Review

A Bibliometric Study of Scientific Publications regarding Hemicellulose Valorization during the 2000–2016 Period: Identification of Alternatives and Hot Topics

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Abstract: A bibliometric analysis of the Scopus database was carried out to identify the research trends related to hemicellulose valorization from 2000 to 2016. The results from the analysis revealed an increasing number of annual publications, a high degree of transdisciplinary collaboration and prolific contributions by European researchers on this topic. The importance of a holistic approach to consider the simultaneous valorization of the three main components of lignocellulosic biomass (cellulose, hemicellulose and lignin) must be highlighted. Optimal pretreatment processes are critical for the correct fractionation of the biomass and the subsequent valorization. On the one hand, biological conversion of sugars derived from hemicellulose can be employed for the production of biofuel (ethanol) or chemicals such as 2,3-butadiene, xylitol and lactic acid. On the other hand, the chemical transformation of these sugars produces furfural, 5-hydroxyfurfural and levulinic acid, which must be considered very important starting blocks for the synthesis of organic derivatives.

Keywords: hemicellulose; valorization; biomass; bibliometric analysis

1. Introduction

The 20th century has been characterized by economics based on fossil fuels (coal, oil and natural gas). The oil refinery, the most representative example of this system, has provided multiple relevant products such as fuels, fine chemicals, pharmaceuticals, plastics, detergents, synthetic fibers, pesticides, fertilizers, lubricants or solvents [1]. However, these fossil resources are not sustainable and their availability in the long term is not assured. Moreover, the variability of the prices of fossil resources has great influence on global and domestic economic activities, employment and prices [2]. The sustainable economic growth that must be promoted in the 21st century requires alternative safe and sustainable resources for reliable industrial production. This transition from a fossil-based to a sustainable economy can be based on biomass, with bioenergy, biofuels and bio-based chemicals as its main pillars [3].

While for energy production a variety of alternative sustainable sources (mainly based on the use of wind, sun or water bodies) has been identified outside bioenergy, the chemical industry is going to be highly dependent on biomass, and more particularly on lignocellulosic biomass. The integral utilization of vegetal biomass instead of oil in the production of chemicals must contribute to the improvement of environmental quality, supply security, and rural economic development [4]. This type of biomass has been identified as a candidate to produce bio-based chemicals, since it offers partially oxygenated functional groups and aromatic structures that could yield platform chemicals [5]. The fuel generation sector can take advantage of the utilization of biomass as raw material. The current high atmospheric concentrations of carbon dioxide must be considered as a consequence of the anthropogenic emissions due to fossil fuels. Transportation fuels comprise about 13% of global emissions of anthropogenic

carbon dioxide, but this percentage is above 25% in some developed countries [6]. Biofuels derived from biomass, either neat or as a blending component, serve as a renewable alternative to fossil fuels that can reduce net carbon dioxide emissions (and other greenhouse gases). Renewable biofuels derived from biomass generally involve contemporary carbon fixation. Moreover, the use of biofuels promotes the security of supply to the regions lacking oil or other fossil resources and represents an opportunity to improve sustainable economic prospects in developing countries from Africa, Latin America and Asia [7–11].

Some characteristics of lignocellulosic biomass that have great influence on its applicability as raw material must be highlighted. On the one hand, lignocellulosic biomass is found in abundance worldwide. It is the most abundantly available material on the earth and must be considered the most promising renewable carbon source that can be converted into chemicals in solid, liquid, and gas forms [12]. To avoid competence with regular food crops, no arable land and alternative resources should be employed for the production of lignocellulosic biomass. Taking into account this consideration, the main available sources can be divided into three categories, namely agricultural wastes, forestry wastes and energy crops [13]. However, the use of this residual lignocellulosic biomass implies higher difficultly to extract valuable chemicals, since a series of physical and chemical treatments might be necessary to convert lignocellulosic biomass to the required products. On the other hand, the complex recalcitrant nature of lignocellulosic biomass prevents a simple direct treatment just by chemicals or microorganisms. This complex nature is due to the three main components of lignocellulosic biomass: cellulose, hemicellulose and lignin. Cellulose and hemicellulose are two carbohydrate polymers, which are tightly bound to lignin, an aromatic polymer. Depending on the biomass source, the relative content of the three types of polymers can vary [14]. Cellulose, as the major chemical component of the cell wall and making up about 50% of both softwoods and hardwoods, is the most abundant organic polymer. It is composed of linear chains of D-glucose linked by β-1,4-glycosidic bonds. Because of its chemical and physical properties derived from its strong tendency to form intra-chain and inter-molecular hydrogen bonds [15], the resulting strength and insolubility in water and most organic solvents allow cellulose to stabilize the overall structure of plants. Hemicellulose ranks second after cellulose in abundance in plant cell walls, representing 25–35% of the total weight. Hemicellulose is a group of heterogeneous polymers of pentoses (xylose and arabinose), hexoses (mannose, glucose and galactose) and sugar acids (uronic acids, such as D-glucuronic and D-galactouronic acids). Hemicellulose has branches with short lateral chains consisting of different sugars [16]. Lignin is the third macromolecular component of wood and represents 20–30% of its dry weight. Lignin can be described as a random three-dimensional network polymer comprised of three main types of monolignols (oxygenated phenylpropane units): coniferyl alcohol, sinapyl alcohol and paracoumaryl alcohol [17].

The traditional industrial sector with more experience in the chemical transformation of lignocellulosic biomass is the pulp and paper industry. However, its main target has been the production of high-quality cellulose as raw material for paper and derived products. With this objective, the valorization of the other fractions (hemicellulose and lignin) has not been considered a primary concern. The recovery of energy has been the most common application of hemicellulose and lignin in the pulp and paper sector [18]. However, the recent attention these fractions deserve as green renewable sources for chemicals has deeply modified the point of view about the management of lignocellulosic biomass. This new scenario imposes the implementation of totally integrated biorefineries as the most sustainable model for the complete valorization of lignocellulosic biomass. A biorefinery is a facility that integrates the biomass conversion processes to produce bioenergy, biofuels and bio-based chemicals from biomass [3]. This biorefinery concept is totally analogous to petroleum refineries, which produce multiple fuels and chemicals from oil. However, biorefineries represent fully integrated systems of sustainable, environmentally and resource-friendly technologies for the holistic material and energetic utilization of biomass [19]. The defined holistic approach cannot consider discarding one main lignocellulosic component to promote the valorization of another: the

main components of biomass must be simultaneously valorized to achieve a sustainable scenario (Figure 1). Therefore, the effective utilization of lignocellulosic biomass, hitherto underutilized, must take into consideration the valorization of lignin and hemicellulose. The alternatives for hemicellulose valorization are gaining importance, since it is a very abundant and economical resource for the production of bio-based fuels and chemicals by thermo-chemical or biological conversion.
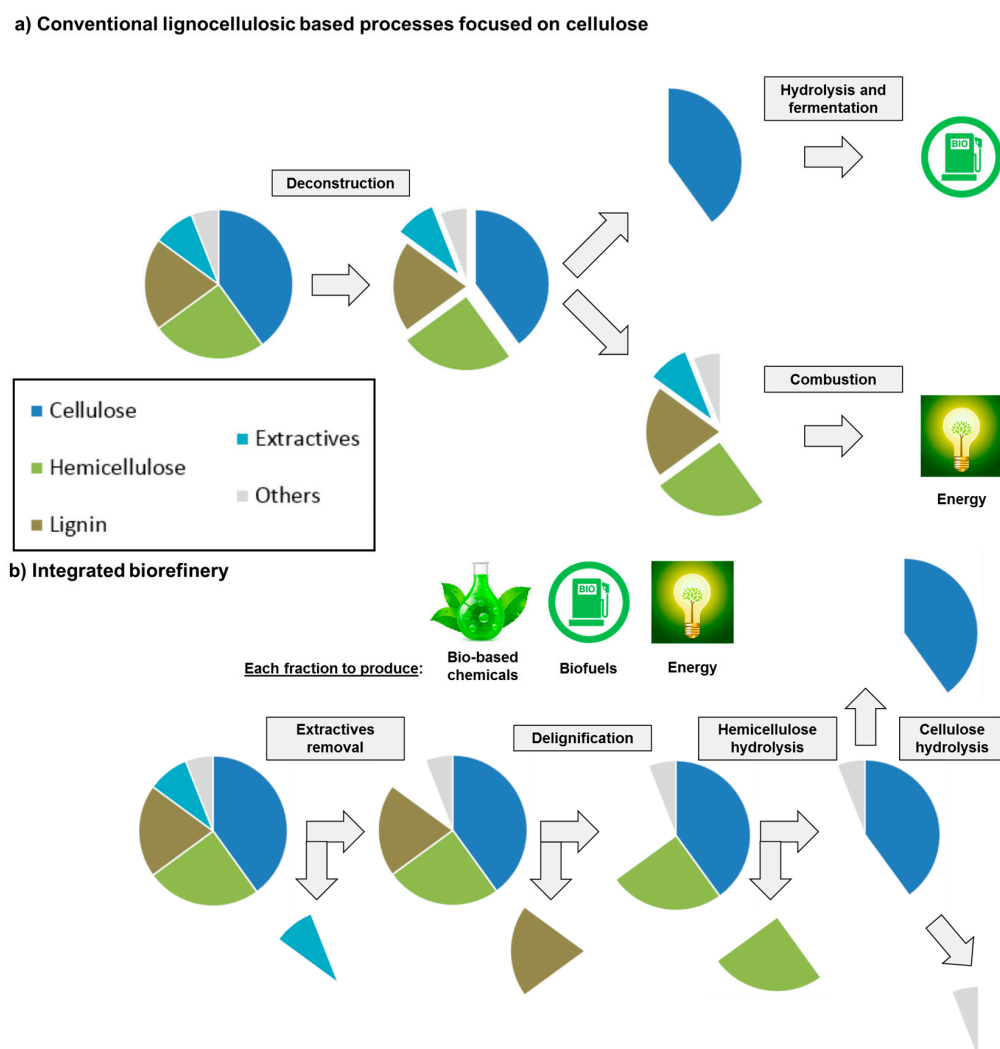

