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Review

An Updated Review of Recent Applications and Perspectives of Hydrogen Production from Biomass by Fermentation: A Comprehensive Analysis

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Abstract: Fermentation is an oxygen-free biological process that produces hydrogen, a clean, renewable energy source with the potential to power a low-carbon economy. Bibliometric analysis is crucial in academic research to evaluate scientific production, identify trends and contributors, and map the development of a field, providing valuable information to guide researchers and promote scientific innovation. This review provides an advanced bibliometric analysis and a future perspective on fermentation for hydrogen production. By searching WoS, we evaluated and refined 62,087 articles to 4493 articles. This allowed us to identify the most important journals, countries, institutions, and authors in the field. In addition, the ten most cited articles and the dominant research areas were identified. A keyword analysis revealed five research clusters that illustrate where research is progressing. The outlook indicates that a deeper understanding of microbiology and support from energy policy will drive the development of hydrogen from fermentation.

Keywords: hydrogen production; fermentation; biological processes; biomass; bibliometric

1. Introduction

The demand for energy in modern society continues to escalate, driven by factors such as population growth, increased living standards, and accelerated industrial development in both developed and developing countries [1]. Currently, over 80% of our energy consumption is derived from fossil fuels, namely, oil, natural gas, and coal, underscoring a significant dependence on these sources [2,3]. Unfortunately, the combustion of fossil fuels results in significant emissions of polluting gases, including CO_2, contributing to adverse climate and ecosystem impacts [4].

To address this critical issue, the "Paris Agreement", which emerged from the 21st Conference of the Parties [5,6] (COP 21), in 2015, united 196 countries to combat global warming. The Agreement set the ambitious goal of limiting the global temperature increase to below 1.5 °C [6,7]. Since then, there has been remarkable progress in green energy technologies as essential solutions to meet global energy needs and promote sustainable development [8,9]. Numerous countries have made efforts to implement environmentally friendly energy policies in pursuit of sustainability and decarbonization [10–13]. For example, the Republic of South Korea outlined its Second Climate Change Response Master Plan in 2019, which aims to reduce greenhouse gas emissions from 709.1 million tons in 2017 to 536 million tons by 2030 and promote a sustainable, low-carbon green society [14,15].

The increasing urgency among countries to curb greenhouse gas emissions has spurred the search for cleaner fuels [16–19]. This search has rekindled interest in the substantial energy potential of hydrogen, which has emerged as a promising alternative for decarbonizing various sectors of modern society [20]. Hydrogen stands out as a "promising future energy source" due to its exceptionally high energy density, abundance on Earth, and emission-free combustion [21,22]. To illustrate this, the energy content of hydrogen, at 122 kJ/g, is approximately three times higher than that released by the combustion of fossil hydrocarbons [23]. Furthermore, hydrogen combustion produces only water and energy [24].

Although hydrogen is the lightest and most abundant element on Earth, it rarely exists in significant quantities in its molecular form [25,26]. Instead, hydrogen commonly combines with other elements [27]. Molecular hydrogen can be obtained from a variety of sources, including fossil fuels, water (fresh or seawater), biomass, and hydrogen sulfide, using a variety of extraction techniques [27–29]. Major energy-consuming sectors, such as industry, transportation, and commerce, are increasingly interested in using hydrogen [30–32]. In addition, hydrogen serves as a raw material in various industrial processes, including petroleum refining, metal treatment in steel mills, glass manufacturing, ammonia and methanol production, and food processing [20,33,34]. Projections indicate that the global demand for green hydrogen could reach 610 million tons per year by 2050 [35].

Although hydrogen has a promising future, producers still rely on fossil hydrocarbons to produce a significant portion of it [36–38]. Steam methane reforming (SMR) of natural gas dominates hydrogen production, followed by petroleum reforming and coal gasification [39]. However, there has been recent exploration of biological processes for hydrogen production. Notable biological methods include biophotolysis of water using green algae and cyanobacteria [40], photofermentation of organic matter by photosynthetic microorganisms [41], and anaerobic (or dark) fermentation of organic compounds by fermentative bacteria [39,42–44]. Out of these pathways, fermentative methods have received increased attention due to their sustainability, absence of polluting gas generation (e.g., CO_2), and potential for environmentally friendly treatment of organic waste for energy production [45]. Various waste streams from the food industry, agro-industrial processes, and wastewater can be reused in this approach [46,47].

In this bibliometric study, we delve into the events of the last 23 years to identify and analyze the progress made, the challenges overcome, and the ones still to come in hydrogen production by fermentation. The visualization of discoveries and knowledge gaps contributes significantly to a comprehensive and up-to-date understanding of this aspect of the contemporary energy landscape. Researchers recognize bibliometrics as an appropriate method to map the scientific activity of a specific field and perform qualitative and quantitative assessments using statistical and mathematical techniques [48,49]. Therefore, the present study aims to provide a comprehensive perspective on the current state of the field, using technological tools, namely, VOSviewer (version 1.6.20) and Microsoft Excel (Microsoft Office Professional Plus, 2019), to process data and interpret results.

2. Materials and Methods

This study builds on previous research [28,50–59] and uses bibliometric analyses with data from the Web of Science (WoS) (https://www.webofscience.com (accessed on 27

December 2023)), a reliable platform for scientific publications that is widely recognized for its high quality and accepted standards in generating research citation data [60,61].

The WoS database was initially searched using the keyword "hydrogen production" with a filter set to "all fields". We selected records from the period 2000 to 2023 categorized as "articles", "review articles", and "proceeding papers", with English as the primary language. This resulted in an initial set of 62,087 documents. Subsequent refinements were made with two additional keyword filters: ("fermentation" OR "fermentative"), which yielded 6182 documents, and ("biological" OR "biohydrogen"), resulting in a final dataset of 4493 published documents. The database was selected and exported on 27 December 2023.

Figure 1 shows the search criteria for database selection and the analytical approach adopted in the research methodology. The current study uses that dataset to address the following research questions (RQs):

- RQ1—What is the pattern of collaboration between journals, countries, institutions, and authors?
- RQ2—Which manuscripts are the most influential in the field?
- RQ3—Which topics are highlighted in the literature?
- RQ4—What should be the agenda for future research in this area?

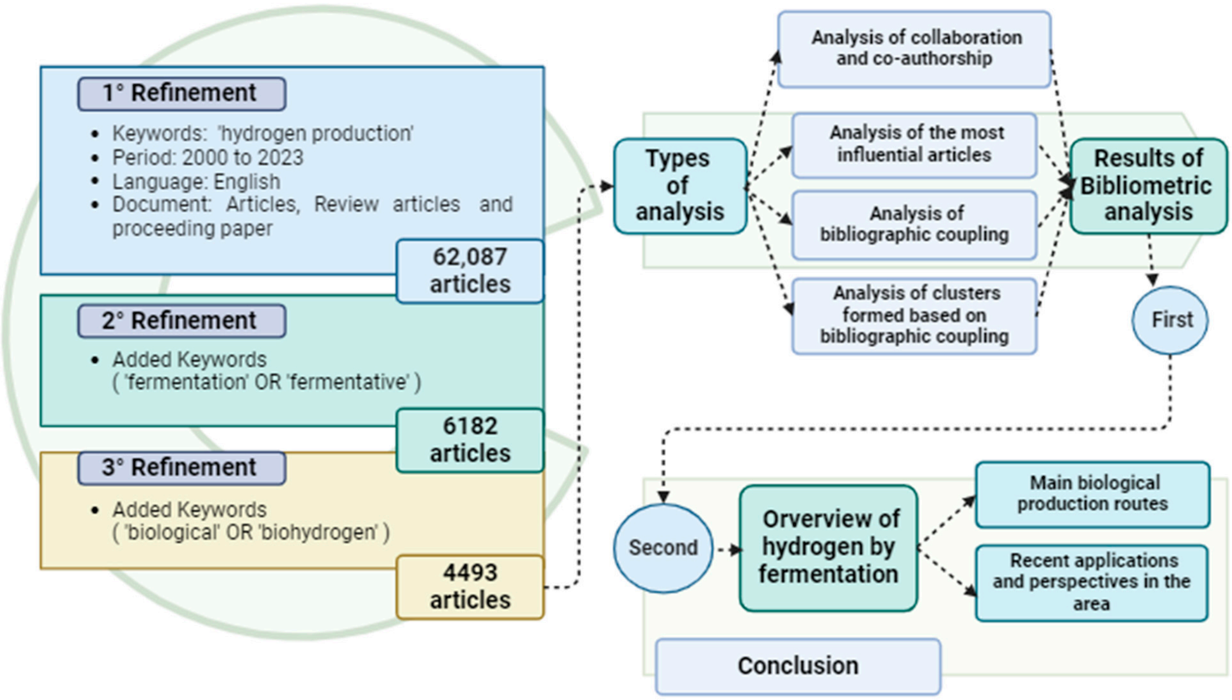

Figure 1. Search and analysis criteria used in the research methodology.

Bibliometric data analysis was performed using VOSviewer (version 1.6.20) to construct and visualize information related to the network of countries, authors, institutions, journals, and keyword occurrences [60]. In addition, standard Microsoft Excel spreadsheets (Microsoft Office Professional Plus, 2019) were used for data analysis and cataloging.

3. Results and Discussion

3.1. Performance Indicators

What is the pattern of collaboration between journals, countries, institutions, and authors?

