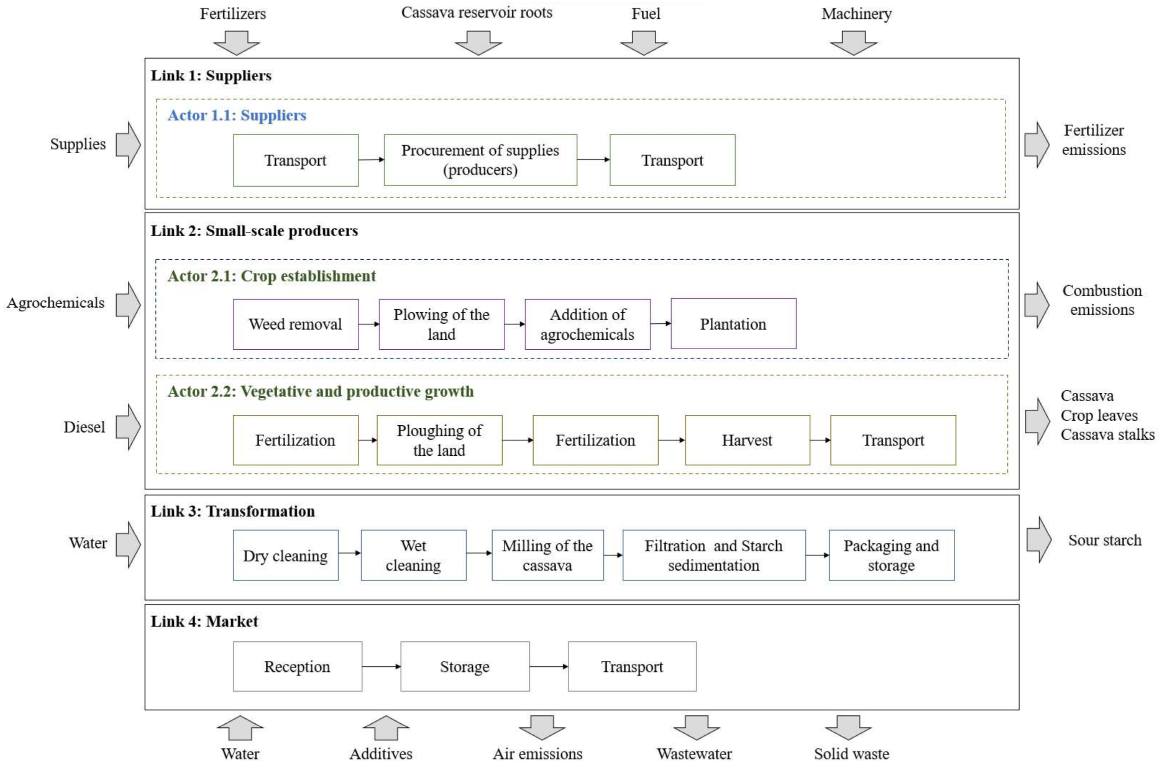


Figure 6.2. System boundaries of the value chain of the cassava in Sucre.

d) Life cycle inventory (LCI)

The environmental life cycle inventory (LCI) was conducted through primary sources such as field visits, surveys, and interviews with farmers and agronomists in the region. Information was collected for sour cassava for the agronomic stage, considering that the region also produces sweet cassava for human consumption [19]. The inventory and considerations for developing the LCI for each link of the cassava value chain were detailed below (see **Figure 6.2**). The mass and energy balances provided by the Aspen Plus software were used for the simulation schemes. **Table 6.1** shows a summary of the life cycle inventory inputs.

Table 6.1. Inventory of the cassava value chain in the department of Sucre for the four links.

Link	Actor	Subsystem	Activity	Inputs			Considerations	Type of work
				Description	Value	Unit		
Suppliers	Input suppliers	Input suppliers	Transportation	Transport of inputs to the producer	35.4	km	An average distance between Since and Sincelejo was considered.	Truck
Producers	Small producers	Crop establishment	Weed control	Scythe	1	Scythe	Weeding is done manually.	Manual
			Layout	NA.	10.000	tree/Ha	Two passes of heavy plows are made in a cross pattern, and one pass of light harrows forms the furrows.	Manual
			Boring	NA.	NA.	NA.		Manual
			Fertilization and addition of agrochemicals	Gramafin (Paraquat)	1.00	L/Ha	Only one application of fertilizers and agrochemicals is considered for this stage.	Manual
				Cipermetrina	0.05	L/Ha	Fertilization is performed every 30 days for five months.	
			Planting	N.A.	N.A.	N.A.	80 cm between plants and 80 to 100 cm between rows was considered.	Manual
		Cultivation - vegetative and productive stage	Fertilization	Gallinaza	2	kg/Ha	Fertilizer application is carried out every three months during the first year.	Manual
			Pruning	Manual scissors	NA.	NA.	Growth pruning and maintenance pruning are carried out.	Manual
		Productivity	**Cassava**	**Cassava**	**20000**	**kg/Ha**	Cassava is harvested between 7 and 10 months, depending on the variety.	Manual
Transformers	Collection centers	Starch production	Dry cleaning	Elimination of cassava peels	N A.	NA.	The peel was removed.	Washing machine
			Wet cleaning	Elimination of impurities	N A.	NA.	The cassava was washed with water in a 1:4.5 ratio.	Washing machine
			Milling of the cassava	Starch extraction with water milling	7.2	kg/kg cassava	The cassava is subjected to a wet milling process	Industrial milling
			Filtration and sedimentation	Starch filtration and sedimentation	8.5	kg/kg cassava	A starch-rich slurry was obtained, which is sedimented in tanks.	Manual
Market	Collection centers	Cassava transportation to the marketer	Transporter	Distance	29.5	km	The distances were taken from a review of maps considering the location of the marketers (Almidones de Sucre SAS) and the processors (Rural rallanderias in Since); in addition, one-way transportation was considered (EURO 3).	Truck

- Input suppliers

The nursery construction was not considered for the cassava crop because the crop is grown directly in the field using the lower stalk of the plant (Cassava reservoir roots) as seed. Therefore, the impact of the supplier link was associated with the transport of agrochemicals and fertilizers from the nearest municipality (Sincelejo) to the crop located in Sincé. A transport of 5 tons was assumed, covering an average distance of 10 km for the supply of inputs.

- Small producers

In the small producers' link, inputs were taken according to the establishment of the crop, the vegetative phase, and the productive phase. First, it was considered that the cassava crop is grown in temperatures between 20 and 30° C, with precipitation between 750 mm and 1250 mm of rainfall, climatic conditions present in the Sincé area. The soil has a long photoperiod with sandy loam soils, deep, organic, good drainage, and acidity between 5.5 and 8.5, allowing yields of 10 to 50 tons/Ha. Before planting, the soil requires adequate weed control with a scythe, before planting the tree. In the soil preparation, two passes of heavy plow, in a cross, and one pass of light harrow were made. If the soil has an acid pH (<5), 1 ton/ha of quicklime was applied after the previous crop. Calcium carbonate was not considered since planting occurred 1-2 months later.