Figure 1. Schematic representation of the transition from (**a**) conventional lignocellulosic-based processes focused on cellulose to (**b**) integrated biorefineries.

Since the amount of published research documents about hemicellulose valorization which are available after a bibliographic search is huge (some review papers that considered the valorization of biomass represent great examples [20–24]), basic managing tools are needed to handle all this information. Bibliometrics is a useful tool to map the literature around a research field. Although most definitions of bibliometrics are too broad, it could be defined as the research methodology employed in library and information sciences that utilizes quantitative analysis and statistics methods to describe the distribution of patterns of publications according to some given categories such as topic, field, source, author or country [25,26]. The bibliometric methodology allows access to relevant information and knowledge about the status of scientific research activities in specific disciplines, which helps researchers to identify novel schemes among research [27]. Moreover, it is a well-recognized technique for conducting systematic analyses about the study of science as a knowledge-generating and

communication system and its interaction with technology [28]. These methods have been successfully applied to investigate research trends of specific fields recently, including multiple examples related to chemical and environmental engineering [29–69].

The main aim of this work was the bibliometric analysis of the literature available in the publications listed in Scopus from 2000 to 2016 related to the research on alternatives for the valorization of hemicellulose. The systematic evaluation of the papers found was useful to determine the quantitative characteristics of the research and provide an overview of trends in this topic, mainly regarding the most important valorization routes, which, to the best of my knowledge, has not been the subject of similar studies previously. Therefore, this paper was prepared to help researchers to understand the global panorama of the research on lignocellulosic biomass for valorization of hemicellulose and identify the most relevant research topics in this area. This study may give clues about the future evolution of the valorization of hemicellulose according to present research.

2. Data Sources and Methodology

The search of the published scientific literature was performed after the selection of the online version of Scopus as the database. This abstract and indexing database with full-text links, which was launched in 2004, is produced by Elsevier and claims to index over 21,500 active titles from more than 5000 international publishers, stating that it is the "largest abstract and citation database of peer-reviewed literature" [70]. The list of indexed titles is selected by an independent and expert advisory board that apply strict criteria based on user demand and market research. Scopus contains more than 38 million abstracts with references back to 1996 (84% of them include references) and more than 22 million records before that year (they go back as far as 1823). Titles from all geographical regions are covered: more than half of Scopus content originates from outside North America, representing various countries in Europe, Latin America and Asia-Pacific regions. Non-English titles are included as long as English abstracts can be provided with the papers. In fact, approximately 21% of titles in Scopus are published in languages other than English, adding up to 40 languages. Therefore, Scopus claims to offer the broadest, most integrated coverage of peer-reviewed literature across the sciences, technology, engineering and medicine (STEM), as well as social sciences and arts and humanities. To improve search recall, in addition to the keywords added by authors, extra index terms are manually included for most of the titles in the database, derived from thesauri that Elsevier owns or licenses.

The online search within Scopus was completed in August 2017 by the selection of "hemicellulose" and "valorization" as keywords in the Article Title, Abstract, Keywords field of the search-engine in order to obtain the complete bibliography with all the articles related to this topic published during the period from 2000 to 2016. Some tests were carried out to demonstrate that the use of spelling variants ("valorisation" instead of "valorization") and singular or plural forms ("hemicelluloses" instead of "hemicellulose") did not affect the number of documents identified by the search-engine. The total number of articles found was 109. This bibliometric analysis is based only on the Scopus database and only two keywords ("hemicellulose" and "valorization") were used as search terms to find the sample documents for the analysis. The results are different with other databases and other search keywords. Therefore, all the statistical results presented in this work should be interpreted in the context of these limitations.

The scientific documents found in the online search were analyzed in detail to provide a firm base for a better understanding of the research panorama, which could help to identify current and future strategies within this field. Therefore, the investigated aspects covered not only the quantitative description of the documents (annual outputs, leading countries and institutions, main journals, languages and Scopus subjects), but also the research trends identified after the analysis of the research papers.

3. Results and Discussion

3.1. Bibliometric Analysis of Research on the Hemicellulose Valorization (2000–2016)

3.1.1. Publication Year, Document Type and Language of Documents

The distribution of annual publications is shown in Figure 2. Firstly, the earliest document found applying the selected criteria was published in 2004, since no publications appeared during the 2000–2003 period. Besides, the production until 2009 was very limited: only 5 documents were found before that date. When the search criteria were modified to remove the time restriction, three pioneer papers published in the late 1980s and 1990s were found [71–73].

The graph in Figure 2 shows that the publication rate followed a quite irregular evolution. Although a general increasing trend can be clearly identified, this trend presented an evident irregular evolution. Until 2012, the production was not constant, but, after that year, the evolution can be represented by a linear increase. Despite the irregularities, the result of the linear fitting was satisfactory, with a R^2 value of 0.900. The assessed slope was 3.6 publications per year, a figure that gives an idea about the increase in the publication rate.
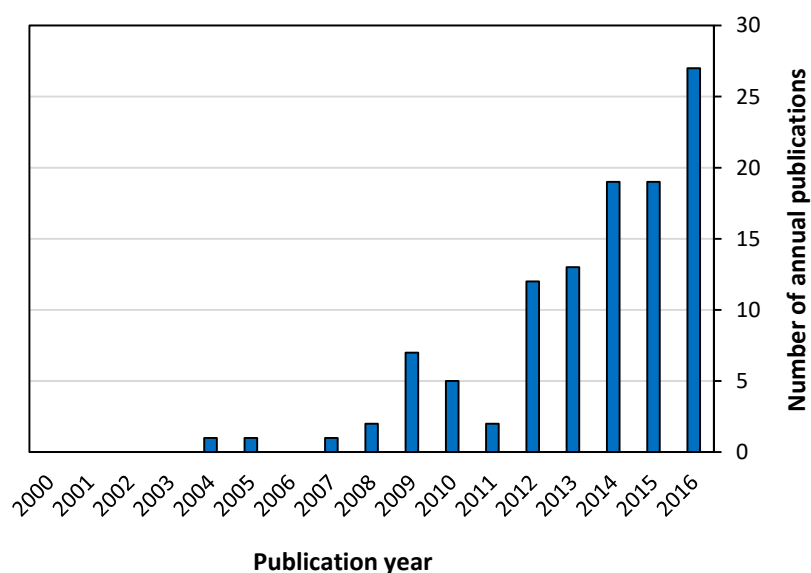

Figure 2. Annual publication output.

The distribution of document types was analyzed. Five different document types were found among the 109 publications from the defined time period. *Article* (80) was the most common document type comprising 73.4% of the publications, but also three *articles in press* were found, which can be added up to attain 76.1%. Articles were followed by *reviews*, with 12 documents comprising 11.0%. The rest of the categories included *book chapter* (7) and *conference paper* (7). The percentages obtained were in agreement with the figures that resulted from other bibliometric studies, which reported the clear prevalence of *articles* over other types of publications in chemical or environmental engineering topics [74,75]. However, in this case, the higher contribution of *reviews* and the lower contribution of *conference papers* when compared to the research trends on other topics in these fields should be mentioned [42].

English was undoubtedly the most used language in the documents found (96.3% of the publications were written in English). Only two other languages were found, but they can be considered anecdotal, since only three documents were written in French and another one in Spanish. Once more, this bibliometric analysis demonstrated that English is the principal language for scientific research, and more specifically in the engineering field [76,77].