3.1.1. Results Related to Publications

The initial search on WoS used the keyword "hydrogen production" and yielded 62,087 academic articles. Upon adding the string ("fermentation" OR "fermentative"), the search yielded 6182 articles. Upon adding the string ("biological" OR "biohydrogen"), the search yielded 4493 articles. The most relevant article was "Biohydrogen production by dark and photo-fermentation processes", published in March 2013 by Akroum-Amrouche et al. [62], which provides an overview of biological processes for hydrogen production, including the most used raw materials and the influencing factors in these processes. As shown in Figure 2, the number of publications related to fermentative hydrogen production has demonstrated remarkable growth, as in 2001 and 2003, only three and four publications were recorded, respectively, representing the lowest values within the period selected for investigation. In 2022, 371 articles were registered. In the last year of the analysis (2023), 235 articles were published up to the date of export of the database, confirming the importance of this topic. The increased interest in hydrogen produced by biological processes can be attributed to the recognition of hydrogen as a clean fuel with a high energy content, without emission of polluting gases into the atmosphere, compared to fossil fuels [63–65]. In addition, methods for the production of fermentative hydrogen can benefit from the use of several low-cost, renewable resources and environmentally sound waste treatment [66–70].

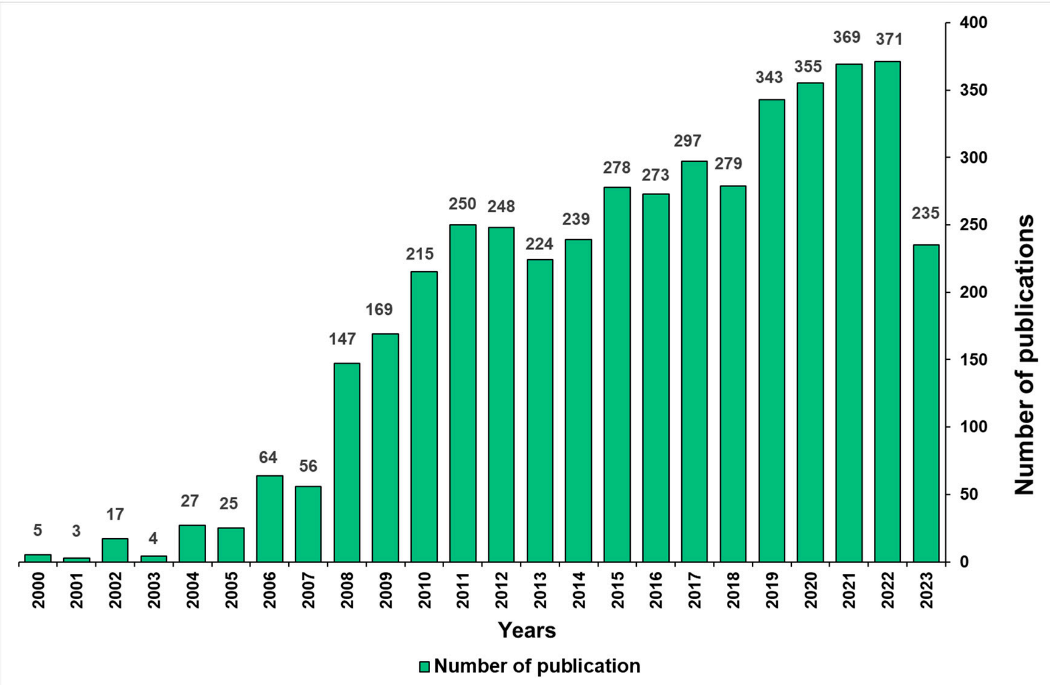

Figure 2. Annual distribution of scientific publications on hydrogen from fermentation (data exported on 27 December 2023).

3.1.2. Distribution of Scientific Journals, Countries, Institutions, and Authors

Articles on hydrogen produced by biological fermentation were published in 541 journals and accumulated 181,769 citations, resulting in an average of 40.46 citations per article between 2000 and 2023. Table 1 shows the ranking of the top ten journals, countries, institutions, and authors. The number of citations and the average number of citations per publication are also shown. Among the ten journals that published the most, the statistical analysis shows that they represented 56.6% of the publications in the field studied. The journal with the highest number of publications and citations is the English *INTERNATIONAL JOURNAL OF HYDROGEN ENERGY*, with 1440 publications, 71,296 citations, and an average of 49.51 citations per publication. The journal *RENEWABLE SUSTAINABLE ENERGY REVIEWS* had the highest average number of citations per publication (117.3). The database analysis also provides information on the countries of origin reported by the corresponding authors of the published articles. China had the highest number of publications with 1117 publications (26.2%) and an impressive 42,795 citations. India and the USA came in second and third with 548 publications and 23,257 citations and 380 publications and 23,805 citations, respectively. Of the countries analyzed, the USA had the highest average number of citations per publication at 62.64. According to the affiliation of the corresponding authors, the top three most published institutions were the *HARBIN INSTITUTE FF TECHNOLOGY* (with 189 publications and 7812 citations), the *FENG CHIA UNIVERSITY* (with 162 publications and 8477 citations), and the Chinese Academy of Sciences (with 136 publications and 5639 citations). *NATIONAL CHENG KUNG UNIVERSITY* was the institution with the highest average number of citations per publication (66.01). The top three authors were Gopalakrishnan Kumar (105 publications and 4412 citations), Sang-Hyoun Kim (98 publications and 3723 citations), and Chiu-Yue Lin (96 publications and 4113 citations), each accounting for about 6% of the total. Chiu-Yue Lin had the highest average number of citations per article (42.84).

Table 1. Ranking of the top ten most published and most cited journals, countries, institutions, and authors over the last 23 years, according to the WoS database.

Ranking		NP	NC	AC
Journals				
1	INTERNATIONAL JOURNAL OF HYDROGEN ENERGY	1440	71,296	49.51
2	BIORESOURCE TECHNOLOGY	579	27,624	47.71
3	RENEWABLE ENERGY	87	2378	27.33
4	FUEL	81	2269	28.01
5	RENEWABLE SUSTAINABLE ENERGY REVIEWS	74	8680	117.3
6	JOURNAL OF CLEANER PRODUCTION	70	2048	29.23
7	BIOMASS BIOENERGY	61	2117	34.70
8	ENERGIES	56	650	11.60
9	BIOTECHNOLOGY FOR BIOFUELS	46	1641	35.67
10	APPLIED MICROBIOLOGY AND BIOTECHNOLOGY	43	2870	66.74
Countries				
1	China	1117	42,795	38.31
2	India	548	23,257	42.43
3	The USA	380	23,805	62.64
4	South Korea	329	13,720	41.70
5	Brazil	246	6775	27.54
6	Mexico	223	6453	28.93
7	Thailand	203	5600	27.58
8	Italy	195	7675	39.35
9	Malaysia	188	8634	45.92
10	Canada	174	10,708	61.54
Institutions				
1	HARBIN INSTITUTE OF TECHNOLOGY	189	7812	41.33
2	FENG CHIA UNIVERSITY	162	8477	52.32
3	CHINESE ACADEMY OF SCIENCES	136	5639	41.46
4	UNIVERSITY OF SÃO PAULO	123	3849	31.29
5	TSINGHUA UNIVERSITY	108	6050	56.01
6	NATIONAL CHENG KUNG UNIVERSITY	104	6866	66.01
7	HENAN AGRICULTURAL UNIVERSITY	97	1883	19.41
8	KHON KAEN UNIVERSITY	81	2357	29.09
9	NATIONAL AUTONOMOUS UNIVERSITY OF MEXICO	77	1782	23.14
10	YONSEI UNIVERSITY	72	1989	27.62
Authors				
1	Kumar, Gopalakrishnan	105	4412	42.01
2	Kim, Sang-Hyoun	98	3723	37.98
3	Lin, Chiu-Yue	96	4113	42.84
4	Zhang, Quanguo	92	1782	19.36
5	Mohan, S. Venkata	79	3962	50.15
6	Reungsang, Alissara	76	2229	29.32
7	Ren, Nan Qi	75	2925	39.00
8	Chang, Jo-Shu	74	4680	63.24
9	Wang, Jianlong	66	4265	64.62
10	Zhang, Zhiping	64	1292	20.18

Note: NP = number of publications; NC = number of citations; AC = average citations (NC/NP).

After analyzing the collected database, we identified eligible works related to the topic in scientific journals. A total of 516 journals were identified, with an approximate average of 8.70 publications per journal. This result highlights the relevance of the topic in several research fields. However, there is still a need to deepen the understanding of this line of research, as it is of great importance to the scientific and industrial community.

The diversity of research groups working in this field is a valuable aspect. It reflects the variety of journals that deal with the topic. The different groups provide the opportunity to experience different methodologies, each unique to its group. This diversity ensures a more comprehensive approach to the topic, enriching the academic community with new ideas and projects.

Figure 3A illustrates the interconnection between journals with at least five publications, using lines that indicate the total link strength (TLS) and clusters to demonstrate this relationship. TLS indicates the degree of connection between two or more distinct journals, while clusters identify each journal by a specific color node. The *INTERNATIONAL JOURNAL OF HYDROGEN ENERGY* stands out for being the journal with the largest number of publications on the topic and for its significant collaboration with other journals, thus positioning itself in the center of the figure with a considerably thicker line. This indicates a high total link strength, highlighting the *INTERNATIONAL JOURNAL OF HYDROGEN ENERGY'S* extensive network of collaborations, mainly with journals such as *BIORESOURCE TECHNOLOGY, RENEWABLE ENERGY, FUEL, RENEWABLE SUSTAINABLE ENERGY REVIEWS, THE JOURNAL OF CLEANER PRODUCTION*, And *BIOMASS BIOENERGY*. Figure 3B illustrates how these relationships became closer over time. Table 1 highlights the importance of the *INTERNATIONAL JOURNAL OF HYDROGEN ENERGY*. It has an impact factor of 7.2, with approximately 1440 articles published on the topic studied, which represents 32% of the total documents collected.