Then, the reservoir roots of the previous crop were the starting point for the new crop. These roots were 15 to 20 cm long and 2.5 cm in diameter with a rough surface texture with oblique growth direction, presenting a cylindrical conformation. The cassava was planted at the top of the furrow, and the stake was placed at 45° to avoid excess shoots. The root should be buried at 95 % of its size to prevent it from dehydrating too quickly, and the planting distance was 80 cm between plants and 80 cm to 100 cm between rows. The root system was formed in the first 2.5 months of plant development, with the first roots disappearing and the second roots reaching a depth of up to 50 cm, depending on the soil texture. At the same time, during the first three months of leaf development, the migration of reserve material (starch) begins. Since it is a tropical plant, it can suffer from the occasional attack of bacterial, fungal, and viral diseases, which were avoided with the addition of Gramafin (Paraquat) and Cypermethrin in doses of 600 g/L. Gramafin is a liquid, concentrated, soluble, non-selective herbicide that acts by contact with the green parts of the plants, does not damage the mature bark, and is immediately inactivated when it comes into contact with the soil. Cypermethrin is an insecticide used to control a wide variety of pests. For the addition of agrochemicals, 360 L/Ha of water was used. In addition, to improve crop productivity, Gallinaza was added in concentrations of 2 kg/Ha, and cleaning was carried out when the plants were between 20-30 cm, with a second application recommended after two months. Finally, hilling was carried out after 2 - 3 months of vegetation in crops that were not mechanized. This ensures the reservoir roots can develop well and prevent rodents or other animal attacks [20].

Finally, the last parameter considered in the environmental analysis was the region's soil organic carbon balance (COS). The COS was calculated according to the methodology of the IPCC 2006 "Guidelines for National Greenhouse Gas Inventories Volume 4 Agriculture, Forestry, and Other Land Use," specifically "Chapter 5 - Cropland, section 5.3.3 Soil Carbon". Due to the scarcity of data, the Tier 1 method was selected [21]. The COS was calculated as the difference between the final COS (year 2022) and the reference COS (year 2011). The reference COS and the final COS were calculated considering the soil organic carbon in the region. Parameters such as bulk density and sampling depth in the study areas were also considered. These data were taken from soil analyses conducted in Sampués and were provided by the producers during field visits. The parameters for COS estimation are shown in **Table 6.2**.

Table 6.2. Parameters used in soil organic carbon estimation.

Year	pH	Bulk density (g/mL)	Sample depth (cm)	Organic matter (%)	Organic carbon (%)
2011	7.29	1.41	20	1.03	0.597
	7.25	1.49	20	0.86	0.499
	7.41	1.49	20	0.86	0.499
2022	7.33	1.50	20	0.87	0.505
	7.60	1.52	20	0.87	0.505
	7.63	1.49	20	0.81	0.470

SD Standard deviation

- Transformation

In the transformer link, the mass and energy balances developed during a technical visit to the facilities of the Almidonera La Victoria starch company, located in the department of Sucre, were considered. The production process was classified based on the stages shown in **Table 6.1**, considering that the principle of the cassava starch extraction process was based on the isolation of its components. The mass balance indicates that an average of 1000 kg/h of fresh cassava was received, and between 231 kg/h and 234 kg/h of sour starch (dry basis) were obtained, which shows extraction efficiencies close to 51 %, values similar to the more technified production processes developed in other countries such as Brazil, where extraction can vary between 56.5 % and 63.0 % [22] The fresh cassava first received a dry wash, in which the peel was removed (9.7 % of the fresh cassava), then the shelled cassava was washed with water at a ratio of 1:4.5 and, the roots were wet grated at a ratio of 1:7 (solid:water). After grating, a starch-rich slurry was obtained after filtering. The mixture was then subjected to a sedimentation process and after obtaining the starch on a wet basis, it was transferred to tanks for 15 to 30 days to obtain sour starch. From this last stage, wet sour starch, stain, and water were obtained and recirculated to the wet washing stage. Of the total water contributed to the process, 45% was used in the grating stage and another 55 % in the filtration stage. After the process, liquid wastes were generated whose effluent was characterized by a high content of carbohydrates and contaminating organic matter (COD = 3,400- 5,400 mg/L) [23]. Traditionally, these wastes were discharged into nearby crops or water bodies without being treated, which triggers a significant environmental load of the waste. Finally, **Table 6.3** summarizes the equipment used during starch extraction at the La Victoria rallanderia.

Table 6.3. Equipment used in starch extraction.

Equipment	Operating voltage (V)	Current (A)	(Power (W)	Consumption (kWh)
Dry-washing machine	330	5.8	1914.0	45.94
Conveyor belt 1	330	1.2	392.7	9.42
Wet washing machine	220	8.7	1922.8	46.15
Conveyor belt 2	330	1.3	419.1	10.06
Milling	330	26.0	8580.0	205.92
Electric pump milling	330	6.9	2280.3	54.73
Filter 1	330	2.4	792.0	19.01
Filter 2	330	2.8	907.5	21.78
Electric pump starch	330	3.9	1287.0	30.89

- Market

The activities of the market link involve the transportation of sour starch from rural transformers to the collection centers in the urban area. This link excludes the companies using sour starch to produce other commercial products. In the department of Sucre, there are two main wholesale centers; the first is in the Corozal municipality, and the second is in Sincelejo (Almidones de Sucre SAS). Therefore, the impact associated with this link depends on the transportation of sour starch to the nearest collection centers (Sincelejo), and this limitation was derived from the need for more valid information to carry out mass and energy balances in the companies where sour starch is processed.

6.3. Results

6.3.1. Life cycle assessment

i) Value chain description of the cassava in Sucre

The analysis of the cassava VC's environmental impact in the Sucre department began with identifying the links and actors involved in the productive chain, which involves different activities specific to the crop and the region. Considering the activities carried out by each actor, it was possible to identify raw materials, inputs, residues, and products generated in each link. Thus, **Figure 6.3** shows the links and value chain actors with the greatest relevance for cassava crops in the department of Sucre. For the first link, which is the input suppliers, the transport of inputs (herbicides, insecticides, and fertilizers) from the city of Sincelejo to the crop in Sincé was considered at a rate of 0.1315 g of agrochemicals/ kg of cassava for approximately 35.4 km.

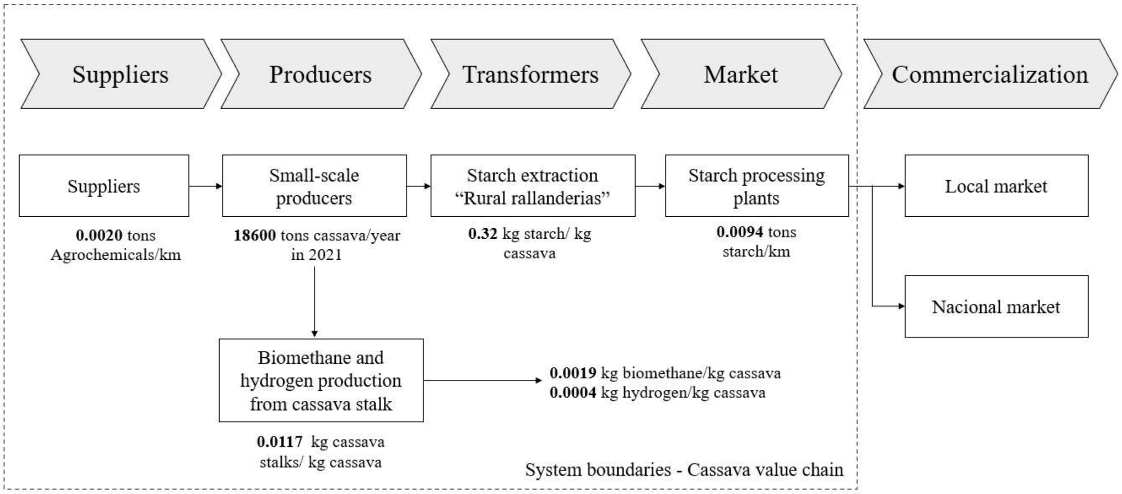


Figure 6.3. Simplified value chain of cassava in the department of Sucre.