3.1.2. Distribution of Output in Subject Categories and Journals

The distribution of research subjects is shown in Table 1, where the eight most common categories are shown. The categories are non-exclusive and a publication can be related to more than one research subject due to interdisciplinary research. As a result, the sum of the number of documents in these categories is above the total number of documents, and a similar result can be found when percentages are analyzed, with results above 100%. The ranking indicated that *Environmental Science* was the dominant category, with a contribution percentage of 36.7%. However, *Chemical Engineering* was almost as relevant, since 35.8% of the documents corresponded to this research subject. Therefore, a great collaboration between environmental professionals and chemical engineers should be expected in the research on valorization of hemicellulose. *Chemistry* and *Agricultural and Biological Sciences* occupied the 3rd and 4th positions respectively, while *Biochemistry, Genetics and Molecular Biology* and *Energy* shared the 5th position, all of them with contribution values above 20%. These results indicated clear evidence of multidisciplinary collaboration focused on hemicellulose valorization among several technical and scientific fields interested in this topic. More information about this multidisciplinary collaboration among subjects with *Chemical Engineering* playing a central role is provided in Figure 3 by means of Venn diagrams.

Table 1. The top eight most common subject categories.

Ranking	Subject Categories	Documents	Percentage (%)
1	*Environmental Science*	40	36.7
2	*Chemical Engineering*	39	35.8
3	*Chemistry*	27	24.8
4	*Agricultural and Biological Sciences*	24	22.0
5	*Biochemistry, Genetics and Molecular Biology*	23	21.1
5	*Energy*	23	21.1
7	*Materials Science*	13	11.9
8	*Engineering*	10	9.2

The analysis of the distribution of publications in journals can be observed in Table 2. The values (year 2016) of Impact Factors (IF) of the Web of Science database and the SCImago Journal Rank (SJR) index of the Scopus database that correspond to the top six journals were also included. Two journals shared the first position in the ranking: *Bioresource Technology* and *Industrial Crops and Products*. Both of them published eight papers, which represented 7.3% of the total amount of documents. On the one hand, *Bioresource Technology* is a journal linked to the *Chemical Engineering* and *Environmental Sciences* subjects, more specifically focused on the areas of biomass, biological waste treatment, bioenergy, biotransformations and bioresource systems analysis, and the complementary technologies. On the other hand, *Industrial Crops and Products* is a journal that is completely centered on the subject *Agricultural and Biological Sciences*, as it covers research on industrial crops and products (excluding those oriented to human food or animal feed), with important concern in bio-based materials. Once again, the significant contribution of different scientific disciplines must be highlighted. This idea can be supported by the rest of the journals included in Table 2, since they cover aspects from microbiology and biotechnology to chemistry and chemical engineering. Moreover, the high quality of the listed journals (all of them with IF values above 3 and a maximal value above 9 for the journal *Green Chemistry*) must be emphasized. Consequently, the research on valorization of hemicellulose can be considered as a very relevant issue within the scientific scenario.
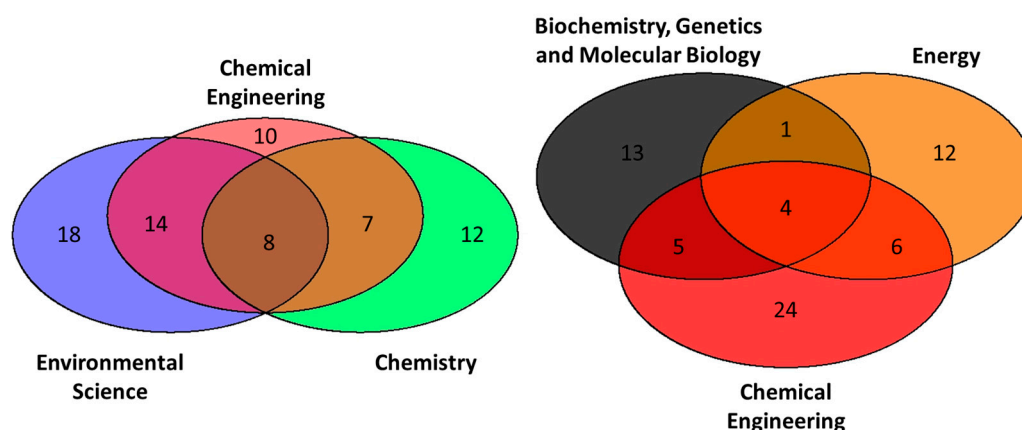
Figure 3. Venn diagrams representing the number of documents shared among the main subjects.

Table 2. The top six most productive journals (Impact Factor (IF) and SCI mago Journal Rank (SJR) values correspond to 2016).

Ranking	Journal	IF (WoS)	SJR (Scopus)	Documents	Percentage (%)
1	*Bioresource Technology*	5.651	2.191	8	7.3
1	*Industrial Crops and Products*	3.181	1.059	8	7.3
3	*Journal of Chemical Technology and Biotechnology*	3.135	0.843	4	3.7
4	*ACS Sustainable Chemistry and Engineering*	5.951	1.523	3	2.8
4	*Applied Microbiology and Biotechnology*	3.420	1.177	3	2.8
4	*Green Chemistry*	9.125	2.564	3	2.8

3.1.3. Publication Distribution of Countries and Institutions

The analysis of the geographical distribution of the authors was based on the documents that provide information about the address and affiliation of at least one author. There were five papers without country identification, so the total number of documents considered for the analysis of country contribution was 104. Researchers from 33 different countries contributed to the publication of retrieved documents. Table 3 shows the top eight countries ranked by the number of total publications. Once more, since the country affiliation is not an exclusive category (a document can be contributed by authors from more than one country), some documents may be classified in more than one country simultaneously due to international collaborations. Nevertheless, the contribution percentages of these top eight countries amounted to 78%. These data confirmed the existence of a reduced number of countries that dominate the publication of documents in this research field, in a similar way to other topics, including the full list of engineering branches [45,78,79].

Table 3. The top eight most productive countries.

Ranking	Country	Documents	Percentage (%)
1	Spain	23	21.1
2	France	19	17.4
3	Portugal	12	11.0
4	United States	8	7.3
5	Belgium	7	6.4
6	Italy	6	5.5
7	Germany	5	4.6
7	The Netherlands	5	4.6

However, a more in-depth look at the countries in Table 3 concluded that the research in this topic was clearly led by European countries, since USA was the unique top country that did not belong to

the European Union. Spain was the most productive country, with 23 documents, which implies a contribution of 21.1%. This leading country was followed by France (19 documents and 17.4%) and Portugal (12 documents and 11.0%). These results were quite surprising, as USA occupied only the fourth position, and other countries that must be considered great contributors to scientific research, such as China, Japan, Canada or South Korea, did not appear in relevant positions. Thus, European countries can be considered as references for the most innovative research in hemicellulose valorization.

The top five institutions were ranked by their number of publications (Table 4). They were the only ones that produced more than four documents. All these institutions were European: a Spanish university led the ranking, while two French institutions and two universities from Germany and Belgium completed the table. All four of these countries appeared among the top eight most productive countries. However, Portugal, which was the third most productive country, did not have any institution situated among the most productive ones, so it can be suspected that the Portuguese research production in this topic was highly distributed among different institutions. In addition, no American institutions were found among the leading contributors, which was not a typical situation, as institutions from USA are frequently among the most productive ones in most research areas [31,80,81].

Table 4. The top five most productive institutions.

Ranking	Institutions	Documents	Percentage (%)
1	University of Vigo (SPAIN)	8	7.3
2	Centre National de la Recherche Scientifique (FRANCE)	4	3.7
2	RWTH Aachen University (GERMANY)	4	3.7
2	University of Reims Champagne-Ardenne (FRANCE)	4	3.7
2	KU Leuven (BELGIUM)	4	3.7

3.1.4. Most Frequently Cited Papers

The 10 most cited papers among the retrieved documents are compiled in Table 5. The range of cites varied from 48 for the paper in 10th position to 442 for the leading article. Although a deeper analysis and further comments on the most important research trends will be made in the next section, a simple examination of the most cited publications can be useful to have an initial idea about some relevant topics that attract the attention of the researchers investigating hemicellulose valorization.

After this quick analysis of the most cited documents, the papers in Table 5 can be classified into three different categories according to their topics. The first category, which can be represented by the articles in positions 1, 7 and 9 [82–84], covered a global approach to biomass fractionation and valorization by implementation of biorefineries. The second category, which can be represented by the articles in positions 5, 6 and 10, included the papers more specifically focused on the valorization of cellulose and hemicellulose fractions of lignocellulosic biomass [85–87]. Finally, the third category, which can be represented by the articles in positions 2, 3, 4 and 8, included documents that mainly focused on lignin valorization [88–91]. Therefore, the clear interdependence of the valorization purposes of the different fractions of lignocellulosic must be highlighted, as the consideration of hemicellulose valorization has to take into account cellulose and lignin within the framework of a totally integrated biorefinery. Lastly, the analysis of the most cited papers revealed that the first two articles were published in relevant journals such as *Science* and *Nature*, so the high importance of this topic in the research scenario can hardly be questioned.