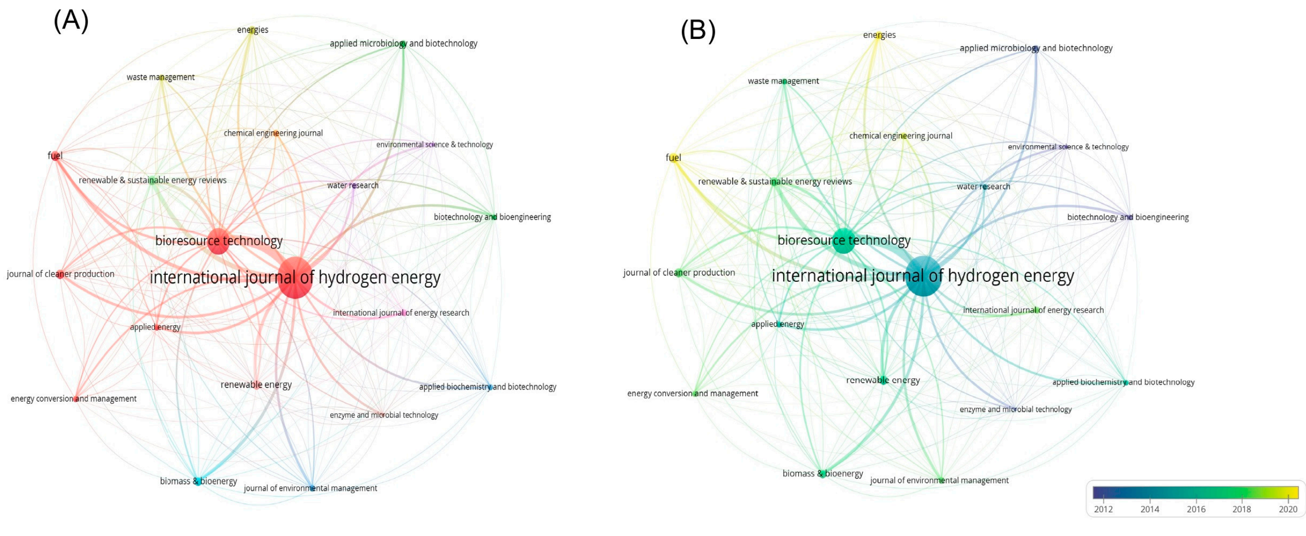

Figure 3. Main journals that published the most in the area of hydrogen generation through biological and fermentative methods in the last five years. (**A**) The 20 journals with at least five documents that published the most and were cited within this theme. (**B**) Temporal map of the number of journals that published the most in the area.

The *INTERNATIONAL JOURNAL OF HYDROGEN ENERGY* stands out not only for the quantity but also for the quality of citations. The second journal in the list, Bioresource Technology, has an impact factor of 11.4, with around 50 articles published on the subject and 747 citations accumulated over time. This represents less than 50% of the publications and citations of the first-place journal, which underscores its importance in the field.

To improve the analysis of the network visualization, a geocoding was created to represent the number of organizations per country. This geocoding expands the possibilities for visualizing and analyzing the geographic distribution of organizations involved in research related to the topic of this thesis. Thus, Figure 4A emerges as a tool to explore the geocoded addresses, revealing a higher density of organizations in regions covering North America and Asia, especially China, with some notable regions in South America just below.

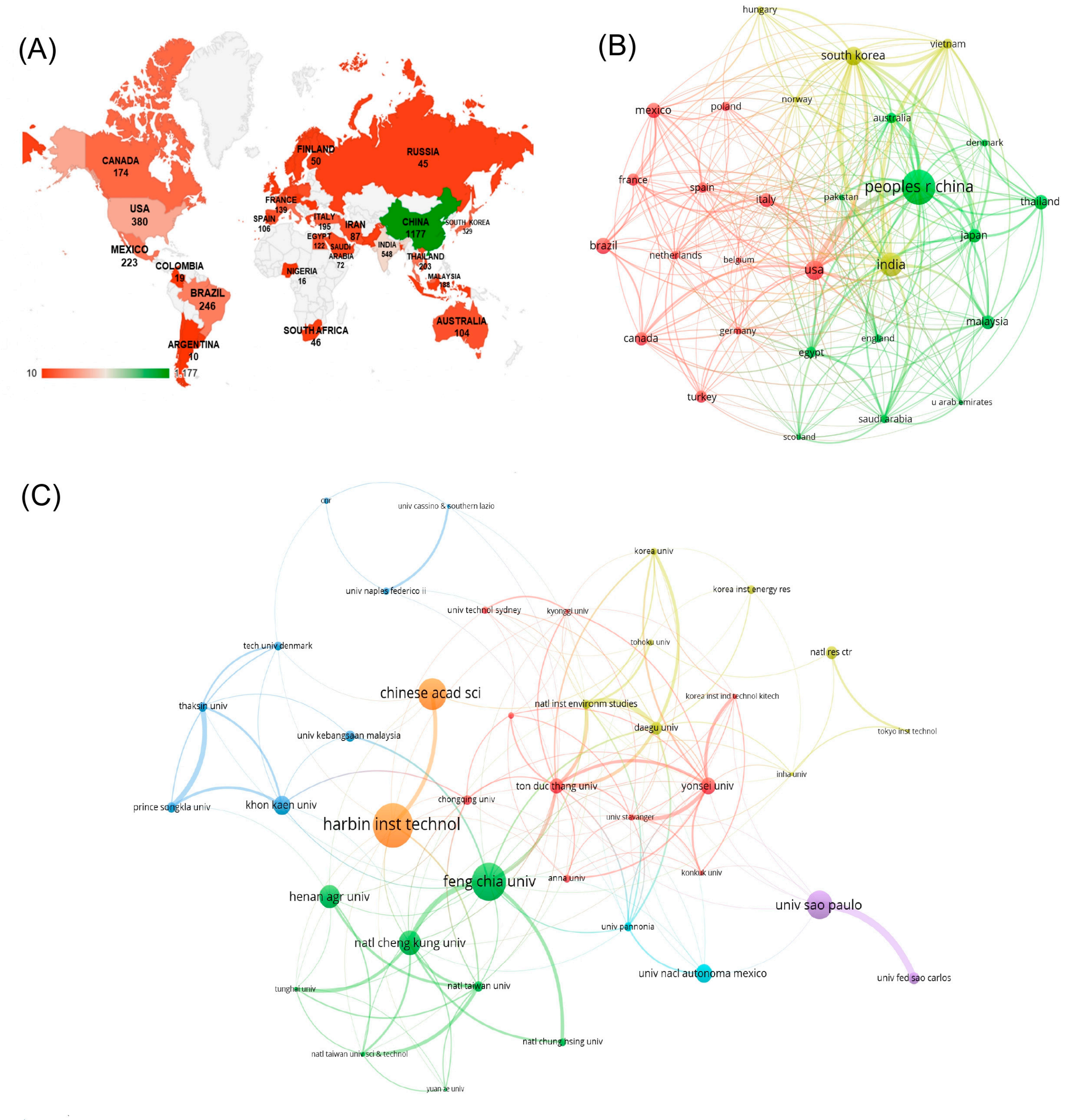

Figure 4. Bibliometric Analysis. (**A**) Cartographic representation of publications by country. (**B**) Network visualization map of the most significant collaborations between countries. (**C**) Co-authorship cluster map between top institutions.

Using the same filters as in the previous figure, Figure 4B illustrates the network of connections or collaborations between countries. The intense interaction between China and the United States is evident, fostering robust cooperation in the exchange of ideas and collaboration in manuscript preparation, even though these countries are located on different continents. To accurately represent the interactions between organizations, a network diagram was created, as shown in Figure 4C. In this context, outstanding organizations include the Harbin Institute of Technology, Feng Chia University, and the Chinese Academy of Sciences, which show the best results in collaboration. Here, the predominance of Chinese institutions stands out as a major contributor to research on the topic addressed.

We identified all the works in the database. This result highlights the widespread nature of research in the field, which is characterized by a considerable diversity of researchers and methodologies applied to the topic. Figure 5A shows the relationship between authors, considering the restriction that each author must have at least one published paper, and Figure 5B illustrates this relationship over time. This visualization shows more restricted sets of collaborations, indicating that virtually all authors are part of an extensive network of collaborations for co-authorship. This again highlights the extensive collaborative network in article production, the local connections between neighboring institutions, and the collaboration between authors from the same institution. Ultimately, all of these collaborations contribute to the strengthening of studies on this topic.