The second link, which corresponds to small producers, those whose work is done manually, was considered. For this, the information provided by COLFEYUCA was considered, which registers that the department of Sucre has 267 registered producers, of which 115 are dedicated to the production of sweet cassava and 152 to the production of industrial or bitter cassava with at least 10 Ha of production [24]. The producers are grouped into various associations with influence in different municipalities, as shown in **Table 6.4**. The activities involved in this link included land preparation with a plow, fertilization, and hoeing to clean the crop. Once the cassava was obtained, the producers transported it to the nearest rallanderias or those offering the best price per kg of cassava (generally, these rallanderias are in the rural areas where the crop was established).

Table 6.4. Associations of cassava producers in the department of Sucre.

Organization	Number of producers	Municipalities
Asoagrocharconiza	14	Corozal, San Pedro, Since and San Juan de Betulia
Coagrobetulia	18	San Juan de Betulia, Corozal and San Antonio de Palmito
Mandioca	44	Corozal, Sincelejo and Sampues
Annpy	14	Corozal, Morroa and Ovejas
Cooimpro	62	Ovejas

The third link, the transformers, was considered. The traditional system of processing cassava to obtain starch was carried out in plants called rallanderias. The rallanderias are low-scale, low-complex systems that can process up to 1000 kg of fresh cassava in 24 hours. The raw material was received from the producer. It was washed, peeled, milled, and filtered, and the cassava pulp mixture was transferred to tanks where the sedimentation, fermentation, and drying process occurred. After extraction, residues such as cassava peel, wastewater with high organic load, and wet starch were obtained in ratios of 0.10 kg/ kg cassava, 16.32 kg/kg cassava, and 0.32 kg/kg cassava, respectively. The wastewater from the rallanderias was characterized by a high organic content, including cyanide (CN^-) carried over from the root crops [25]. In Sucre, 11 small companies (Rallanderias) are dedicated to starch production in Sampués, Galeras, Sincelejo, Sincé, and La Unión. Similarly, 10 agro-industrial companies are also producing dried cassava chips and sour starch in San Juan de Betulia, San Antonio de Palmito, Los Palmitos, Corozal, Ovejas, and San Pedro. This group of companies comprises the transformers link, with a total of 21 in the region.

Finally, the fourth link (market) involved the transportation of sour starch from the rallanderias to the large starch processors or distributors in the region. The department of Sucre has companies dedicated to transforming sour starch, the most important being Almidones de Sucre S.A.S [26]. Finally, although the consumer and distributor links were not considered, it should be noted that in the department of Sucre, two wholesale centers are the market located in the municipality of Corozal and the city of Sincelejo, as local distributors, and in the national distributors are those market centers located in other cities of the country such as Montería, Cartagena, and Barranquilla.

ii) Environmental impact of the cassava value chain in Sucre

The environmental analysis, which considered 1 kg of cassava as a functional unit, showed the existence of different dynamics among the links in the VC. The results of the environmental impact are shown considering a percentage contribution of the different impact categories (categories that were calculated for each link and each activity within the VC). **Figure 6.4** shows the carbon footprint for each link of the VC, and it should be noted that all indicators were established without considering carbon sequestration by the crop in the department of Caldas. The processing of fresh cassava to produce sour starch and the waste generated in this activity represented about 98.6 % of the environmental impact associated with the carbon footprint, followed by the market with a contribution of 1.0 % and the supplier and producer links with contributions of 0.4 %. The market link has a greater impact compared to the supplier's link, even though both considered only the transportation of materials, and this was because the distance between Sincelejo and Sincé was 35 km with loads greater than 1 ton, while from Sincé to the Almidones de Sucre SAS company was 29 km with loads less than 0.5 ton. Similarly, the producers' link does not imply a significant carbon footprint because cassava is a crop with low agrochemical demand. It does not require previous processes, such as the construction of nurseries, which reduces the supply-demand and the impact associated with them.

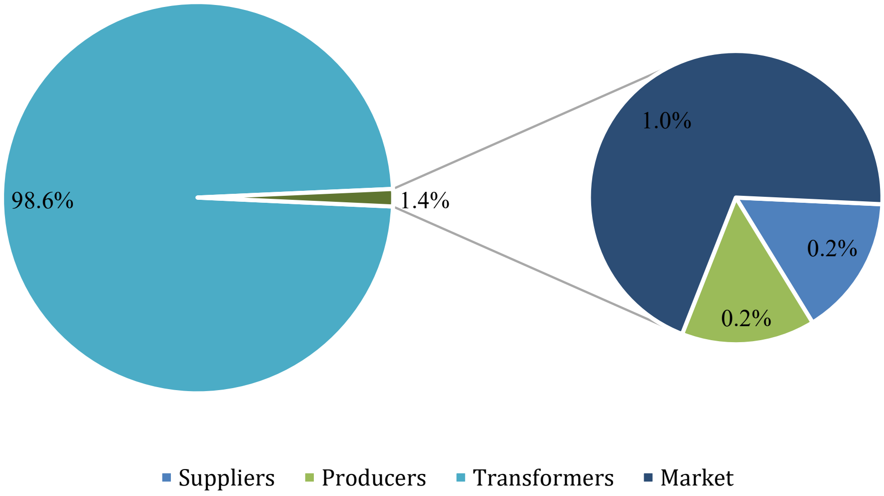


Figure 6.4. The carbon footprint of the value chain of cassava in Sucre for each link.

Table 6.5 shows the emissions of agrochemicals used in the second link of the cassava VC. Emissions were classified according to their destination. Thus, the categories with the greatest impact were emissions to air, where the greatest contributor was N_2O, followed by NH_3. On the other hand, in emissions to water, the greatest contributor was NO^{3-}. The impact generated by emissions to air and water was due to the addition of multiple agrochemicals such as Gramafin, an herbicide whose active ingredient is Paraquat, in the form of a dichloride salt, which is known to be a quaternary ammonium herbicide [27]. On the other hand, phosphorus emissions to the soil were since cassava is a crop that extracts large amounts of nutrients, mainly nitrogen, phosphorus, potassium, calcium, and magnesium. Therefore, an important aspect to highlight within fertilizers for cassava crops is their high phosphorus content [28]. Finally, the estimation of soil organic carbon allowed determining that for 2011, the values were at 15.526 ± 1.14, and for 2022, it was already at 14.827 ± 0.72, which implies a difference of -0.063. Initially, the amount of COS stored in each soil depends on the balance between the amount of C entering and leaving the soil. C can leave the soil as C-based respiration gases from microbial mineralization and, to a lesser extent, from soil leaching as dissolved organic carbon (COD). Thus, it can be assured that, locally, in the department of Sucre, the soil loses more carbon than it can store. At the regional level, C can be lost through soil erosion or deposition, leading to the redistribution of soil C at the local scale. Therefore, it is important to consider changes in agricultural practices for cassava crops to control COS storage levels by managing the amount and type of organic residues deposited on crops (i.e., organic C input to the terrestrial system) and minimizing soil C losses [29].