Table 5. The top 10 most cited papers.

Ranking	Articles	Times Cited
1	Title: Valorization of biomass: Deriving more value from waste Author(s): Tuck, C.O., Pérez, E., Horváth, I.T., Sheldon, R.A., Poliakoff, M. Source: *Science* Published: 2012	442
2	Title: Formic-acid-induced depolymerization of oxidized lignin to aromatics Author(s): Rahimi, A., Ulbrich, A., Coon, J.J., Stahl, S.S. Source: *Nature* Published: 2014	193
3	Title: Adipic acid production from lignin Author(s): Vardon, D.R., Franden, M.A., Johnson, C.W., Karp, E.M., et al. Source: *Energy and Environmental Science* Published: 2015	96
4	Title: Review: Oxidation of lignin using ionic liquids-an innovative strategy to produce renewable chemicals Author(s): Chatel, G., Rogers, R.D. Source: *ACS Sustainable Chemistry And Engineering* Published: 2014	85
5	Title: Cellulose and hemicellulose valorisation: An integrated challenge of catalysis and reaction engineering Author(s): Delidovich, I., Leonhard, K., Palkovits, R. Source: *Energy and Environmental Science* Published: 2014	79
6	Title: Optimization of sugarcane bagasse conversion by hydrothermal treatment for the recovery of xylose Author(s): Boussarsar, H., Rogé, B., Mathlouthi, M. Source: *Bioresource Technology* Published: 2009	76
7	Title: The forest biorefinery and its implementation in the pulp and paper industry: Energy overview Author(s): Moshkelani, M., Marinova, M., Perrier, M., Paris, J. Source: *Applied Thermal Engineering* Published: 2013	56
8	Title: Lignin-degrading enzymes Author(s): Pollegioni, L., Tonin, F., Rosini, E. Source: *FEBS Journal* Published: 2015	55
9	Title: Novel pre-treatment and fractionation method for lignocellulosic biomass using ionic liquids Author(s): Magalhães Da Silva, S.P., Da Costa Lopes, A.M., Roseiro, L.B., et al. Source: *RSC Advances* Published: 2013	51
10	Title: Valorisation of hardwood hemicelluloses in the kraft pulping process by using an integrated biorefinery concept Author(s): Mendes, C.V.T., Carvalho, M.G.V.S., Baptista, C.M.S.G., et al. Source: *Food and Bioproducts Processing* Published: 2009	48

3.2. Analysis of Author Keywords and Hot Topics of the Research on Hemicellulose Valorization

Author keywords are selected to point out the most significant information of the research presented in an article. The most frequently used author keywords are among the best indicators that can be used to identify research topics and trends in a certain field [92].

The most frequently used keywords, which were mentioned by at least six of the retrieved documents, are listed in Figure 4. Singular and plural forms were considered together to simplify the list. Surprisingly, *Cellulose* was the most common keyword (selected in 68 papers), while *Hemicellulose(s)* was the second most common keyword (selected in 43 papers). In addition, *Lignin* occupied the third position in the ranking (included as a keyword in 41 papers), while *Valorization*, which was selected as a keyword to be introduced in the search engine, appeared only 11 times. Once again, the high interconnection between hemicellulose and cellulose and lignin (the other two main components of lignocellulosic biomass) was revealed and it is obvious that the valorization of hemicellulose must be carried out simultaneously with the rest of biomass components within biorefineries (*Biorefinery(ies)* was found among the most frequently used keywords with 30 appearances).
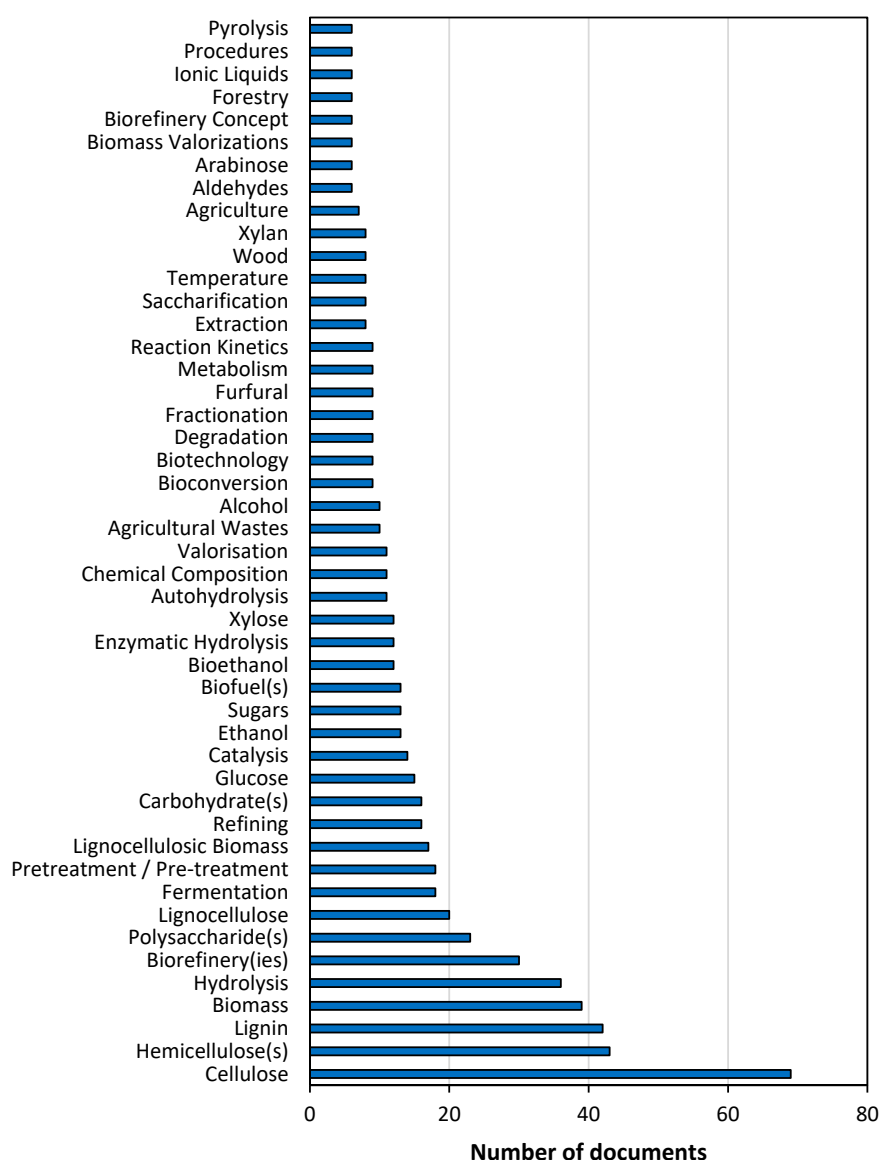

Figure 4. Most frequently used keywords.

Other keywords in Figure 4 provide additional information about the research trends in this field. Expressions such as *Hydrolysis* (36 appearances), together with *Enzymatic hydrolysis* and *Autohydrolysis* (12 and 11 appearances respectively) or *Fermentation* (18 appearances) and *Sacharification* (8 appearances), clearly confirmed the main route for hemicellulose valorization: the cleavage of the

chemical bonds among sugar monomers in the hemicellulose chain to obtain fermentable sugars. The most common purpose of this fermentation process is the production of ethanol to be used mainly as fuel (*Ethanol* had 13 appearances, the same number than *Biofuel(s)*, while *Bioethanol* appeared 12 times). Moreover, the analysis of the chemical compounds listed in Figure 4 demonstrated the supremacy of the saccharides over other chemicals. *Carbohydrate(s)* appeared 16 times, followed by *Glucose* with 15, and 13, 12 and 6 appearances for *Sugars*, *Xylose* and *Arabinose*, respectively. Nevertheless, another interesting chemical appeared in the list: *Furfural* was mentioned 9 times. Furfural has recently been identified as one of the top value-added chemicals that can be derived from biomass, being emphasized as one of the key chemicals to be produced in lignocellulosic biorefineries [93]. The polysaccharides can be hydrolyzed to pentoses (mainly xylose), which are subsequently dehydrated to obtain furfural [94]. Therefore, in addition to biofuels, biomass-based chemicals also appear to be a very interesting option, specifically since these chemicals have gained a better competitive position against oil derivatives in recent years. The next section will present the most recent remarkable topics about these options for the valorization of hemicellulose.