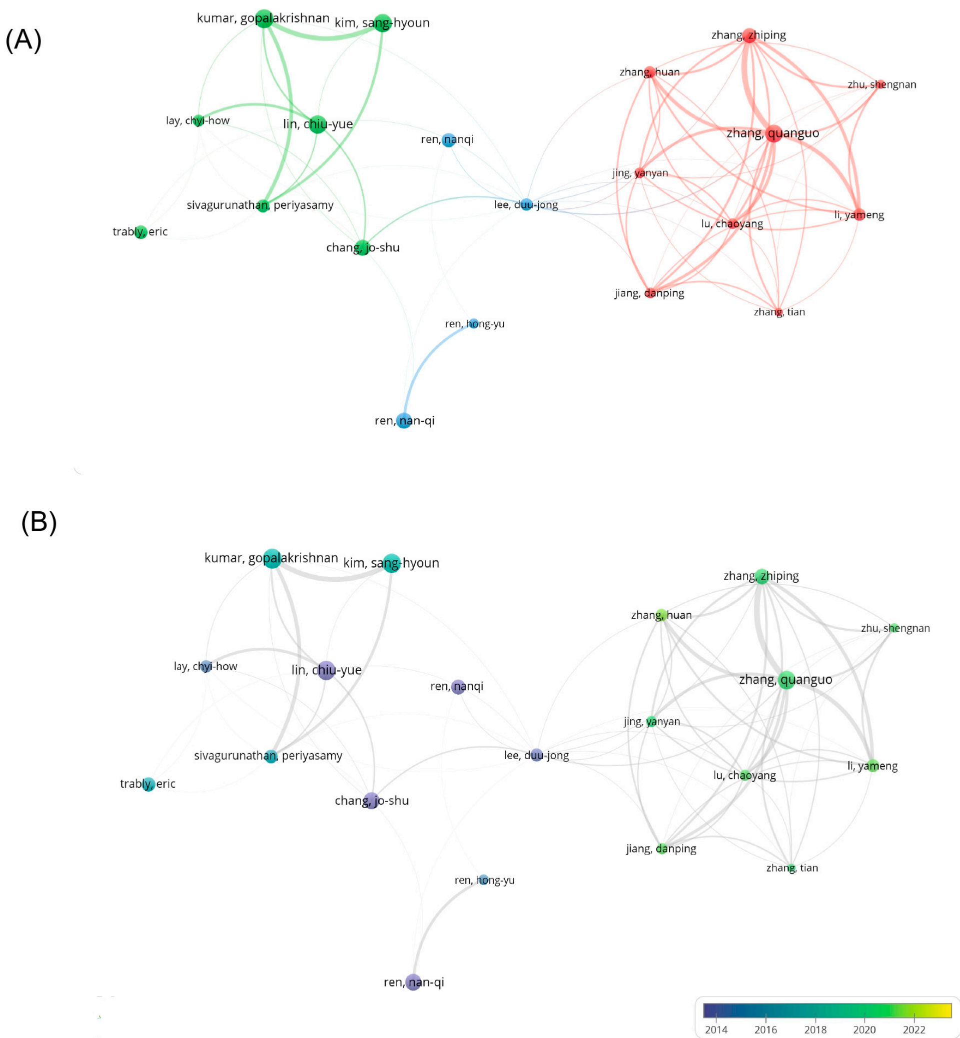

Figure 5. Bibliometric Analysis. (**A**) Grouping map of authors with the highest number of co-authorships. (**B**) Authors' production over time.

However, despite the diversity of connections between authors, the three outstanding authors, Kumar, Gopalakrishnan, Kim Sang-Hyoun, Lin, and Chiu-Yue, are located within the same cluster. The close relationship between these authors has resulted in a significant number of publications, leading to a dominance in this area of study. Thus, these prominent names appear when discussing a specific topic, i.e., hydrogen production by fermentation.

3.2. Research Points

What are the most influential manuscripts in this field?

The Most Cited Articles

The ability to statistically analyze the publication of papers on a given topic, as well as the evolution of the scientific community in this field of research, is one of the important features of bibliometric analysis. As a result, Table 2 lists the ten most referenced works on hydrogen synthesis by fermentation using biomass as a raw material, together with their year of publication and average citation per year.

Table 2. The most cited articles in research on fermentative hydrogen production obtained from WoS.

Rank	Title	Authors	Journal	Year Published	Citations Total	Average Annual Citations	Reference
1	Hydrogen production by biological processes: a survey of literature	Das, D.; Veziroglu, T.N.	International Journal of Hydrogen Energy	2001	1539	66.91	[71]
2	Hydrogen production from renewable and sustainable energy resources: Promising green energy carrier for clean development	Hosseini, S. E.; Wahid, M. A.	Renewable and Sustainable Energy Reviews	2016	1260	157.5	[72]
3	Bio-hydrogen production from waste materials	Kapdan, I.K.; Kargi, F.	Enzyme and Microbial Technology	2006	1204	66.89	[73]
4	Biohydrogen production: prospects and limitations to practical application	Levin, D.B.; Pitt, L.; Love, M.	International Journal of Hydrogen Energy	2004	1106	55.3	[74]
5	An overview of hydrogen production from biomass	Ni, M.; Leung, D.Y.C.; Leung, M.K.H.; Sumathy, K.	Fuel Processing Technology	2006	857	47.61	[75]
6	Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell	Liu, H.; Cheng, S.A.; Logan, B.E.	Environmental Science & Technology	2005	765	40.26	[76]
7	Biological hydrogen production: fundamentals and limiting processes	Hallenbeck, P.C.; Benemann, J.R.	International Journal of Hydrogen Energy	2002	732	33.27	[77]
8	Sustainable fermentative hydrogen production: challenges for process optimisation	Hawkes, F.R.; Dinsdale, R.; Hawkes, D.L.; Hussy, I.	International Journal of Hydrogen Energy	2002	721	32.77	[78]
9	Production of bioenergy and biochemicals from industrial and agricultural wastewater	Angenent, L.T.; Karim, K.; Al-Dahhan, M.H.; Domíguez-Espinosa, R.	Trends In Biotechnology	2004	718	35.9	[79]
10	Factors influencing fermentative hydrogen production: A review	Wang, J.; Wan, W.	International Journal of Hydrogen Energy	2009	667	44.47	[80]

The most cited article is titled "Hydrogen production by biological processes: a survey of literature". It was published in 2001, has an average of 66.91 citations per year, and provides an overview of biological mechanisms for hydrogen synthesis. The authors present and discuss the metabolic processes and microorganisms involved in hydrogen production. As a result, they argue that fermentation is among the most widely applied biological processes for hydrogen production [71].

Secondly, the article "Hydrogen production from renewable and sustainable energy resources: A promising green energy carrier for clean development", published in 2016, has an average of 157.5 citations per year. The authors provide an overview of using renewable and sustainable energy resources for hydrogen production, emphasizing supercritical water gasification from biomass as the most economically effective thermochemical method. They also present the energy required to pressurize the product in the storage tank. Finally, they point out challenges that need to be overcome, such as the low efficiency of photovoltaic systems, with a focus on solar cells, as electricity prices are critical for the economic sustainability of the process [72].

The authors of "Bio-hydrogen production from waste materials", published in 2006 and with an average citation of 66.89, present a review of the technologies involved in the production of biohydrogen. The article also explores topics such as bioprocessing methods, wastes with potential use, bioprocessing environments, and potentially useful microbial cultures [73].

In "Biohydrogen production: prospects and limitations to practical application", published in 2004, with an average of 55.3 citations per year, the researchers recommend listing the achievements and limitations of biohydrogen production in practice on an industrial scale [74].

The article "An overview of hydrogen production from biomass", published in 2006, has an average of 47.61 citations per year and discusses the importance of converting biomass to hydrogen. This section describes and reviews alternative thermochemical and biological processes for current and future use. Thermochemical processes include pyrolysis and gasification. Biogenic processes include biophotolysis and fermentation [75]

3.3. Background Research Topics

A segmented investigation allows us to understand the current gaps and difficulties in a complete research topic or in a specialized sector to be analyzed. As a result, the current study on this topic divides lists and identifies the key research topics for biological hydrogen production.

Research Areas

The database contains publications from 50 different fields of study. Many publications cover more than one field of study, and 28 of them have fewer than ten linked papers. Figure 6 shows the top seven research areas. Energy fuels was the most frequently researched topic, with 2811 articles and about 26.5% of all records. Chemistry and electrochemistry followed with 1617 and 1458 articles, respectively, representing 15.3% and 13.8% of the total articles. Biotechnology and applied microbiology ranked fourth with 1225 articles (11.6% of the total). Other specialties accounted for 12% of the total.

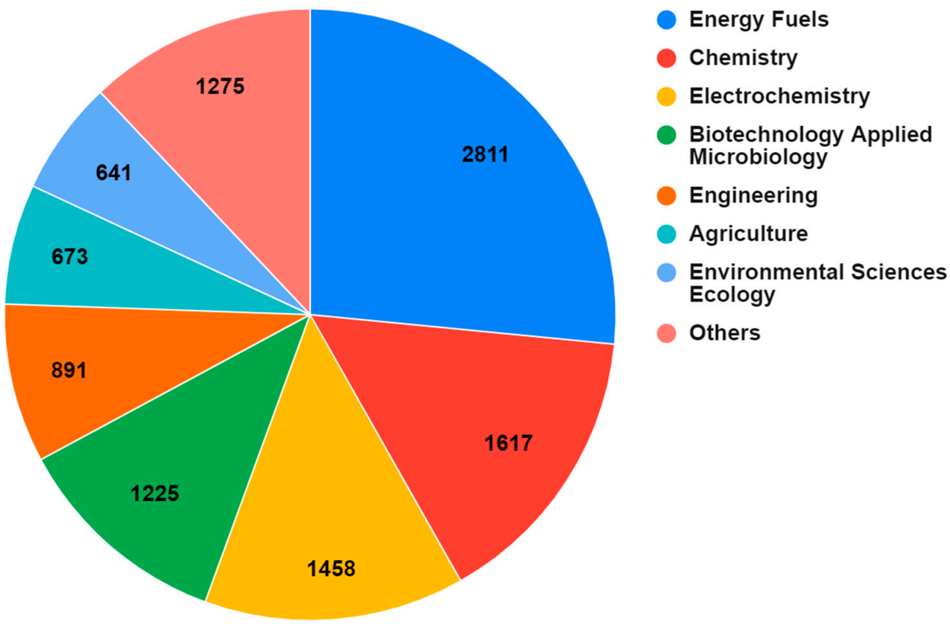

Figure 6. Distribution of research areas related to fermentative hydrogen production.

Figure 6 shows that the research area with the most publications was energy fuels, highlighting the importance of this topic in the scientific community for the development of alternative technologies for increasingly sustainable fuel production. This enables advances in industrial applicability through economic viability. Chemistry and electrochemistry are the next topics covered, emphasizing the application of theoretical principles from these areas to develop innovative and environmentally friendly approaches.