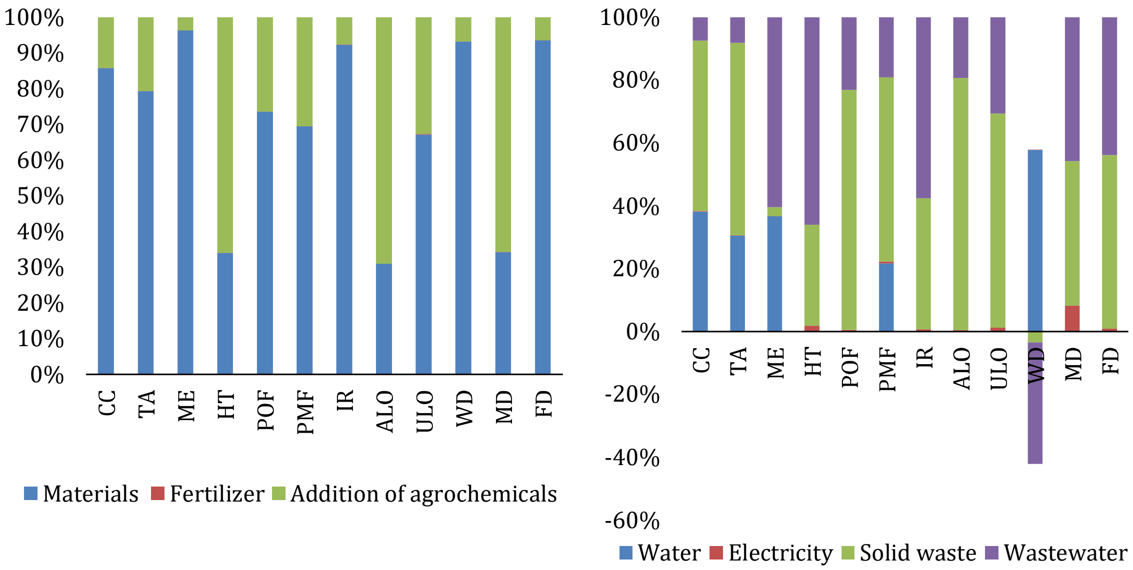
Table 6.5. Cassava crop emissions in Sucre.

Emissions to air	Value	Unit
Emissions de N_2O – Direct – air	28.078	kg N_2O/Ha
Emissions de N_2O – Indirect – air	2.935	kg N_2O/Ha
Emissions de NH_3 – air	21.697	kg NH_3/Ha

Emissions de CO_2 – air	0.880	kg CO_2/Ha
Emissions to water		
Emissions de NO^{3-} - water	268.02	kg NO^{3-}/Ha
Emissions de PO^{4-} - water	2.81	kg PO^{4-}/Ha
Deposition of heavy metals in water		
Cd	0.11	mg/ (Ha year)
Cu	481.68	
Zn	551.10	
Pb	0.10	
Cr	347.91	
Emissions to soil		
Emissions P - soil	3.18	kg P/Ha

Considering that the small producers and transformers were the links with the greatest environmental impact, it is important to highlight that the categories that had the greatest influence were climate change (CC), terrestrial acidification (TA), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (POF), particulate matter formation (PMF), ionizing radiation (IR), agricultural land occupation (ALO), urban land occupation (ULO), water depletion (WD), metal depletion (MD) and fossil depletion (FD). **Figure 6.5** shows the relative percentage contribution of the activities carried out in the second and third links (small producers and transformers). In the producer actor, the addition of agrochemicals such as Cypermethrin, Gallinaza, and Gramafin was the activity that generated the greatest impact. The use of materials represents about 85 % of the CC and 96 % of the ME categories. Some authors suggest that the deposition of heavy metals in water generates the proliferation of harmful algae and the death of aquatic species because of eutrophication, which occurs when the environment is enriched with nutrients [30]. Additionally, for the materials in the cassava crop, it was necessary to use up to 360L/Ha of water, which produces an increase in the impact of WD, representing 93 % in this impact category.

In the transformer link, the activities that generated the greatest impact were wasted in general. Solid waste includes stains, bran, and peel. Liquid wastes include wastewater from cassava mills with high levels of organic matter and traces of cyanide present in the cassava. Recent studies show that the level of cyanide released from cassava tubers ranges from 15 to 200 mg per kg of tuber, calculated based on the fresh weight of the tuber pith since even the peel can have a much higher cyanide potential [31]. For this reason, the high volume of residues generated in rallanderias can cause negative effects on flora and fauna because of the accumulation of organic matter, which produces soil acidification (TA) and secondary atmospheric pollutants such as photochemical oxidants formed by the action of sunlight on nitrogen oxides (POF).



A) Producers B) Transformers

Figure 6.5. Relative percentage contribution to the environmental impact of different impact categories for (a) producers (second link), (b) and the transformers (third link). Climate change (CC), terrestrial acidification (TA), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (POF), particulate matter formation (PMF), ionizing radiation (IR), agricultural land occupation (ALO), urban land occupation (ULO), water depletion (WD), metal depletion (MD) and fossil depletion (FD).

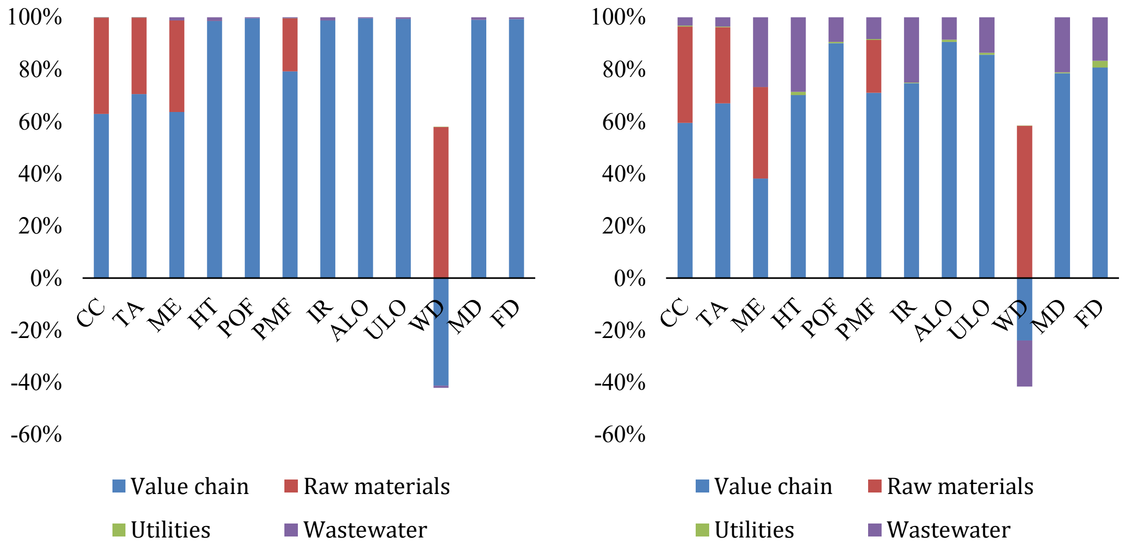
Finally, the production of 1 kg of cassava in the department of Sucre generates 1.22 kg of CO_2 eq through the entire VC and 2.44 g CO_2 eq through a crop stage. These results are similar to those reported by other authors such as Alexander et al., who estimate the generation of 2.72 g CO_2 eq /kg cassava [32], and Namchancharoen et al., who estimate that the production of cassava chips generates an impact of 2.92 g CO_2 eq /kg cassava [33]. Likewise, Morales A. et al. report a 1.96 kg CO_2 eq generation over Peru's entire cassava VC [34]. Although the results of the LCA are dependent on the context, level of technological maturity, and the study area, it is evident that kg CO_2 eq emissions from cassava production in the department of Sucre are similar to those reported by other authors in different areas, because agricultural practices for cassava production are non-technified systems and have been practiced for a long time.