3.3. Review of the Main Alternatives for Hemicellulose Valorization and Current Trending Topics

3.3.1. Pretreatment of Lignocellulosic Biomass for Hemicellulose Valorization

The utilization of the saccharides derived from hemicellulose is essential for its efficient transformation to biofuels (mainly ethanol) or other high value-added chemicals. These two alternative purposes for hemicellulose valorization can be attained by chemical or biological conversion of the hemicellulosic monomers. Hemicellulose can be depolymerized into monomeric and oligomeric components with high purity and yield by chemical, enzymatic or thermal processes [14]. This hydrolysis of hemicellulose is only possible after effective fractionation of the biomass to obtain significantly pure fractions of the different components, since, for instance, lignin can cause drawbacks to cellulose and hemicellulose processing [95]. The pretreatment of lignocellulosic biomass is a crucial step that disrupts its original structure, separates the different fractions and allows the optimal valorization of each fraction. Therefore, multiple research efforts have been applied to find the most adequate pretreatment options to fractionate biomass taking into consideration the different feedstocks and possible valorization routes. Pretreatment alternatives can be divided into either physical, chemical or biological methods.

The most frequent physical treatment of lignocellulosic biomass is wood size reduction through mechanical means to increase the accessible surface area available for further chemical or biological methods. However, thermal methods for biomass treatment can be considered attractive due to the fast rate of the conversion process and the broad range of allowed feedstocks [96]. The most investigated example of thermal pretreatment is pyrolysis, which implies fast heating of biomass in the absence of oxygen to produce a liquid product (known as bio-oil) along with syngas and solid char [97]. Pyrolysis is applied to the raw biomass (it does not require previous fractionation) and cellulose, hemicellulose and lignin are simultaneously converted to solid, liquid and gaseous compounds. This way, hemicellulosic oligomers and monomers cannot be obtained. Thermal studies including decomposition profiles, reaction kinetics and thermal stability of the raw biomass are required to improve the modelling of pyrolysis reactors. Biomass pyrolysis kinetics have been studied extensively in the last years by means of several technologies, but thermogravimetric analysis is the technique generally applied [98,99]. Bio-oil is similar to tar and has levels of oxygen too high to be considered a hydrocarbon. This high oxygen content results in characteristics that impede its direct use, such as thermal instability, high tendency to polymerization or immiscibility with fossil fuels. Therefore, after biomass pyrolysis, catalytic conversion of the bio-oil is required so that it can be further processed in an analogous way to conventional oil refineries. One alternative strategy that has been proposed to produce simpler intermediate streams is staged thermal fractionation (also called staged degasification), which can be preceded by biomass torrefaction and the corresponding partial

conversion of hemicellulose to compounds such as furfural and furan carboxyl aldehydes or ketones and alcohols [100]. The staged thermal fractionation is guided by the order of thermochemical stability of the biomass constituents, which increases from hemicellulose as the least stable fraction to the most stable cellulose. Different vapor product streams of enhanced purity and decreased complexity can be obtained [5]. Nevertheless, although staged degasification is an elegant conversion option to valorize lignocellulosic biomass, more research efforts are still required to increase the yield and selectivity for effective valorization of the hemicellulosic fraction [101]. In addition, alternative physical treatments not only based on thermal processes have been investigated, including turbo-fractionation technology, which comprises particle separation according to their size and density; or electrostatic fractionation, which is based on the separation of particles according to surface properties such as chemical composition and charge [102,103].

Depending on the process and conditions used during the chemical pretreatment of lignocellulosic biomass, the fractionation process can result in the transfer of hemicellulose from solid to liquid phase, but degradation of the hemicellulosic sugars to weak acids, furan derivatives and phenolic compounds can also occur, as well as dissolution of chemicals derived from cellulose and lignin [104]. These compounds may inhibit posterior fermentations or interfere with other processes required for the valorization of the sugars derived from hemicellulose, so the selection of the most adequate chemical pretreatment must consider the whole processing of lignocellulosic biomass. Nonetheless, autohydrolysis and acid or alkaline pretreatment must be highlighted as preferred solutions to valorize hemicellulose. Further information about all the available alternatives for chemical pretreatment of biomass for hemicellulose valorization can be found in the bibliography [105].

Autohydrolysis, also known as hydrothermal pretreatment, employs compressed liquid hot water (temperature around 200 °C and pressure above the saturation point) to convert hemicellulose into soluble saccharides with high yield and low byproducts formation. An easily separable solid residue rich in cellulose and lignin results from autohydrolysis, so high hemicellulose recovery can be attained without the presence of catalysts or auxiliary chemicals [106]. The autohydrolysis process has been optimized for increasing the recovery of hemicellulose in the form of monomeric sugars (such as xylose, mannose and galactose) or the respective oligo-saccharides, as well as for improving the production of glucose in the subsequent enzymatic hydrolysis of the cellulosic fraction [107]. In addition to its application to traditional wood species, such as eucalyptus [108], or fast-growing energy crops, such as Paulownia [109], autohydrolysis has been successfully employed for the valorization of the hemicellulosic content of vegetal byproducts or waste materials, such as barley straw [110], rapeseed cake [111], vine shoots [112] and invasive species such as gorse [113]. The development of kinetic models has provided fundamental understanding for the identification and evaluation of the most appropriate conditions for optimal autohydrolysis processes [114]. These models allow the satisfactory interpretation of the time courses of the main products and their degradation compounds [115] and can be employed as a powerful tool for scale-up procedures [116]. Nevertheless, autohydrolysis can be followed by another chemical pretreatment to improve the valorization of the hemicellulosic fraction. Examples of posterior acid pretreatment to enhance the hydrolysis of hemicellulose to monomers [86] or alkaline pretreatment to increase hemicellulose recovery [117] are worth mentioning.

Acid and alkaline hydrolysis are the two most reported technologies for chemical pretreatment of lignocellulosic biomass to obtain high sugar yields at low cost [13]. Acid treatments favor hydrolysis of the hemicellulose fraction, whereas alkaline hydrolysis targets the lignin fraction (Figure 5). Acid hydrolysis processes can be divided in two groups: concentrated acid at low temperature or diluted acid at high temperature [100]. Since the processes based on concentrated acid are quite expensive and may cause operation problems (equipment corrosion), diluted acid processes are more common, with sulfuric acid in the range between 0.5% and 2.5% being the most representative case [118]. Raw hemicellulose prehydrolyzate streams originating from lignocellulosic materials by autohydrolysis can be improved after a further acid hydrolysis of partially degraded and non-degraded hemicelluloses that may still exist [119]. Alkaline pretreatment can be based on the use of ammonia

or hydroxides (soda, potash or lime). Although alkaline hydrolysis has been used extensively to separate lignin from cellulose and hemicellulose, this treatment modifies the structure of the remaining solid biomass and makes it more amenable to enzymatic hydrolysis, which can enhance the options for hemicellulose valorization [4]. In some cases, alkaline pretreatment solutions include additional chemicals to increase the delignification, such as oxidants [120] or ionic liquids [121].
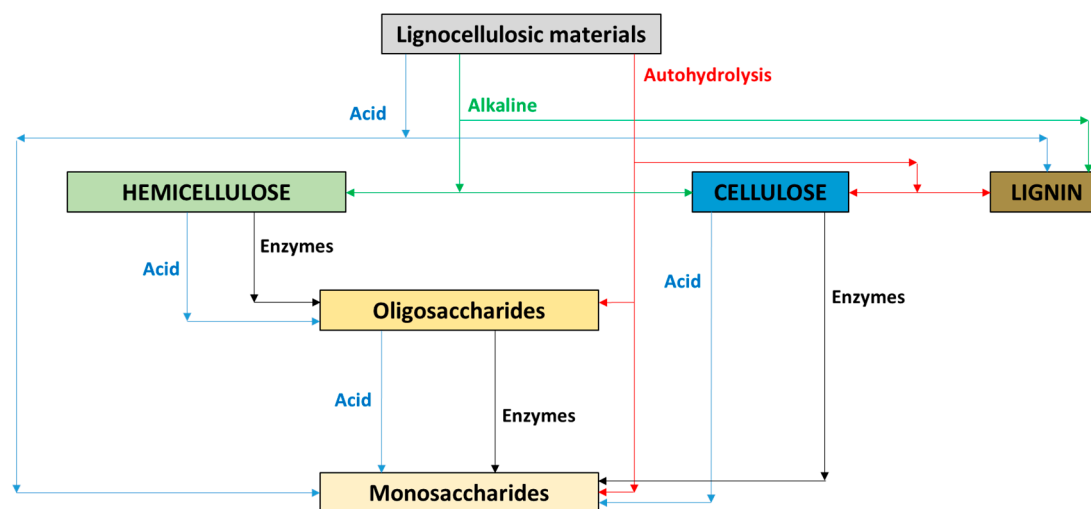

Figure 5. Traditional hydrolysis processes for biomass fractionation (adapted from [100]).