3.4. Emerging Areas of Research

What could be the agenda for future investigations in this field?

The line of investigation that the academic community has developed in hydrogen production by fermentation from biomass points in promising directions. The improvement of fermenting microorganisms [81–83] to increase the production potential is a future field of research. To improve hydrogen production, future research may converge on the identification of adapted microorganisms, allowing a more comprehensive substrate exploration [84–86], in particular, the search for more sustainable solutions for an immense variety of wastes from industrial production processes.

The development of co-digestion techniques to influence the rate of hydrogen production from biomass fermentation [87–89] reveals a potential line of development. The simultaneous processing of a range of substrates can reveal aspects related to microbial inhibition and beneficial association with the process. Focusing on research in these areas has promising potential to expand the range of substrates to be used as well as advance process optimization to contribute to applicability. There ought to be direct reflection on the economic viability of hydrogen production via microbial fermentation of biomass.

Quantitative Analysis of Frequent Keywords

The present bibliometric analysis examined the most popular keywords within the study area in question. In Table 3, the 20 most used keywords in the bibliometric study are ranked according to their frequency of occurrence. These most used keywords were grouped into clusters. The network map shown in Figure 7A is composed of four main clusters, in which the keywords presented are directly related to their importance and influence. The distance between the clusters represents a connection between the words. As seen in Figure 7A, the keyword "biohydrogen production" occupies a central position in the biomass fermentation process, and the importance of this keyword can be evidenced by the high number of links between it and other terms.

Table 3. Ranking of the 20 most relevant keywords in the area of hydrogen production through fermentation obtained from VOSviewer.

Rank	Keywords	TOs	TLS	Rank	Keywords	TOs	TLS
1	Biohydrogen production	2194	5905	11	Pretreatment	555	1893
2	Biohydrogen	1414	3937	12	Optimization	518	1736
3	Dark fermentation	1306	4062	13	Anaerobic digestion	504	1763
4	Fermentation	1075	3150	14	Glucose	493	1606
5	Hydrogen production	984	2553	15	Hydrogen production	477	1332
6	Fermentative hydrogen production	780	2126	16	Biomass	474	1513
7	Wastewater	733	2424	17	Methane production	464	1705
8	Food waste	676	2459	18	Sludge	456	1623
9	pH	623	2093	19	H2 production	329	995
10	Hydrogen	586	1723	20	Microbial communities	311	1158

Note: TOs = total occurrences; TLS = total link strength.

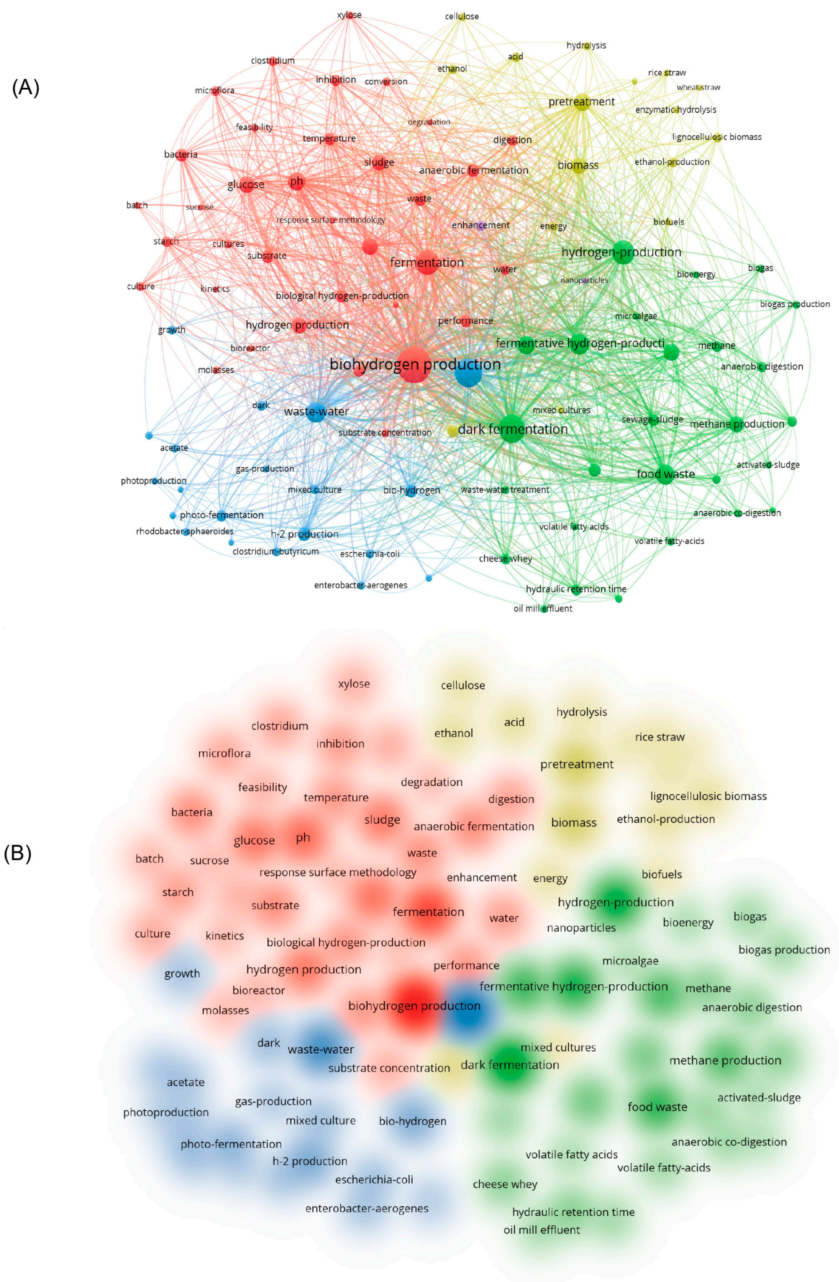

Figure 7. Occurrence-based keywords: (**A**) Network visualization map of the 100 keywords with at least five occurrences. (**B**) Density map of the most relevant keywords.

In the density map of the most relevant keywords (Figure 7B) generated in VOSviewer, it was possible to observe several terms related to numerous aspects. The words "biohydrogen production", "dark fermentation", "production", "pretreatment", "wastewater", "pretreatment", and "biomass" stand out because they have darker and larger nuclei. In addition, the proximity of the nuclei of the last two words suggests a conceptual relationship between them.

The first cluster with the highest number of keywords, shown in Table 4, demonstrates the broad spectrum related to hydrogen production via anaerobic fermentation. In particular, it highlights the microorganisms, substrates, and processes involved. The second position, with a total of 27 keywords, emphasizes processes related to biogas production and waste treatment. The third cluster relates to techniques for hydrogen production through bacterial metabolism.

Table 4. Clusters of essential keywords obtained from the VOSviewer software.

Cluster	Items	Keywords in the VOSviewer Network
#1	35	Anaerobic fermentation, bacteria, batch, biohydrogen production, biological hydrogen production, bioreactor, clostridium, conversion, culture, cultures, degradation, digestion, feasibility, fermentation, generation, glucose, hydrogen production, inhibition, kinetics, microflora, molasses, optimization, performance, pH, reactor, response surface methodology, sludge, starch, substrate, substrate concentration, sucrose, temperature, waste, water, and xylose
#2	27	Activated sludge, anaerobic co-digestion, anaerobic digestion, anaerobic digestion, bioenergy, biogas, biogas production, cheese whey, co-digestion, dark fermentation, fermentative hydrogen-production, food waste, hydraulic retention time, hydrogen, hydrogen production, methane, methane production, microalgae, microbial community, municipal solid waste, oil mill effluent, organic fraction, organic loading rate, sewage sludge, volatile fatty acids, volatile fatty acids, and wastewater treatment
#3	20	Acetate, biohydrogen, clostridium butyricum, crude glycerol, dark, dark fermentation, enterobacter aerogenes, escherichia coli, gas production, growth, h-2 production, metabolism, mixed culture, photofermentation, photoproduction, photosynthetic bacteria, rhodobacter sphaeroides, and wastewater
#4	16	Acid, biohydrogen production, biofuels, biomass, cellulose, corn stover, energy, enzymatic hydrolysis, ethanol, ethanol production, hydrolysis, lignocellulosic biomass, mixed cultures, pretreatment, rice straw, and wheat straw
#5	2	Enhancement and nanoparticles

4. Overview of Hydrogen Produced by Fermentation

Hydrogen production is carried out by anaerobic bacteria [90] that decompose organic matter [91,92], generating molecular hydrogen (H_2) as one of the by-products [93]. This process, which does not require oxygen, allows the collection of hydrogen, which is then compressed, purified, and stored for future use [94–96].

The efficiency of hydrogen production by fermentation depends on several factors, including proper selection of microorganisms, optimization of fermentation conditions in terms of temperature and pH, and appropriate substrate selection [97–100]. In contrast to conventional methods, which often involve energy-intensive processes and significant carbon emissions, hydrogen fermentation is a promising alternative with lower environmental impact [99] and geographical flexibility. Factors such as geographical location or availability of specific resources do not become limiting factors compared to other sources (e.g., solar and wind), as fermentation offers a higher degree of adaptability and can be implemented in different regions [101]. This contributes to the decentralization of energy production and provides a circular approach by reusing organic waste and transforming it into a valuable renewable and clean energy source.

Despite this great potential, we must overcome several technological and economic challenges to optimize the efficiency of hydrogen production from biological processes [102]. Continued research and innovative investments are essential to improve the efficiency of the microorganisms involved, develop more scalable processes, and reduce the associated costs.