iii) Environmental impact of the cassava stalk valorization for hydrogen production

The environmental analysis of the biomethane and hydrogen production schemes from cassava stalk considered the environmental impact of cassava crops and biorefineries. **Figure 6.6** presents the relative percentage contribution of the different impact categories for the biomethane and hydrogen production schemes. The most representative and highest impact categories in the production schemes were climate change (CC), terrestrial acidification (TA), marine eutrophication (ME), human toxicity (HT), ionizing radiation (IR), agricultural land occupation (ALO), water depletion (WD), metal depletion (MD) and fossil depletion (FD). In both valorization schemes, the strong impact generated by the VC can be appreciated, contributing 62.9 % and 59.5 % of the environmental impact to the biomethane and hydrogen production schemes, respectively. This strong impact is because multiple wastes are generated in the chain, especially in the transformer stage, causing an increase in the overall impact.

The production of energy carriers such as biomethane allowed the production of 330.92 kWh of energy that allowed supplying the energy needs of the biorefinery and supplying up to 72 % of the energy of the transformation process, reducing the impact generated by this link, reducing the energy demand from 0.44 kWh/kg cassava to 0.12 kWh/kg cassava. Likewise, the hydrogen production scheme allowed the production of 305 kWh/kg cassava, supplying the needs of the biorefinery and 58% of the needs of the transformation stage, reducing energy consumption to 0.18 kWh/kg cassava. Both biorefineries present improvements at the environmental level, given that they reduce emissions generated by crop residues (cassava stalk) and allow the generation of usable energy carriers within the slabs, reducing the consumption of fossil fuels to produce such energy. In addition, the valorization schemes that are integrated into the VC allow for the reduction of the carbon footprint up to 1.20 kg CO_2/kg cassava.

Figure 6.6-A shows that for the biomethane production scheme, the second highest impact parameter was the raw materials, especially the sludge used for the anaerobic digestion of the cassava stalk. Sludge contributes about 99 % of the impact associated with CC and 98 % associated with WD due to GHG emissions caused by the digestion and production of this sludge. **Figure 6.6-B** shows that in hydrogen generation, as in biomethane production, the VC and raw materials have some environmental impact due to waste and the use of digestion sludge affecting the overall environmental impact of the scheme. Thus, the value chain and raw materials, utilities contribute about 4 % of the environmental impact due to the demand for services such as steam to reach the necessary temperatures in the reforming and WGS processes. The demand for these utilities promotes the use of fossil fuels for their generation, which increases the impact of these schemes. The contrary is the case with biomethane since the process does not require high temperatures or emissions, reducing the impact of these services by up to 0.2 %. In addition, CO_2 capture allowed to establish a 10 % reduction of CC due to the VSA system. However, CO_2 capture allowed a 10 % reduction in CC to be established due to the VSA system. With this, it can be assured that carbon sequestration and storage systems (CCS) are established as a tool for the environmental improvement of energy processes.



A) Biomethane production B) Hydrogen production

Figure 6.6. Relative percentage contribution to the environmental impact of different impact categories for hydrogen production schemes.
Climate change (CC), terrestrial acidification (TA), marine eutrophication (ME), human toxicity (HT), ionizing radiation (IR), agricultural land occupation (ALO), water depletion (WD), metal depletion (MD) and fossil depletion (FD).

Changes in the chemical properties of the soil and water bodies affect categories such as TA and ME due to the deposition of minerals (specifically nitrogen and sulfur). Deposing these elements produces acidification of soils and the proliferation of toxic plants that affect aquatic ecosystems. Other authors have previously reported these phenomena, such as Cortés et al., in methane reforming processes for hydrogen production [35] and due to the addition of nitrogen agrochemicals in soils [36]. On the other hand, the HT category is an index that reflects the potential harm of a unit of chemical released into the environment and is based on both the inherent toxicity of a compound and its potential dose. Thus, HT was affected by processes such as SBMR, where GHGs were released that directly or indirectly affect human health [37]. Likewise, ionizing radiation was generated through reactions at very high temperatures, such as those reached in reforming reactors and WGS, affecting the IR category. The ALO indicator was influenced by the agricultural use of the land to produce cassava, and the WD was favored because the liquid currents of the production schemes were treated in the Wastewater Treatment Plants (WWTP) that clean the wastewater so that it can be safely returned to the environment. Some authors even claim the possibility of using WWTP water for biogas generation, increasing the system's productivity [38]. Metal depletion (MD) was affected by crop due to irrigation and fertilizer application, generating a deposition of heavy metals in water, such as Cu, Zn, and Cr, mainly (see **Table 6.5**) [39]. Finally, the FD indicator had a greater impact on process utilities due to the steam demand necessary to reach high temperatures in the reactors. In the simulations, the steam used in the production schemes comes from coal combustion, increasing this fossil resource's consumption.

Finally, biomethane production is the scheme with the greatest opportunity and best energy yields to be implemented in a rural VC, such as cassava in Sucre. Although hydrogen is a vector with higher energy density, the process presents high levels of complexity that can hardly be installed in rural areas such as the rallanderias for using such energy. In addition, the process must be rigorously controlled to avoid accidents, which decreases the possibility of being installed in areas without rigorous control systems. In addition, the biomethane process has less demand for complex operating conditions and can be introduced in areas far from urban centers for in situ use.

6.4. Conclusions

The producers and transformers were the links with the greatest environmental impact in the cassava value chain in Sucre. In the producers, the most influential activity was the materials and addition of nitrogenous agrochemicals, affecting indicators such as terrestrial acidification, marine eutrophication, water depletion, and metal depletion due to N_2O emissions into the air and the deposition of heavy metals in the water. In the transformer link, the greatest impact was attributed to solid and liquid wastes from rural companies (rallanderias), wastes with high levels of organic load, and with important effects on adjacent ecosystems. Similarly, value chain and raw materials were responsible for the greatest environmental impact in biomethane and hydrogen production schemes. However, this study showed that the inclusion of the valorization schemes allows to reduce the environmental footprint of the value chain and the CO_2 capture scheme allows a reduction of up to 10 % in the climate change category. This reduction may become more relevant due to the increase in production flow since this study considered a local analysis, which generated a relatively low flow for an energy-driven biorefinery. Therefore, in schemes with higher flows, the reduction of environmental impact may be more representative. In addition to the climate change category, the most influential categories were fossil depletion due to the depletion of coal in combustion processes for steam generation and human toxicity due to the release of GHG during biomethane reforming. Finally, the production of 1 kg of cassava in the department of Sucre generates 1.22 kg of CO_2 eq throughout the value chain, with the transformer link having the greatest impact, and the production schemes estimate the generation of 1.20 kg CO_2 eq /kg cassava considering CO_2 capture. Thus, the biomethane production scheme considering agricultural residues such as cassava stalk was presented as a viable alternative capable of supplying the energy needs in the links of the value chain, reducing the overall impact of the agricultural system and allowing the use of residues.