Organosolv pretreatments are based on the employment of aqueous solutions of organic solvents (solvent concentration ranges from 40 to 80%), such as acetone, methanol, ethanol, butanol or ethylene glycol. Organosolv fractionation recovers cellulose as solid phase, while most of hemicelluloses and lignin are dissolved in the solvents. The dissolved lignin can be further precipitated by water addition and recovered as a solid product, while hemicellulosic sugars remain in the liquid stream [122]. This approach allows an efficient utilization of all the major biomass components to produce platform chemicals and various final products. Acid catalyzed organosolv treatments highly increased the digestibility of the remaining cellulosic fraction, both by a decrease of lignin fraction and the improved accessibility of polysaccharides [123]. In addition, the presence of acid catalysts increased the recovery of hemicellulosic fermentable sugars [124]. Nevertheless, the nature of the catalyst (Lewis or Brønsted acid) has great influence on the yield and characteristics of the obtained products [125]. Alkaline catalysts can be employed in the organosolv process too, but as it occurred with the case of alkaline hydrolysis, these pretreatments are more focused on the recovery of the lignin fraction whereas hemicellulose remains in the solid residue with cellulose [126,127].

Recently, more advanced chemical pretreatments have been investigated to fractionate lignocellulosic biomass. A promising approach that has been identified is the combination of traditional chemical pretreatments and transition-metal catalysis [128]. In these catalytic fractionation processes, lignocellulosic biomass is treated at high temperatures (160–230 °C) in water, classical organosolv solvent (with methanol and ethanol as the most typical examples), or a mixture of both in the presence of a heterogeneous transition metal-based catalyst, such as Ni, Ru, Rh, Pt, Pd, or Cu [129–133]. These processes can separate all the three main lignocellulose components, where cellulose is retained as a solid and is delignified to a high degree, the hemicellulose is partially solubilized, and lignin is selectively converted to a set of monomers and oligomers that together form a separate phase of "lignin oil" that can be easily fractionated by distillation. Nevertheless, in some cases, the selected conditions defined an alternative scenario characterized by the retention in the residual pulp of the hemicellulosic fraction [134]. In order to further exploit these processes, a clear understanding of the catalyst's role in the fractionation is required for optimal reactor designs and scale-up initiatives [135].

In addition, examples of more complex pretreatment systems that use ionic liquids or deep eutectic solvents as media must be mentioned. Ionic liquids (and ionic liquid-based mixtures) have been extensively studied for their application in pretreatments for the deconstruction and fractionation of lignocellulosic biomass [136–138]. Most cases are based on the selective dissolution of cellulose [139–143] or lignin [144–147], but attempts to dissolve the whole lignocellulosic biomass have been carried out as well [148–151]. Nevertheless, in most cases, a solid residue was left at the end of the dissolution experiment and even the studies that reported complete dissolution of biomass stated that their solutions were hazy and non-uniform [152]. Although hemicellulose has not been the main target of these pretreatments, ionic liquids can be also applied to separate cellulose and hemicellulose [153,154]. Deep eutectic solvents are formed by mixing a hydrogen bond donor and a hydrogen bond acceptor, which interact by means of hydrogen bonds to form eutectic mixtures with a melting temperature lower than the melting points of the constituents [155]. They share solvent characteristics with ionic liquids but some advantages over ionic liquids are claimed, such as lower prices, chemical inertness with water and easy preparation by mixing its constituents at moderate temperature. In a similar way to the application of ionic liquids, research about deep eutectic solvents for biomass fractionation has been focused on the dissolution of cellulose and lignin and the extraction of these constituents from lignocellulosic biomass [156]. These solvents have displayed outstanding performance for the dissolution of lignin, whereas cellulose can barely be dissolved [157]. The combination of deep eutectic solvents and microwave irradiation had a significant synergetic effect on efficiently cleaving the lignin–carbohydrate complex [141]. This proposed pretreatment promoted an efficient lignin-first biorefinery approach while keeping the dissolved hemicellulosic saccharides and undissolved cellulose available for further utilization. The pretreatment with different deep eutectic solvents in sequential stages achieved effective hemicellulose and lignin removal, affording readily accessible cellulose [158].

When residual biomass with a high content in hemicellulose to be valorized is available, the biomass fractionation process can be replaced by the selective extraction of the hemicellulose-rich fraction. Examples of this approach have been proposed to be applied to residual matter remaining after the processing of fruits, seeds and grains, such as almond shell [159] and olive oil cake [160]; or leaves from plants, such as the giant knotweed *Fallopia sachalinensis* [161] and the drinn *Aristida pungens* [162].

Enzymatic hydrolysis is the most promising option to selectively depolymerize hemicellulose to monosaccharides. Xylans are the most characteristic components of hemicellulose and can be represented by a *β*-(1-4)-linked-D-xylopyranosyl main chain with a variable number of side groups, such as L-arabinosyl, D-galactosyl, acetyl, feruloyl, p-coumaroyl and glucuronosyl residues [163]. The frequency and composition of these branches depend on the biomass source. Due to this complex structure, the hydrolysis of the hemicellulose needs the action of several hemicellulases [164]. The most important xylanolytic enzyme is the endo-*β*-1,4-xylanase, which hydrolyzes the insoluble xylan backbone into shorter soluble xylo-oligosaccharides, but different accessory enzymes are required [165]. Further information about the applications of hemicellulases and their structure/function relationships can be consulted in the bibliography [166]. The development of efficient enzymatic strategies for the hydrolysis of hemicellulose remains a challenge in the pursuit of viable biorefineries. The production and characterization of optimal enzymatic cocktails of hemicellulases can improve the hydrolysis process significantly [167–179].

3.3.2. Chemicals from Hemicellulose

The hydrolyzed hemicellulosic sugars can be transformed to a variety of chemicals, which must be considered primary substrates to obtain important industrial compounds. This section will present a brief review on the most relevant research topics, which have been identified as current trending topics during the bibliographic analysis of the found references, about the biological or chemical conversion of saccharides derived from hemicellulose to biofuels and bio-based compounds.

Ethanol

Second-generation ethanol, which is produced from lignocellulosic materials as feedstock, is an environmentally friendly renewable energy source. Once hydrolyzed, the fermentable sugars derived from hemicellulose could be used to produce ethanol [180]. The sugar mixture obtained after hydrolysis may contain xylose, arabinose, glucose, galactose, mannose and other monosaccharides. However, the lack of microorganisms that efficiently perform the simultaneous conversion of pentoses and hexoses to bioethanol under industrial conditions is the main problem for the direct fermentation of these hydrolyzates [84]. For instance, *Saccharomyces cerevisiae*, the most frequently used industrial fermentation microorganism, can ferment hexoses (such as glucose), but not pentoses (such as xylose and arabinose). Therefore, research efforts have been applied to the development of co-fermentation microorganisms.

Different microorganisms able to produce ethanol from pentoses have been identified, including bacteria, yeasts and fungi [181]. As compiled in Table 6, each organism presents some advantages and disadvantages for their industrial implementation [158]. Among these alternative organisms, *Escherichia coli*, *Zymomonas mobilis* and *Pichia stipitis* are worth mentioning, but others can be cited, such as *Candida shehatae*, *Pachysolen tannophilus*, *Klebsiella oxytoca* and *Fusarium oxysporum* [182–184]. Nevertheless, despite extensive research in this field, the majority of the studies concerning xylose (as the most relevant pentose) conversion to ethanol have been performed with only these few yeast species. This trend has recently changed after studies describing the isolation, description and application of new xylose-fermenting yeasts from particular habitats, such as wood-boring insects and rotting wood [185]. These new species belong to the xylose-fermenting clades *Spathaspora* and *Scheffersomyces* [186].

Another option for valorization of hemicellulose to ethanol is the genetic modification of microorganisms specifically engineered to overproduce ethanol from mixed sugar substrates [187]. The most practical approach proposes the introduction of the pentose-utilizing capability into efficient ethanol producers such as *S. cerevisiae* and *Z. mobilis* [135,188,189]. The introduction of xylose isomerases that function well in other xylose-fermenting yeasts is the preferred solution to overcome the limitations caused by xylose to these host organisms [190,191].

Moreover, the combination of typical ethanol producers from hexoses with other organisms that consume xylose to produce alternative products has been proposed [192,193]. In these cases, the sugar mixture can be diversified to obtain different products from hexoses and pentoses. These sequential fermentations of the monosaccharides released by hydrolysis can produce bioethanol and other chemicals with complete sugar consumption and improve the performance of separate fermentations.

Table 6. The main advantages and disadvantages of various natural microorganisms for industrial fermentation (adapted from [163]).