4.1. Main Biomasses Used

In the production of hydrogen by fermentation, various biomasses can be used as a substrate for the microorganisms that carry out the fermentation process. The most commonly used biomasses include:

I. Agricultural waste

Agricultural materials, such as cereal straw, sugar cane bagasse, and rice husks, are widely used in hydrogen production. They have an advantage over competitors because they contain a lot of cellulose, which microorganisms can break down and thereby release sugars that can be fermented [103]. In addition, the abundant availability of these wastes and their potential for anaerobic fermentation [104] contribute to their attractiveness.

However, these biomasses pose significant challenges. Their different compositions require adaptations in the biological processes [105,106], making continuous research essential to optimize and adjust specific parameters [107] because of the great diversity of these residues. In addition, the logistical costs associated with transporting these materials to production centers represent a critical consideration to be weighed when using these biomasses for hydrogen production [104].

II. Forest residues

Wood waste, bark, and other forest debris make up this biomass category, which is a promising source for producing hydrogen [108]. These materials contain cellulose and hemicellulose in their composition, substances that can be converted into sugars and subsequently fermented [109,110]. They are considered important players in the diversification of biomass sources to produce H_2. However, some crucial aspects must be considered for the effective use of these materials, such as the analysis of the environmental impacts resulting from the process of collecting these wastes, in order to ensure balance and sustainability [111]. Implementing coherent strategies is crucial to overcome waste-handling difficulties and optimize production [112,113].

III. Food Waste

Using fruit peels, vegetables, and food processing wastes in hydrogen production represents a sustainable way to recycle these materials [114]. These residues, rich in fermentable carbohydrates, are considered favorable substrates used to produce H_2. However, this source requires attention because of the diversity of these wastes, which require specific methodological approaches for each type [115,116]. In addition, rigorous analyses and controls must be carried out to detect the presence of contaminating chemicals in these materials and to take the necessary preventive measures to mitigate the emission of pollutants and odors associated with the processing of these wastes [117,118].

IV. Agro-industrial effluents

Waste from the agri-food industry, such as vinasse and cheese whey, can serve as useful materials to reduce waste [29]. These sources are characterized by their fermentation potential, which makes them relevant for the diversification of biomass sources used for hydrogen production [29].

However, there are some challenges associated with this source, including the need for prior treatment to remove contaminants before hydrogen production can begin [119–123]. In addition, the costs associated with the treatment of these effluents and the management practices implemented to avoid negative impacts on the local ecosystem and neighborhood are aspects to be considered [124,125].

V. Herbaceous Biomass and Microalgae

Herbaceous plants (e.g., grasses and microalgae) have emerged as promising biomass sources for hydrogen production [126–129]. These plant sources are rich in organic compounds that can be fermented by microorganisms and are characterized by their ability to be cultivated in different regions [129,130], thus offering geographical flexibility. This fermentation potential, combined with geographic adaptability, makes them attractive options for hydrogen production.

Despite the benefits, some initial challenges need to be overcome. The specific implementation for the cultivation and harvesting of microalgae requires initial investment [131,132] and is an issue to be considered.

VI. Urban Organic Waste

Organic waste from urban solid waste, such as food waste, is a valuable source of hydrogen production [133]. Besides contributing to the production of clean energy, this waste plays a crucial role in reducing the amount of solid waste in urban centers. This reuse not only opens space for the creation of production centers in urban areas but also contributes to reducing the logistical costs associated with transporting waste [134], which is considered a challenge, as we have discussed in previous sources.

However, to ensure the efficiency of this process, rigorous selection processes to control contamination and to perform prior treatments on organic wastes must be implemented [135–137]. In addition, urban restrictions and regulations that may affect both the collection and use of these wastes in hydrogen production must be considered [135,137].

4.2. Fermentative Processes

Generating hydrogen through biological means is seen as one of the most promising approaches for the future. Despite the absence of industrial facilities specialized in biological hydrogen production, it is essential to highlight the significant growth in research in this field [138].

The production of hydrogen by dark fermentation using biological systems has attracted great interest, mainly due to its higher efficiency compared to other biological processes [29]. The fermentative process also allows using different types of waste as substrates, such as lignocellulosic materials, glycerol, and food and dairy waste [139]. The ability to work in the absence of light makes this method advantageous, allowing the use of simpler reactors and energy savings.

Dark fermentation is described as any process in which sugars are broken down. Thus, in the production of hydrogen by facultative fermentative bacteria, they will oxidize a type of substrate rich in organic matter to simpler compounds, such as volatile organic acids, alcoholic acids, methane, carbon dioxide, and hydrogen [140,141].

In photofermentation, photosynthetic bacteria convert organic acids or biomass to hydrogen in the presence of light and under anaerobic conditions [140,142]. Photofermentation is a biological process in which organic matter is converted to simpler compounds using light as an energy source. This occurs primarily in photosynthetic organisms, such as photosynthetic bacteria and certain algae. Photofermentation differs from classical photosynthesis in that it does not involve the net production of oxygen [141].

When fermentative bacteria digest a substrate, they can only break it down into H_2 and organic acids, whereas photofermentative bacteria use light energy to break down all organic compounds and produce even more H_2. In addition to a large amount of energy, photosynthetic bacteria also require the activity of nitrogenase in their fermentation process [143].

Hydrogen production by photofermentation depends on parameters such as the activity of nitrogenase and hydrogenase enzymes, the proportion of carbon and nitrogen in the production media, the age of the PNS bacterial inoculum, the source and intensity of light applied, pH, and temperature, among other factors that affect production efficiency and yield [142].

Although industrial effluents rich in organic compounds have been extensively studied as substrates for hydrogen production, there is a growing interest in developing research on the interaction between dark fermentation and photofermentation processes [144].

Dark-phase fermentation of organic residues produces not only hydrogen and carbon dioxide but also intermediates such as organic acids. In the subsequent photofermentation step, these acids can be converted to hydrogen by photosynthetic bacteria under anaerobic conditions and with a high C/N ratio in the presence of light [141,144].

The hybrid system offers complementarity in the hydrogen production stages, allowing its integration in one or two stages. Most studies consider the approach of dividing the process into two stages, allowing the application of optimal operating conditions for each system. In many cases, the transition between the stages requires a pretreatment to remove the dark-phase biomass and to dilute the substrate. However, segmenting the stages implies the need to maintain two bioreactors, resulting in increased costs [145].

Although the co-fermentation of fermentative and photofermentative bacteria in the same bioreactor is less explored in the literature [145], this integration has the potential to optimize the process and reduce costs. With this method, the need for pretreatment for stage change and frequent pH adjustments would be eliminated, since the acids generated could be consumed simultaneously by photofermentative bacteria. Furthermore, a decrease in fermentation time and an increase in hydrogen yield are expected.

4.3. Influential Factors in the Production Process

As with most biological processes, fermentation requires attention to process variables (e.g., substrate, temperature, pH, and nutritional variables) to optimize production yield and minimize costs. Proper selection of the microorganisms to be used is also critical to ensure efficient results [143,146].

There is a wide variety of feedstocks that can be used in the anaerobic hydrogen production process, including food waste, municipal solid waste, industrial wastewater, agricultural and agro-industrial waste, glycerin, etc. These feedstocks must contain fermentable sugars such as sucrose, glucose, lactose, and xylose to ensure high yields, as these sugars are easily broken down during the process [73,147].

One of the key factors directly affecting hydrogen production by anaerobic fermentation is temperature. Overall, these processes are carried out at temperatures close to ambient, i.e., they are performed by mesophilic microorganisms (25 °C to 40 °C). The authors of [141,148] investigated the effect of different temperatures, ranging from 20 °C to 55 °C, on H_2 production through mixed batch cultures. The experimental results, using glucose as a substrate, showed that the substrate degradation efficiency and H_2 production potential increased with increasing temperature from 20 °C to 40 °C. However, a decrease in these parameters was observed with an increase in temperature from 40 °C to 55 °C.

pH plays a significant role in the process of producing H_2 by fermentation. To determine the ideal pH for H_2 production, two different types of experiments have been conducted. The first consists of adjusting different initial pH values, while the second consists of controlling and maintaining a constant pH throughout the fermentation process [141]. Studies indicate that the ideal pH for H_2 production is in the range of 5 to 7, with a pH around 5.5 being associated with the best yields in H_2 production. Maintaining the pH within this range favors the activity of the enzymes involved in the H_2 production process while also allowing for the inhibition of H_2-consuming microorganisms present in the fermentation medium [149–152].

The hydrogen production process by anaerobic fermentation can be carried out using mixed microbial cultures derived from natural environments or pure cultures selected from bacteria specialized in the production of H_2 [29].

Several bacterial strains have been used to produce H2 from various substrates. The use of pure cultures offers advantages in terms of substrate selectivity, more precise manipulation of metabolism by adjusting growth conditions, obtaining high H2 yields, and reducing unwanted by-products. However, pure cultures are more susceptible to contamination, require aseptic conditions in most cases, and increase the overall cost of the process [153]. The use of mixed cultures in large-scale processes is considered advantageous due to the ease of control and operation of the process, especially when non-sterile media are used, which contributes to reducing the overall cost [153]. This is even more evident when mixed cultures are derived from natural sources (e.g., soil, sewage sludge, animal excreta, or waste) [154,155].

Most studies related to H_2 production by anaerobic fermentation have been conducted in batch reactors. The advantage of these reactors is their simplicity, flexibility, and ease of operation. For large-scale operations, continuous production processes are preferred due to waste storage and economic factors [148].