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Conclusions and recommendations

Conclusions

The development of this thesis made it possible to establish different premises in the evaluation of hydrogen production schemes in the Colombian context. In the first place, it was possible to establish the importance and usefulness of heuristic analysis. Through this tool, it was possible to establish a global overview of the different hydrogen production pathways and technologies and their level of development at commercial and research levels. It was also possible to establish the main challenges these technologies face that aim to be the starting point for an energy transition towards carbon-neutral societies, considering the development of an energy economy based on hydrogen. As the main results of the heuristic analysis developed during this work, it was possible to establish that the pathways with the greatest opportunity for development and a high level of performance were the petrochemical and thermochemical pathways. On the contrary, the electrolytic and biological pathways face low conversion levels, low energy utilization, and high operating costs. Additionally, within these processing pathways, it was also possible to establish, from a database of technologies, which were the ones with the highest level of development, considering operational and design parameters. It was thus possible to conclude that steam methane reforming, gasification, alkaline electrolysis, and dark fermentation were the technologies with the highest level of development.

Once the heuristic analysis was carried out, the results of this first objective allowed the establishment of the experimental tests developed below. In the experimental trials, it was possible (i) to obtain biogas with yields of 160 g H_2/kg raw material, considering the biomethane potential of the raw materials and considering methodologies widely reported in the literature, (ii) to obtain synthesis gas with the gasification of biomass with a downdraft gasifier, obtaining yields of 33 g H_2/kg raw material (iii) to perform alkaline electrolysis trials considering energy from the national electricity grid and considering energy from solar panels with yields of 11.0-13. 5 g H_2/kg of raw material and (iv) it was possible to obtain hydrogen form in dark fermentation tests considering the microorganism Thermoanaerobacter *thermosaccharolyticum* W16, which allowed obtaining yields of 6.24 g H_2/kg of raw material. These yields indicate that biomethane production and biomass gasification are the technologies with the highest mass yield and energy efficiency. On the contrary, the alkaline electrolysis and dark fermentation schemes presented lower yields, but the operating conditions were less severe, which reduced the operating cost of the procedures.

Once the experimental trials were developed, the results were the input for the different technologies to be scaled in simulation schemes developed in the Aspen Plus software, considering high-scale flows (25 tons/day) and economic parameters of the Colombian context. The development of the simulation schemes included the separation and purification stage, considering the yields reported in the literature. Once the different schemes were scaled up, they were evaluated, considering a sustainability index. This index was developed considering different dimensions: techno-energetic, economic, environmental, and social. The sustainability index (S_{Id}) evaluated the performance of products, mass, and energy indicators in the techno-energetic dimension; in the economic dimension, it evaluated the CapEx, OpEx, gross income, and cost of hydrogen production. In the environmental dimension, we evaluated the carbon footprint and two indicators derived from the life cycle assessment. Finally, in the social dimension, we evaluated employment generation, water use at the industrial level, and biomass consumption through simulation schemes. All these indicators were considered for the analysis of the sustainability index.

According to the results of the sustainability analysis, the steam biomethane reforming (SBMR) and gasification (GF) schemes showed the best techno-energy yields and the lowest production costs, ranging from 2.0 to 6.0 USD/kg H_2. However, the thermochemical processes had a high environmental impact, with a carbon footprint of 4.79 kg CO_2 eq/kg H_2, affecting the environmental dimension and decreasing the S_{Id}. In the case of SBMR, maximum levels (≥90%) were reached if the techno-energy dimension was considered due to the high energy and mass efficiencies of the system. On the contrary, if the economic dimension was considered, the S_{Id} for SBMR decreased to 75%, as it required higher CapEx and OpEx investments. After the SBMR processes, the processes with the highest S_{Id} were the electrolytic processes (EL). They presented the lowest CapEx and OpEx costs with 1.54 M-USD and 1.57 M-USD/year, respectively, and the lowest pollutant rates. Finally, the biological processes (DF) presented low techno-energy efficiency, high operating costs, and high levels of environmental pollution. As a consequence, the price of hydrogen for these processes was USD 6.96/kg H_2, which reduced their ability to enter the market. However, improved VFA purification processes present an opportunity to reduce both the CapEx and OpEx of the process, lowering the cost of hydrogen production. Therefore, each scheme presents critical points that must be studied and optimized to provide hydrogen with development pathways that allow its expansion in the shortest possible time.

Considering the results of the sustainability analysis, it is possible to conclude that the scheme with the greatest opportunity for development, considering the Colombian socioeconomic context, was the biomethane steam reforming scheme. Based on this, to establish the environmental performance of this technology, the possibility of including this energy vector in value chains already established at the national level was evaluated. To this end, the cassava value chain, which generates waste at the product stage, such as the cassava stalk that can be used to produce biomethane and hydrogen, was evaluated. The main results showed that producers and transformers were the links with the greatest environmental impact in the cassava value chain in Sucre. For producers, the most influential activity was the use of materials and the addition of nitrogenous agrochemicals. In the transformer link, the greatest impact was attributed to the solid and liquid residues of the rural enterprises (rallanderias), residues with high levels of organic load, and with important effects on the adjacent ecosystems. Similarly, the value chain and raw materials had the greatest environmental impact in the biomethane and hydrogen production schemes. However, this study showed that including valorization schemes allows for reducing the environmental footprint of the value chain. The production of 1 kg of cassava in the department of Sucre generates 1.22 kg of CO_2 eq throughout the value chain, being the transformer link the one with the highest impact, and the production schemes estimate the generation of 1.20 kg CO_2 eq /kg cassava considering CO_2 capture. Thus, the biomethane and hydrogen production scheme considering agricultural residues such as cassava stalk was presented as a viable alternative capable of supplying the energy needs in the links of the value chain, reducing the overall impact of the agricultural system and allowing the use of residues. However, the development of hydrogen at the national level is still at an early stage, which makes implementing this type of technology an even greater challenge. Thus, the development of this work allowed the identification of the most viable technologies for hydrogen production and the bottlenecks of these processes to focus future collective efforts on the development and solution of these problems to accelerate and expand the opportunities of hydrogen in the national energy matrix.

Additionally, the development of the thesis is framed in favor of implementing several objectives established in the hydrogen road map developed by the Ministry of Mines and Energies, which promotes the development of research works that seek to evaluate and analyze the implementation of hydrogen production processes in Colombia. Finally, the development of this thesis also allows identifying the multiple difficulties faced by an economy based on hydrogen, where the safety of the process is a pillar still under study and is one of the major bottlenecks, even more so when this energy carrier has multiple applications in the transportation sector. Therefore, it is necessary to carry out more studies to solve these challenges rather than accelerating the inclusion of processes that may pose a risk to industry, governments, and users.

Recommendations

Following the development of this thesis, some issues can be further explored in subsequent research. Some of the recommendations suggested by the author are:

- ✓ To perform an experimental analysis of a wider range of alternative technologies to hydrogen production, technologies derived from catalytic schemes or new innovative developments.

- ✓ To deepen the proposals for hydrogen storage and transport, since these are highly relevant issues in terms of safety, to establish the viability of this energy vector.

- ✓ Determine the concentration profiles of products and reactants throughout the pretreatments and reactions to determine possible chemical kinetics. As observed in this thesis, all processes allow the generation of by-products, such as inhibitors in biogas production, syngas exhausted after biomass combustion, oxygen in the electrolysis schemes, and volatile fatty acids in the dark hydrogen fermentation.

- ✓ From the simulation point of view, a market analysis with projections of hydrogen consumption and utilization in Colombia.

Annexes

Supplementary material-Appendix A

Sustainability of hydrogen production towards a neutral carbon society

1. Hydrogen production flow diagrams

The symbology used in the operating units was described in **Table A0**.