Organism	Natural Sugar Utilization Pathways					Main Products		O₂ Required	Tolerance			PH Range
	Glucose	Mannose	Galactose	Xylose	Arabinose	Ethanol	Others		Alcohol	Acids	Hydrolysate	
S. cerevisiae	+	+	-	-	-	+	-	-	++	++	++	Acidic
E. coli	+	+	-	+	+	-	+	-	-	-	-	Neutral
Z. mobilis	+	-	-	-	-	+	-	-	+	-	-	Neutral
P. stipitis	+	+	+	+	+	+	-	+	-	-	-	Acidic

Furfural, 5-Hydroxymethylfurfural (HMF) and Levulinic Acid (LeA)

Furfural, an aldehyde of furan, is a highly versatile and key derivative from hemicellulose with diverse applications (Figure 6). Hydrogenation of furfural produces furfuryl alcohol, which is a useful intermediate for the manufacture of furan resins. These are used in thermoset polymer matrix composites, cements, adhesives, coatings and casting/foundry resins. Further hydrogenation of furfuryl alcohol leads to tetrahydrofurfuryl alcohol, which is used as a nonhazardous solvent in agricultural formulations and as an adjuvant to help herbicides penetrate the leaf

structure. The synthesis of other derivatives including furoic acid, furan, tetrahydrofuran, 2-methyltetrahydrofuran and related resins is also proposed [82].

Furfural can be produced by the acid catalyzed dehydration of pentoses, particularly xylose. Xylose undergoes a triple dehydration in the presence of acid catalysts (mainly sulfuric acid) to form furfural. The first commercial process for furfural production from biomass was designed in the 1920s and used oat hulls as raw material [194]. Traditional operation conditions include temperature in the 200–250 °C range and the presence of sulfuric acid as catalyst, but alternative acids have been proposed, such as formic acid [195]. However, efforts to improve the process by heterogeneous catalysis have been carried out [196–199] and the recent employment of ionic liquids as catalysts has opened a new opportunity to furfural production [200,201].
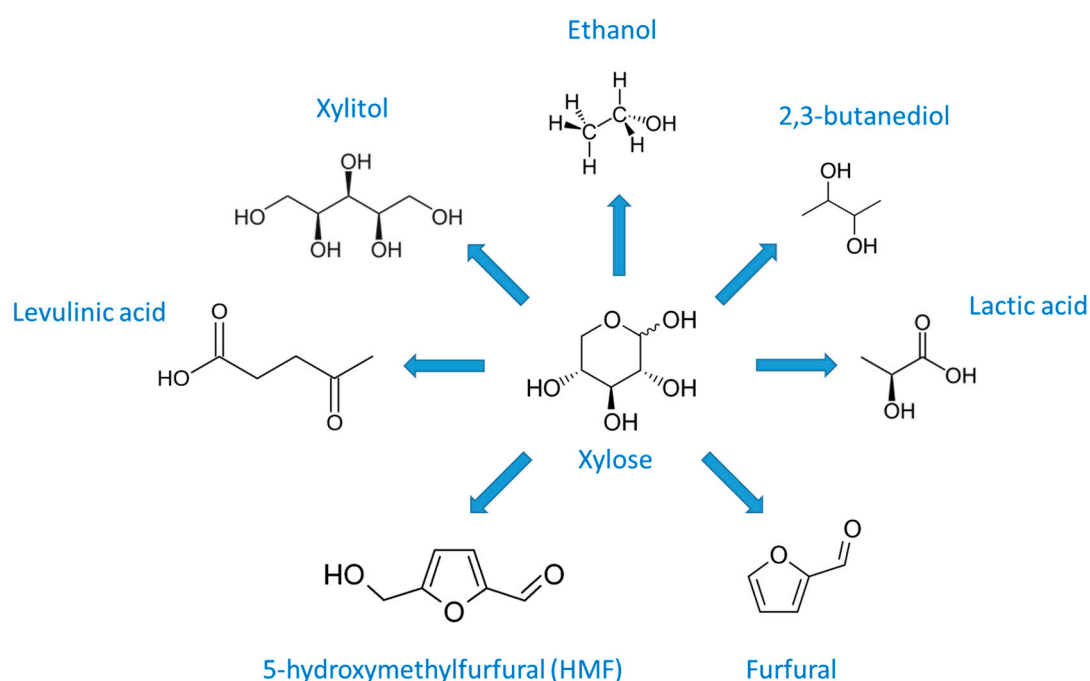

Figure 6. Main chemicals that can be obtained from xylose for hemicellulose valorization.

Although furfural can be the starting block for the synthesis of a series of furan derivatives with high commercial interest [87,202], 5-hydroxymethylfurfural (HMF) is an even more attractive platform [203]. HMF (Figure 6) is an organic product formed by the dehydration of hexoses. As for furfural, the molecule consists of a furan ring, but in this case, an alcohol group accompanies the aldehyde group. HMF is the precursor of 2,5-furandicarboxilic acid (FDCA), a molecule that can be directly used as a replacement of terephthalic acid in the production of polyethylene terephthalate (PET) and other polymers [204]. Besides, HMF can be converted to dimethylfuran, which has applications as both solvent and transportation fuel, so HMF combines two key criteria for the valorization of biomass: it retains a reasonable proportion of the original chemical complexity, and it can also be converted to high-tonnage chemicals [82].

HMF can be obtained from all hexoses derived from lignocellulosic biomass, but fructose has been the most common carbohydrate source for HMF production [205]. Because of this predominance, catalysts for the triple dehydration of fructose to HMF have been deeply investigated, including mineral acids, metal salts, zeolites and other functionalized materials [206]. However, much effort has been applied to the synthesis of HMF from glucose and other hexoses instead of fructose over different catalysts in order to reduce costs [207]. Nevertheless, only a few reaction systems could selectively convert glucose into HMF. The consideration of the reaction media is very important for HMF production. The low cost and excellent solution properties of water as solvent are limited by

the rehydration of HMF, so alternative non-aqueous solvents should be preferred. However, the removal of these organic solvents, which can be required in high amounts, creates additional technical and environmental problems. Therefore, the catalytic systems based on the biphasic system that could concurrently extract HMF into an organic phase immediately after its formation in the reactive phase appeared as a more promising option [208]. Research works have proved that ionic liquids are a promising alternative in this field and open up a broad variety of new opportunities for HMF production from hemicellulosic hexoses [209].

Levulinic acid (LeA) is a C_5-chemical that contains a ketone group and a carboxylic acid group (Figure 6). These two functional groups make levulinic acid a potentially very versatile building block for the synthesis of several organic bulk chemicals. LeA derivatives, such as ethyl and n-butyl levulinates, have been successfully blended with fossil-based diesel up to 20%. LeA can also be hydrogenated selectively to γ-valerolactone, which can be used as a precursor of gasoline and diesel fuels (alkane mixtures), green solvents in fine chemicals synthesis, food additives or intermediates in the synthesis of other value-added chemicals, such as 1,4-pentanediol and methyl pentenoate [210,211]. Moreover, diphenolic acid, which can be employed to replace bisphenol-A in the production of polycarbonates, can be easily obtained by reaction of LeA with phenol [87,163]. The controlled thermal degradation of hexoses in the presence of diluted mineral acids is the most widely used approach to obtain LeA from lignocellulosic biomass [195]. HMF is formed as intermediate, which reacts with water to give LeA and formic acid as by-product. The operation conditions define a range of temperature between 190 and 220 °C for 15 to 40 min with acid concentration in the 1–5% range [212]. Conversion of lignocellulosic biomass to LeA by using enzymes has been recently investigated [213], and even some ILs has been reported for this conversion [214]. In addition, life cycle assessment methodology has been applied to compare the potential of the LeA valorization route to alternative routes in order to identify the most sustainable biorefinery scheme [215].

2,3-Butanediol (2,3-BD)

2,3-Butanediol (2,3-BD) is another example of a bulk chemical that can be obtained from lignocellulosic biomass (Figure 6). Although its microbial production was investigated more than 100 year ago, 2,3-BD became of special interest during WWII as a precursor of 1,3-butadiene, which is a very relevant intermediate for synthetic rubber production [216]. However, despite the satisfactory efficiency of the process, further improvements were discarded since less expensive petroleum-based routes became available. Currently, the microbial production of 2,3-BD from renewable resources is regaining more attention, especially with regard to biorefinery [217]. In addition, 2,3-BD has potential applications in the manufacture of printing inks, perfumes, fumigants, moistening and softening agents, explosives, plasticizers, and pharmaceuticals.

Bioproduction of 2,3-BD has been achieved through aerobic fermentation by various bacteria such as *Klebsiella oxytoca* and *Klebseilla pneumonia*. Although *K. oxytoca* is capable of utilizing both glucose and xylose, it preferably utilizes glucose first, followed by xylose [126]. Alternative microorganisms, such as *Bacillus licheniformis*, produce 2,3-BD starting from hexoses, but are not able to ferment pentoses [218]. However, co-production of organic acids (acetic, lactic, formic, and succinic acids) always occurs, which adversely impacts product recovery and yield. To address these issues, substrate selection and process optimization are needed to improve the yield of 2,3-BD and its purity. Nevertheless, novel strains capable of producing high concentrations of 2,3-BD using low-cost carbon sources with minimal production of by-products are highly desirable [219]. After high-throughput screening for safe efficient microorganisms able to produce 2,3-BD [220], metabolic engineering can be applied [221,222]. Finally, genetic modifications have been performed for improvement of 2,3-BD productivity and yield, elimination of byproducts synthesis, enhancement of the ability to utilize complex substrates (most preferably without pretreatment) and resistance to environmental stresses [223,224].