4.4. Applications of Fermentative Biohydrogen

4.4.1. Industrial Applications

In the last 10 years, many research centers worldwide have turned their attention to the development of alternative renewable/green energy sources [156–158]. Due to the scarcity of energy resources and the rise in prices of foods such as corn and sugar [135,156,158–160], researchers are looking for new renewable energy sources [156,159]. One approach is to convert agricultural waste into hydrogen through sustainable methods such as fermentation. This has led to adopting green hydrogen as an alternative energy source in industries such as steel and agriculture [157,161–164].

The main advantage of green hydrogen perceived by these industries is its low calorific value (120 MJ/Kg), making it a more efficient fuel than fossil fuels based on non-renewable hydrocarbons [156,158]. The textile and food industries therefore generate large amounts of industrial waste, commonly known as industrial effluents. They are generally rich in harmful products but also contain organic matter that can be used as a source for green hydrogen production.

According to Runjavec (2023), many industries have used these effluents as raw materials for biohydrogen production as a promising approach to treating industrial wastewater and generating clean energy [70]. Based on research by Kane and Gil 2022, there is a prospect of massive implementation of wastewater and industrial waste reuse for biohydrogen production in the food industry. The study also reports that more than 500 million tons of green hydrogen will be produced by 2050. These researchers report that several industries in Europe, particularly in Germany, are directing their research toward optimizing green hydrogen production [70,157].

The construction materials industry is also racing to efficiently utilize green hydrogen as an energy source to optimize its manufacturing processes. According to Muhsen et al. (2023), this will be one of the most polluting industries by 2024, thereby generating more CO_2 [163]. Researchers emphasize that in the Middle East, Jordan stands out as one of the major cement producers, as its key industries have an ongoing plan for a total production of around 11.2 million tons/year, well above the local demand of approximately 3.1 to 4.1 million tons/year [70,157,163].

The oil refining sector is the third-largest stationary source of global emissions, responsible for 40% of oil and gas lifecycle emissions and 6% of total global industrial emissions, according to Muhsen et al. (2023) [163]. The author also reports that due to insufficient oil reserves, many specialized centers have turned their attention to green hydrogen, which is one of the most promising alternatives for this energy source. Based on the study of the Jordan Petroleum Refinery Company (JPRC), the demand for pure hydrogen reaches 700 kg/h (5.88 million kg/year), which is consumed in hydrotreating and hydrocracking processes [70,135,159,163]. This order of magnitude is justified by the scarcity of non-renewable energy resources and the high cost of other sources. The JPRC is considering changing its operations to rely exclusively on green hydrogen when biohydrogen production is optimized and the price becomes more competitive [135,160,163].

The agricultural industry also stands out in investing its financial resources in the development of new ammonia production methods, primarily using green hydrogen to minimize the impacts of current ammonia production [70,157,162]. Several researchers, including Gaetano and Nicita (2023), emphasize that hydrogen produced from biomass is CO_2-neutral and can be used directly to produce high-value fertilizers and pesticides [162]. The ability to convert industrial waste into something of value is part of the circular economy concept.

4.4.2. Transport Applications

The technological evolution in producing renewable energy for the sustainable production process of biofuels can be one of the most exciting alternatives to satisfy the planet's energy needs as much as possible [165–169]. The versatility of biohydrogen allows it to be used in a variety of market sectors. Automobile manufacturers are aware of the energy insufficiency of petroleum derivatives and are therefore betting on the development of new fuels [165,166,170–172]. Thus, using biohydrogen is a promising option that has already been tested in some countries. Puricelli et al. (2021) [173] reported that the use of biohydrogen in transport vehicles resulted in a 70% reduction in emissions compared to gasoline and diesel fuels. Furthermore, the ability to convert any biodegradable waste into H_2 is its main advantage [173]. The adoption of sustainably produced and renewable fuels to replace fossil fuels in the transportation sector will significantly improve combustion efficiency, reduce toxic gas emissions that contribute to the intensification of the greenhouse effect, and also contribute to lower prices, efficiency, and ecologically correct goals in the transportation system, which invests heavily in this improvement [165–167,171,174].

Hydrogen is a fuel with zero carbon production and can be used to power internal combustion engines and vehicles [157,171]. On the other hand, a factor that is recurrently discussed with alternatives to fossil fuels is the autonomy of cars powered by hydrogen or electricity. For hydrogen vehicles, an important aspect of autonomy is the amount of H_2 that can be stored inside the vehicle [157,158,169–173].

In conclusion, research into the application of biohydrogen is still in its infancy but is promising and appears to be a sustainable alternative for replacing cars powered by the combustion of fossil fuels with hydrogen cars that do not emit toxic gases.

4.4.3. Energy Sector

Biohydrogen is one of the few efficient ways to decarbonize sectors that have no sustainable alternatives. The energy sector is one of the largest emitters of carbon to the atmosphere [165,175,176]. Uniquely, biofuels are increasingly being used in the transportation, electricity, and thermal energy production sectors. Biohydrogen produced from industrial waste can be optimized through government subsidies to reduce the price of fuel and meet the needs of industry [165,172,175,176].

According to Dawood and Shafiullah (2020), the hydrogen economy has been extensively studied through analysis and directing capital toward its development [177]. Case studies and some reports have been instrumental in understanding investors in the energy sector who see biohydrogen as a viable alternative to resource scarcity. In particular, peer-reviewed research is gaining renown for meaningfully discussing the environmental, economic, and other factors that influence the market. Many international bodies have invested time and resources in developing this promising alternative [172,175,177].

In addition, some industries are already experimenting with the combination of electricity and biohydrogen as energy sources for their daily use. Srivastava et al. (2020) [172] report that a total of 112,642 workers are employed in bioenergy electricity generation and biofuel sub-technologies. They also report that South Korean industries are analyzing the transition from fossil fuel-based electricity generation to biohydrogen and other sustainable sources [165,172,175].

To this end, Srivastava et al. (2020) [172] report that wood waste has been used to produce biohydrogen, which has been used to generate electrical power for paper and other industries. The use of co-firing systems has helped to reduce greenhouse gas emissions with gases such as SO_2 and SO_3. In summary, biohydrogen has become one of the most important energy sources for various industrial sectors [172].

4.5. Recent Technological Advances in Hydrogen Production from Biomass

The global landscape has witnessed significant progress in the development of novel techniques and technological processes for the production of hydrogen from biomass [178]. The exploration of biodegradable materials as an alternative to conventional methods has gained momentum due to the abundant availability of biomass and the high efficiency of enzymes in conjunction with other processes [179]. This synergy has paved the way for a more environmentally friendly route to hydrogen production.

Primary sources of biomass used in green hydrogen production include agro-industrial residues directly obtained from sugar cane plantations, cereals, and various crops [180]. In addition, plantations associated with green fuel or vegetable oil production, such as bamboo and palm trees, serve as direct biomass sources [181]. Waste from the wood industry, such as sawdust, and even domestic organic residues can be used for hydrogen production through fermentation [182].

Investment in and development of these emerging technologies is essential to optimize the fermentation of available biomass [183]. Fermentation bioreactors offer several advantages, including the use of biomass that might otherwise be contaminating or polluting, thereby contributing to waste reduction and neutralization. Non-conventional bioreactor methods, particularly dark fermentation, offer the advantage of not requiring the presence of light, thereby streamlining the overall process [184].

Dark fermentation has emerged as a promising strategy, either alone or in combination with other processes, to advance hydrogen production [185]. Kumar et al. (2018) [186] demonstrated the use of dark fermentation to optimize biomass utilization by integrating it with advanced electrochemical and oxidative processes. Similarly, Nguyen et al. (2020) [187] applied dark fermentation to algal biomass and combined it with a microbial electrolysis cell to improve yield and overall efficiency.

In evaluating recent advances, Kirtay et al. (2011) [188] highlighted the advantages and disadvantages associated with different types of fermentation. Photofermentation, while versatile in utilizing various waste materials, is limited by the energy requirements of light [189]. Dark fermentation, on the other hand, is promising, especially when combined with other processes [190]. In particular, it operates effectively without the need for artificial or natural light, allowing for the utilization of a wide variety of biomasses [191].

Advantages of dark fermentation include the absence of oxygen control requirements due to the anaerobic nature of the microorganisms involved. This technique also produces valuable by-products, such as acetic and lactic acids, which can be isolated and utilized through additional techniques [130]. Some disadvantages, such as production time and residue formation, can be mitigated by combining dark fermentation with other techniques. For example, hybrid reactors integrating photofermentation with dark fermentation have shown a potential to significantly improve the hydrogen production process [145].

4.6. Challenges to Overcome and Gaps

The challenges of biohydrogen production, such as low yields and high production costs, are significant hurdles [179]. Research indicates a promising trend of advancements aimed at improving the efficiency of biohydrogen production by using nanomaterials to support microbial growth and development [192,193]. Examples include carbon nanoparticles, metal/metal oxides, and hydroxyapatite [192]. The unique photoelectrochemical properties of nanomaterials show remarkable potential for enhancing biohydrogen production [194]. Nanotechnology can play a critical role in various stages of dark fermentation for biohydrogen production [195]. In dark fermentation, the use of certain metal nanoparticles has shown a significant increase in biohydrogen production (5.4–230%) [194]. In addition, microbial enzymes (e.g., cellulases, laccases, and xylanases) may be immobilized on nanomaterials, allowing repeated use in multiple cycles for the degradation of complex substrates during biological pretreatment [195].

The major barriers to fermentation are the limitations imposed by the metabolic pathways involved [182]. Genetic modification has led to the development of mutant strains capable of producing biohydrogen more efficiently [65,196–198]. Genetic engineering approaches can reconfigure metabolic pathways and networks to enhance hydrogen production [196]. Metabolic engineering can create reliable biotechnological host organisms capable of producing pure hydrogen from organic substrates [197]. The carbon source used in fermentation controls hydrogen production, and studies with *E. coli* have shown maximum yields ranging from 1.95 to 17 times the original strain [65]. Modified microorganisms can process previously inaccessible feedstocks, opening opportunities for new markets where specific types of biomass are available [198].