Table A0. Symbology used in flow diagrams.

Symbology		Symbology	
D-101	Dryer	SS-101	Stripper
M-101	Milling	PSA	Pressure swing adsorption
S-101	Screening	VSA	Vacuum swing adsorption
T-101	Tank	ST-101	Electrolysis stack
R-101	Reactor	MM-101	Membranes
SP-101	Separator	TB-101	Turbine
C-101	Compressor	CH-101	Chillers
E-101	Heat exchanger	F-101	Filter
P-101	Pump	CD-101	Distillation column
CA-101	Absorption column		

1.1. Steam biomethane reforming

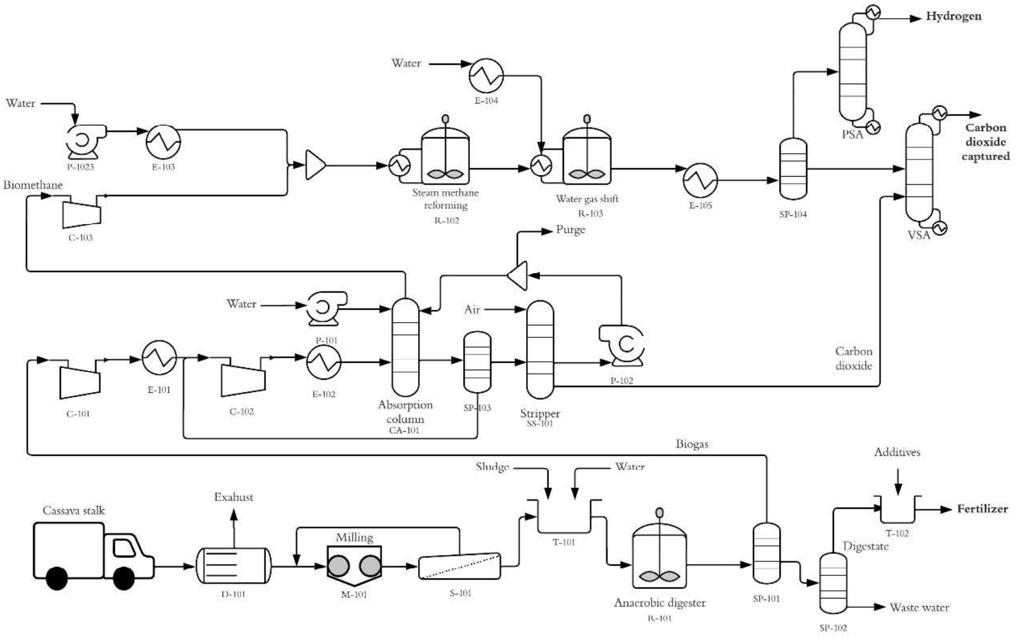

Figure A1. Steam biomethane reforming flow diagram.

1.2. Gasification

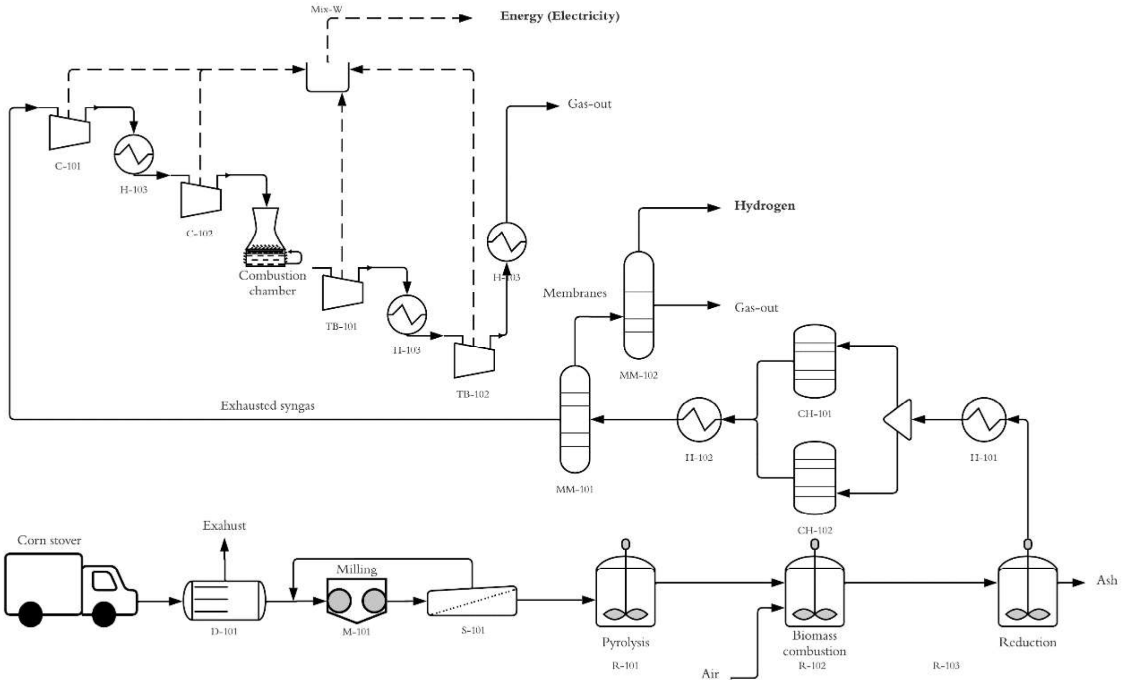

Figure A2. Biomass gasification flow diagram.

1.3. Electrolysis

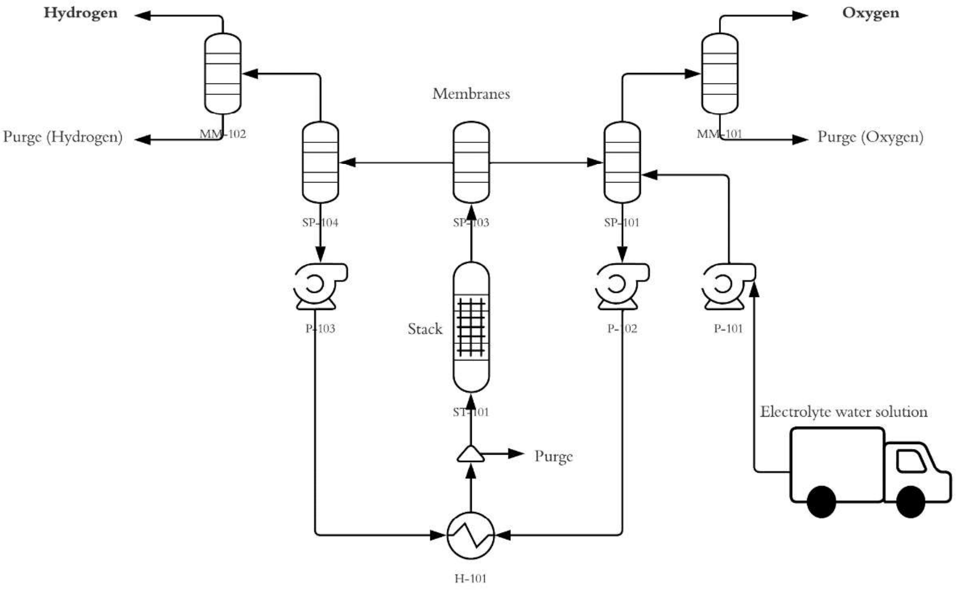

Figure A3. Alkaline electrolysis flow diagram.