Xylitol

Xylitol is a pentose sugar polyol (Figure 6), with sweetness similar to sucrose, but it does not produce caries and is tolerated by diabetic people. Moreover, its caloric value is lower than sucrose [225]. Although xylitol occurs in some fruits and vegetables, its extraction is not economically viable. The traditional synthesis route to produce xylitol has been the catalytic hydrogenation of xylose from hemicellulosic hydrolyzates or sulfite liquors. The hydrogenation can be assisted by different catalysts, being Raney nickel the most frequently used, but noble metals have been applied as well [226,227]. Nevertheless, nickel-based catalysts suffer easy poisoning and deactivation. The required operation conditions include temperatures above 100 °C and elevated pressure (40 bar or higher). Besides, the purification of the raw xylose solution is a crucial step of this process that increases the economic costs. The selective extraction of the hemicellulose fraction from lignocellulosic biomass has been proposed to improve the process [85]. However, taking all the circumstances into account, sorbitol produced from sucrose appeared as a more attractive sweetener.

Nowadays, the bioconversion of xylose to xylitol results in a more interesting alternative to the chemical route and makes xylitol a promising chemical for hemicellulose valorization. The employment of microorganisms allows the direct conversion of xylose to xylitol without previous purification tasks and avoids the use of catalysts. Although some bacteria and fungi are able to produce xylitol from xylose, the relative low production of xylitol has not attracted too much interest in these organisms [228,229], and, as a consequence, yeasts are preferred. The organisms of genus *Candida* and *Debaryomyces* are among the best-known producers of xylitol, including species such as *C. guilliermondii*, *C. pelliculosu*, *C. parapsilosis*, *C. tropicalis*, *C. pseudotropicalis*, *C. units*, *D. hansenii* or *D. nepalensis* [229,230]. In order to increase the production of xylitol by biological routes, optimal operation conditions must be identified. Research works have demonstrated the great influence of the raw lignocellulosic material on the performance [231,232]. Moreover, conditions such as temperature, pH, oxygen availability and xylose concentration affect the fermentation process [233–235]. The presence of chemicals toxic to the microorganisms must be taken into consideration and the implementation of different detoxification processes has been analyzed [119,183].

Lactic Acid (LA)

Lactic acid (LA) is a versatile chemical used in food, cosmetic, pharmaceutical, textile and chemical industries (Figure 6). Over the past few years, its application has been extended also to biodegradable plastics to produce polylactide (PLA), which has properties similar to those of petroleum-derived polymers [236]. LA can be synthesized chemically, but racemic mixtures of the isomers are obtained. As chirally pure LA is required for PLA production, currently LA is obtained on an industrial scale by fermentation of pure sugars or edible crops by bacteria (mainly *Lactobacillus* genus), which typically have complex nutritional requirements. Alternatively, it could be produced by fermentation of hemicellulosic sugars derived from lignocellulosic biomass with alternative bacteria. For example, *Bacillus coagulans* has been reported to possess many valuable fermentation features, such as conversion of pentoses and hexoses, thermophilic trait, simple nutrition requirements and high carbon-efficiency [124]. Despite the application of these versatile organisms able to ferment complex sugar mixtures, the sequential fermentation of hydrolysate derived from lignocellulosic biomass can be selected for the selective conversion of pentoses and hexoses. Some hexoses, particularly glucose, can exert a negative effect on the xylose metabolism to xylitol because of repression and competitive inhibition of the xylose transport system. Therefore, sequential production of LA from hexoses by *L. rhamnosus* and xylitol from pentoses by *D. hansenii* has been reported [233]. Alternatively, LA production by *L. plantarum* can be proposed to ferment the remaining pentoses after the production of bio-ethanol by *S. cerevisiae* from hydrolysates of exhausted sugar beet cossettes [193].

Xylo-Oligosaccharides (XOSs)

Although the hydrolyzed hemicellulosic sugars must be considered primary intermediates to be transformed to more valuable chemical blocks and final products, new chances for their direct valorization have merged. Xylo-oligosaccharides are sugar oligomers made up of xylose units through *β*-(1-4)-xylosidic linkages. The oligomers containing from 2 (xylobioses) to 6 (xylohexoses) monomers have demonstrated a positive influence on several aspects of human health, in addition to their potentiality to work against several gastrointestinal disorders [237]. XOSs naturally appear in some foods, such as fruits, vegetables, milk, and honey, but their concentration is not enough to exhibit the prebiotic effects [238]. Since XOSs can be obtained as direct products of the hydrolysis of xylan, which is present in most lignocellulosic biomass, XOSs generated from lignocellulose, a cheap and highly available resource, have great potential as additional ingredients for the nutraceutical sector.

In a similar way to the hydrolysis of lignocellulosic biomass for fractionation, the production of XOS on an industrial scale from lignocellulosic materials rich in xylan can be performed by chemical and enzymatic methods. The simplest option is autohydrolysis, which provides a selective separation of hemicellulose that results in maximal XOS production and a minimal amount of monosaccharides [116]. However, due to the side processes that can take place simultaneously with the hydrolytic xylan degradation, other undesirable products can be produced [115]. Therefore, the enzymatic route is preferred by the food industry because of the minimization of these undesirable side reactions and by-products [232]. Nevertheless, although examples of direct enzymatic hydrolysis without previous chemical or thermal pretreatment of the biomass can be referred [239,240], most researchers report pretreatments. Although acid and alkaline hydrolysis [241–243], even with additional microwave-assisted processing [244], have been employed as pretreatments, the combination of an initial autohydrolysis step followed by the enzymatic hydrolysis of the obtained xylan can be mentioned as a more promising option [106,245,246].

4. Conclusions

This work completes a bibliometric overview of the research on the valorization of hemicellulose during the 2000–2016 period, with the data related to annual publications, document types, languages, subjects, journals, countries and institutions. The very relevant contribution of different scientific disciplines, such as *Environmental Sciences*, *Chemical Engineering*, *Chemistry* and *Agricultural and Biological Sciences*, must be highlighted to confirm the great multidisciplinary approach proposed for the valorization of hemicellulose. European countries, with Spain, France and Portugal as leaders, must be considered reference points for the most innovative research in hemicellulose valorization. In contrast, USA occupied only the fourth position and other countries that are great contributors to scientific research (China, Japan, Canada or South Korea) did not appear in relevant positions of the ranking.

Further analysis identified the most relevant options for hemicellulose valorization and the corresponding research emphases and trends. The analysis of keywords demonstrated the high interconnection of all the components of the biomass. Consequently, the simultaneous valorization of the three main components of lignocellulosic biomass (hemicellulose, cellulose and lignin) has been proposed. Therefore, the valorization of hemicellulose must be based on the inclusive approach proposed by biorefineries to avoid discarding one main lignocellulosic component to promote the valorization of another. The pretreatment of the biomass for a satisfactory fractionation is a crucial step for the posterior valorization of hemicellulose. Autohydrolysis and acid pretreatment can be mentioned as advantageous options when effective valorization of hemicellulose is desired, but the search for an optimal fractionation process for the complete valorization of lignocellulosic biomass is still a very hot topic. The application of ionic liquids and deep eutectic solvents can provide new opportunities for innovative pretreatment processes.

The hydrolysis of hemicellulose results in complex mixtures of sugars, being pentoses (xylose and arabinose) and hexoses (mannose, glucose and galactose) the main compounds. The biological

or chemical conversion of these saccharides to biofuels and bio-based chemicals is the best option for hemicellulose valorization. Several alternatives appear as interesting options for this conversion. The fermentation of sugars to produce bioethanol is a well-stablished valorization route for cellulose, but further adaptations are required for the case of hemicellulose. Since pentoses are not directly fermented by *Saccharomyces cerevisiae*, genetically modified strains or alternative microorganisms must be considered. Other fermentation options are available for the valorization of pentoses, such as the production of 2,3-butanediol, xylitol or lactic acid. The chemical valorization of hemicellulose may be highlighted to produce furfural and 5-hydroxymethylfurfural (or related compounds such as levulinic acid), which have high potential as building blocks for more complex chemicals. Xylo-oligosaccharides, which can be obtained by incomplete hydrolysis of the hemicellulosic polymer chain, are gaining interest because of their employment as prebiotics.

Nevertheless, the different potential valorization scenarios for lignocellulosic biomass must be evaluated and compared from a sustainability perspective (process engineering and life cycle assessment methodology can be very useful tools) in order to identify the most sustainable biorefining routes, taking into consideration the economic, environmental and social aspects. Moreover, even after this holistic consideration, the resulting optimized proposals cannot be easily extrapolated from one case to another. Different raw biomasses, geographic locations and target applications or markets are going to require different solutions.

Conflicts of Interest: The author declares no conflict of interest.

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