Despite the promising potential at the laboratory level, practical challenges hinder the realization of biohydrogen production methods. The construction of bioreactors and other hydrogen production systems requires significant capital investment [192]. Future improvements should focus on developing local, small-scale production facilities, as they are better suited for small-scale operations. The high production costs of current systems make them less competitive than thermochemical conversion processes. Optimization of bioreactors and the development of new bacterial strains are essential steps [102]. Further studies are needed to bridge the gap between technical–economic viability and realistic, practical applications in commercial biohydrogen production [192].

Another critical aspect of sustainable biohydrogen production is its enrichment and purification. The purity of hydrogen required for specific applications should be around 99.99% [199]. Biohydrogen faces challenges related to high production costs, storage limitations, transportation costs, and distribution. Storage is particularly challenging due to the very low density of biohydrogen (0.09 kg/m^3) at ambient pressure and temperature [180]. Current storage methods include physical storage (compressed gas) and material-based storage, where biohydrogen is reversibly stored by adsorption or absorption [171].

5. Future Perspectives

Fermentative hydrogen production is an emerging field with the potential to revolutionize the energy sector [200,201]. However, due to the current challenges of low efficiency and high cost in biohydrogen production, it still does not meet the requirements for large-scale industrial production [194]. To guide this technology in a scientifically sound manner, several future perspectives are essential. While various substrates have been explored for hydrogen production by fermentation, the availability of sufficient and suitable substrates is crucial for optimizing the process [135]. A comprehensive understanding of the microbiology involved in fermentative processes is essential to analyze microbial communities, their diversity, and their impact on hydrogen production [202,203]. Optimization of these processes is essential to improve energy efficiency.

The design of dark fermentation bioreactors plays a critical role in biohydrogen production [204]. Well-designed bioreactors can provide optimal conditions for microbial activities, thereby maximizing hydrogen production [205,206]. Technologies such as membrane bioreactors or fixed bed reactors can be instrumental in achieving this goal [207,208]. In addition, the integration of anaerobic fermentation processes with other technologies, such as photocatalysis and electrocatalysis, has significant potential to increase the efficiency of hydrogen production, making it more economically and environmentally attractive [194,209]. Using reinforcement learning in machine learning, the bioreactor can be optimized and operated at its full potential [69].

The development of this research area will be driven by favorable energy policies and a growing emphasis on sustainability. At the same time, there is an increasing need to develop suitable storage and transport solutions for hydrogen to establish it as a versatile energy source. Hydrogen production from organic waste fits seamlessly into the principles of the circular economy and will become even more relevant as society seeks sustainable approaches to resource use [208,209].

6. Overview

The scenario of publications on hydrogen production through biological fermentation has shown significant evolution. This is reflected by the substantial increase in the number of articles published, the expansion of journals that cover the topic, and the growing impact of these publications, expressed by the volume of citations. This field of study began with a modest number of publications in the initial years of research but has seen impressive growth, with a peak of 371 articles in 2022 and 235 articles by the last database update in 2023. These results draw attention to the increasing importance attributed to research in the area of fermentative hydrogen [156,171,210]. Furthermore, the number of journals publishing work related to this topic has reached 541, accumulating an impressive total of 181,769 citations. This diversification in publications and the collaboration between different research groups highlight the multidisciplinary nature of the field and a continuous effort for innovation, strategies, and advances in knowledge about hydrogen production via fermentative processes [156,210,211]. This quantitative increase also signals an increase in interest in and study of the topic, attracting the attention of the scientific and industrial community to anaerobic fermentative processes [23,212,213].

Collaboration between institutions can significantly impact the progress of research in the area of fermentation for hydrogen production, as shown by the bibliometric analysis that highlights, among other aspects, collaboration agreements between different institutions and significant partnerships [28,52,54,58]. These collaborative networks are valuable for accumulating knowledge and resources, bringing a diversity of approaches to the field, where different institutions can contribute with specific focuses, from microbiology to energy policies, enriching research by addressing hydrogen production from various perspectives [214–217]. A bibliometric review, evaluating many articles, suggests that contributions from multiple institutions can broaden the database available for analysis, providing a more comprehensive view of the current state and trends in research [52,54,55]. Thus, identifying prominent countries, institutions, and authors makes it easier to visualize international collaboration, mapping the closest relationships that allow interaction between researchers from different parts of the world to accelerate the dissemination of knowledge and the implementation of discoveries globally [28,218–220]. Furthermore, collaboration also facilitates the transfer of technology between institutions, accelerating the practical application of scientific discoveries, especially when there is adequate interaction between academic and industrial researchers, and can lead to an improvement in the quality of studies by allowing different institutions to approach gaps in knowledge [42,55,218,221,222]. Such interaction promotes technological innovation, with the combination of skills and resources leading to the development of new techniques, methodologies, or technologies to drive the advancement of hydrogen production [182,223,224].

In summary, we see that different substrates, such as lignocellulosic biomass, glycerol, sludge, and wastewater, can be used in the production of fermentative hydrogen, and this reflects efforts towards more sustainable and economically attractive raw materials, taking advantage of industrial waste and by-products [189,225–227]. Lignocellulosic biomass is valued for its abundance and sustainability, transforming waste into energy and minimizing dependence on fossil fuels [66,102,212]. However, it faces challenges such as the need for pretreatments to obtain sugars and the complexity of conversion processes [212,228]. Glycerol, derived from biodiesel production, stands out for its availability and reduced cost, offering an opportunity to value an industrial by-product. However, glycerol's purity and catalysts' efficiency present challenges [61,226,228]. In turn, using sludge and wastewater treated by anaerobic digestion, though it solves waste management problems and generates renewable energy, faces the challenges of optimizing biogas production and infrastructure costs [46,70,79,229].

Furthermore, several microbial species transform organic substrates in fermentative processes to produce hydrogen [65,76,187,230]. Such processes can occur in the absence or presence of light and are known as dark fermentation and photofermentation, respectively [44,225,231]. In dark fermentation, anaerobic microorganisms, such as species of the genus *Clostridium* (e.g., *Clostridium butyricum*, *Clostridium cellolosi,* and *Clostridium acetobutylicum*), play a fundamental role in converting sugars and other organic compounds into hydrogen, in addition to generating organic acids (e.g., lactic acid, acetic acid, and butyric acid) and alcohols [185,232]. Another essential genus is *Enterobacter*, with species such as *Enterobacter aerogenes* also contributing to hydrogen production under anaerobic conditions [63,232,233]. Photofermentation depends on solar energy to generate hydrogen, with phototrophic bacteria such as *Rhodobacter sphaeroides* and *Rhodopseudomonas palustris* leading this process [234–236]. These microorganisms work by capturing solar energy, allowing the transformation of organic substrates into hydrogen [232,235]. Within the fermentation environment, microbial interactions are complex and directly influence hydrogen production efficiency [44,153,185,231]. Competition for substrates between different microorganisms can affect the distribution of resources. At the same time, syntrophic associations, in which the metabolic products of one species serve as substrates for another, can optimize the hydrogen production process [65,83,119,182,205].

Fermentative hydrogen production is a sustainable alternative, with advantages such as using organic waste and low greenhouse gas emissions, contributing to waste management and the transition to a low-carbon economy [44,199,237]. However, it faces significant challenges, including the need for large amounts of biomass to compete with food production, the impact on ecosystems through land conversion, and increased water consumption [119,153,185,231]. Furthermore, the efficiency and competitiveness of the process, the management of by-products, and the impact on biodiversity are relevant concerns [156,185,187,205]. An integrated approach and sustainable practices at all stages are essential to maximize environmental benefits and effectively contribute to more sustainable energy sources and climate change mitigation [44,193,203,237].

Innovations and collaborations are required on several fronts to accelerate development in this field of research to achieve a low-carbon economy. Improvements in engineering technologies are essential to increase efficiency and reduce costs, while integration with renewable energies such as solar and wind promotes more sustainable systems [63,235]. The efficient use of renewable raw materials (e.g., agricultural and forestry residues) and interdisciplinary collaboration between research, industry, and government are fundamental to overcoming challenges [44,185,238]. Incentive policies, investments in infrastructure, and specialized education are essential to support the energy transition [239,240]. Public–private collaboration and the internationalization of research are vital to promoting advances [63,191,241,242]. Thus, exploring these opportunities can accelerate innovation in hydrogen production through fermentation and contribute to a more sustainable economy [23,242,243].

7. Conclusions

Anaerobic digestion is a sustainable strategy for environmentally sound waste treatment. In this process, microorganisms, typically fermentative bacteria, break down complex organic compounds such as carbohydrates, proteins, and lipids into simpler volatile organic acids, producing hydrogen as a by-product. A bibliometric analysis revealed a significant increase in publications on this topic, with journals such as the International Journal of Hydrogen Energy and Bioresource Technology leading in terms of numbers of articles. China has emerged as a pioneer in the production of articles, surpassing other countries such as India and the USA. The Harbin Institute of Technology stood out as the institution with the most publications, and Gopalakrishnan Kumar was the most cited author. The publication areas showed a considerable diversity of applications and a multidisciplinary approach, with many articles overlapping in different areas of interest. The keyword network analysis identified five thematic groups, emphasizing biohydrogen production, the diversity of substrates such as lignocellulosic biomass, glycerol, sludge and wastewater treatment, and fermentation process optimization. Accurate understanding and control of the microbial community is crucial to optimize hydrogen production and ensure an efficient and stable process and represents one of the major future challenges in this area of investigation.

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