1.4. Dark fermentation

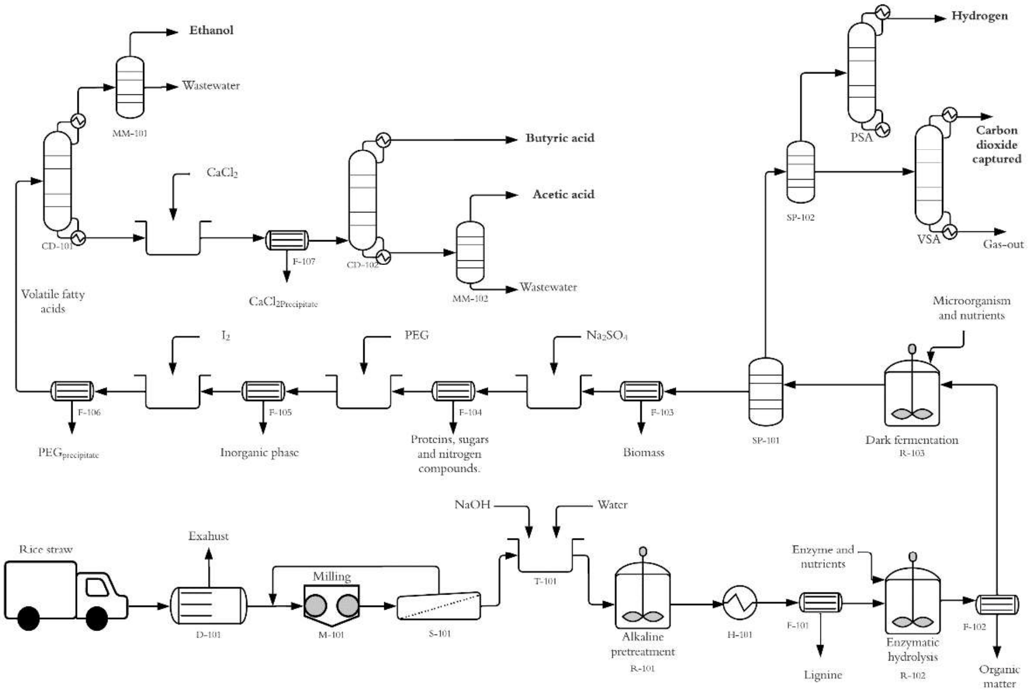

Figure A4. Dark fermentation flow diagram.

2. Social indicators, risk scale, and impact scores for the sLCA

Table A1 and **Table A2** summarize the stakeholders, categories, and subcategories used in the social assessment.

Table A1. Stakeholder, category, and subcategory

Stakeholder	Subcategory	Indicator	Equation
Workers	Fair salary	Minimum wage per month	$M_W = \frac{\text{Minimum wage}_{\text{Colombia}}}{\text{Minimum wage}_{\text{Latin America}}}$
	Working time	Hours of work per employee per week	Working hours per shift
Local community	Access to material resources	Level of industrial water use (related to total withdrawal)	$LW_H = \frac{W_{\text{Process}} + W_{\text{Cooling water}}}{W_{\text{Colombia Withdrawal}}}$
		Level of industrial water use (related to total internal renewable water resources)	$LW_H = \frac{W_{\text{Process}} + W_{\text{Cooling water}}}{W_{\text{Colombia Renewable}}}$
		Extraction of biomass (related to area)	$E_B = \frac{\text{Flow rate}_{\text{Raw material}}}{A_{\text{Raw materials crop}}}$

		Extraction of fossil fuels	$E_F = \frac{\text{Energy}_{\text{Coal}}}{\text{National energy demanda}_{\text{Colombia}}}$
	Local employment	Job generation	Jobs
	GHG Footprints	Embodied CO_2-eq footprint	$P_{CO_2} = \frac{CO_2\text{ released}}{CO_2\text{ Colombia}}$

Table A2. Risk scale, score, and denotation of subcategory.

Stakeholder	Subcategory	Indicator	Risk scale	Risk score	Risk denotation
Workers	Fair salary	M_W	$M_W > 1.8$	0	Very low
			$1.8 \gg M_W > 1.3$	1	Low
			$1.3 \gg M_W > 0.9$	2	Medium
			$0.9 \gg M_W > 0.5$	3	High
			$M_W \gg 0.5$	4	Very high
	Working time	H_W	$40 \gg H_W > 48$	1	Low
			$48 \gg H_W > 55$	2	Medium
			$55 \gg H_W > 60$	3	High
			$H_W \gg 60$	4	Very high
Local community	Access to material resources	LW_H LW_R	$0 \gg LH > 10$	0	Very low
			$10 \gg LH > 20$	1	Low
			$20 \gg LH > 30$	2	Medium
			$30 \gg LH > 40$	3	High
			$LH \gg 40$	4	Very high
		E_B	$0 \gg E_B > 200$	0	Very low
			$200 \gg E_B > 400$	1	Low
			$400 \gg E_B > 600$	2	Medium
			$600 \gg E_B > 800$	3	High
			$E_B \gg 800$	4	Very high
		E_F	$0 \gg E_F > 10$	0	Very low
			$10 \gg E_F > 20$	1	Low
			$20 \gg E_F > 30$	2	Medium
			$30 \gg E_F > 40$	3	High
			$E_B \gg 40$	4	Very high
	Local employment	J_G	-	-	-
	GHG Footprints	P_{CO_2}	$P_{CO_2} > 3$	0	Very low
			$3 \gg P_{CO_2} > 6$	1	Low
			$6 \gg P_{CO_2} > 9$	2	Medium
			$9 \gg P_{CO_2} > 12$	3	High
			$P_{CO_2} \gg 12$	4	Very high

3. Sustainability index S_{Id}

Table A3 and **Table A4** summarize the indicators and statistical distribution used in assigning weights for each dimension in the sustainability assessment

Table A3. Indicators used in sustainability assessment.

Dimension	Indicators	Unit
Tecno-energetic (T)	Product yield	kg H_2 kg Raw material
	Process mass intensity	kg Inlet streams/ kg Products
	Specific energy consumption	kW/ kg Raw material
	Self-generation (Hydrogen)	
Economica (Ec)	OpEx	M-USD/year
	CapEx	M-USD
	Gross income	M-USD/year
	Production cost	USD/kg
Environmental (Ev)	Carbon footprint	kg CO_2 eq /kg H_2
	Human toxicity	kg 1,4-DB eq
	Agricultural land occupation	m^2a
Social (S)	Local employment	Jobs/year
	Extraction of biomass (related to area)	ton/km^2
	Level of industrial water use (related to total withdrawal)	%

Table A4. Statistical distribution.

	Dimensions (w_i %)				S_{Id} (%)			
Combinations	T	Ec	Ev	S	SMR-Ty	GF-Tm	EL-Wat	DF-Pa
T	70	10	10	10	90.52	47.50	52.94	23.72
Ec	10	70	10	10	76.47	63.28	59.48	10.75
Ev	10	10	70	10	88.62	64.31	80.40	10.22
S	10	10	10	70	71.75	48.92	65.87	57.54
TEcEvS	25	25	25	25	81.84	56.00	64.67	25.56
TEc	35	35	15	15	82.94	55.60	59.03	20.01
EcEv	15	35	35	15	82.31	61.20	68.19	15.51
EcS	15	35	15	35	76.69	56.07	63.34	31.28

T: Techno-energetic, Ec: Economic, Ev: Environmental, and S: Social.