



On the R&D Landscape Evolution in Catalytic Upgrading of Biomass

Atif Emre Demet, Nathalie Tanchoux, Gabriele Centi, Rita de Luca, Siglinda Perathoner, Francesco Di Renzo, Walter Vermeiren

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SECTION 2

BIO-BASED PROCESSES AND BEYOND

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CHAPTER

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On the R&D Landscape Evolution in Catalytic Upgrading of Biomass

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OUTLINE

1 Introduction	3	5 Conclusions	22
2 Methodology	5	Acknowledgments	23
3 Overall Trends and Patterns of Evolution	7	References	23
4 Technical Analysis of Catalytic Conversion of Renewable Biomass	12		

1 INTRODUCTION

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Biomass, from vegetable or animal origin, is constituted by organic materials essentially consisting of carbon, hydrogen, and oxygen, along with significant amounts of nitrogen and small

amounts of other essential elements required for the metabolism of living material. The energy source of biomass is sunlight and the material source is carbon dioxide, converted through photosynthesis into carbohydrates. Other enzymatic metabolic mechanisms produce fatty acids, amino-acids, proteins, and complex aromatics, which are the basis of lignin

in plants. Plant biomass, which is essentially lignocellulose, stores solar energy and is often used as feed for animals—plants and animals together, forming the food for mankind. Other biomass types, such as wood, are used as construction materials and heat generation. Burning of biomass has always been the most direct way to use its contained energy, although two main constituents of certain biomass types are being converted into fuels to be blended with fossil-based gasoline and diesel. Biofuel production has been incentivized for sustainability reasons to reduce the carbon footprint of human transportation. Sugars (or starch) and triglycerides are the most accessible components for large amounts of energy storage in plants. Simple sugars can readily be fermented into ethanol and triglycerides can be catalytically converted into the corresponding methyl-esters, which can be blended with either gasoline or diesel. These constituents of first-generation biofuels are in competition with resources of food for humans and feed for ~~domesticated animals~~. The complex nature of biomass energy (lignin, carbohydrates, proteins, etc.) has limited its use to burning for heat and electricity generation. A further development has been to convert wood and food waste, agricultural residues, animal manure, and human sewage into biogas by fermentation into a mixture of methane and carbon dioxide.

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p0015

In the last decade a lot of progress has been made in diverting complex biomass to fuel applications. Hereto, lignocellulose is decomposed into its constituents, cellulose, hemicelluloses, and lignin. Cellulose and hemicelluloses can enzymatically be depolymerized, and the obtained simple sugars can be fermented into ethanol. Biotechnology research has flourished enormously and has resulted in plentiful applications to convert sugars into other chemicals (isobutanol, isoprene, isobutylene, farnesene, butanediols, lactic acid, succinic acid, etc.). At the same time, the scientific community and industrial developers have evaluated the

potential of nonenzymatic catalysis for biomass conversion. Catalysts have the advantage over enzymes to sustain higher temperature and pressure. On the other hand, they are generally less specific in product formation. Although in the fossil-based petrochemical and chemical industries, 85%–90% of the conversion processes employs catalysts and probably every marketable product has been in contact with a catalyst at least once. Still, most of the biomass-derived products are produced via fermentation or enzymatic pathways. The essential features of catalysis (whether heterogeneous, homogeneous, or enzymatic) is that they accelerate reactions, and according to the implied mechanism, they can do this with selectivity for one desired product.

Science and technology monitoring can be performed by the following two methods: state-of-the-art search, or innovation watch. The state-of-the-art search mainly focuses on the prior art of the related technology (one knows what one is looking for). It is a useful type of search method to determine the patentability of a product as part of a specific patent application or to prepare for new research projects (requiring background information). However, innovation watch is typically performed for technology landscape studies to comprehend beyond the state-of-the-art search in order to study the technological evolution of a particular field to identify and detect emerging technologies [1].

p0020

In 2015 and 2016, respectively, 2,887,300 and 3,127,900 patent applications were filed worldwide. Put another way, for the first time ever, more than 3 million patent applications were filed globally in 2016 in a single year, up 8.3% from 2015 [2,3]. China, the United States, and Japan are the first three main drivers of global scientific and technological growth. However, it is impressive that China by itself received more applications than the combined total for the United States, EPO, Japan and the Republic of Korea.

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Of all the global patent applications filed in 2016, 21.8% were in chemistry-related fields.

p0030

2. BIO-BASED PROCESSES AND BEYOND

TABLE 8.1 Published Patent Applications Worldwide by Field of Technology in Chemistry [3]

Field of Technology in Chemistry	2005	2010	2015	Share (%) of 2015	Average Growth (%) 2005–2015
Food chemistry	22,391	27,659	63,150	2.5	10.9
Microstructural and nanotechnology	2145	3366	4725	0.2	8.2
Materials, metallurgy	29,406	37,377	63,835	2.5	8.1
Basic materials chemistry	39,075	44,451	82,202	3.3	7.7
Environmental technology	20,880	25,776	42,979	1.7	7.5
Chemical engineering	33,619	36,887	60,479	2.4	6.0
Macromolecular chemistry, polymers	27,965	28,531	45,576	1.8	5.0
Surface technology, coating	27,962	32,222	42,671	1.7	4.3
Biotechnology	38,296	39,068	55,499	2.2	3.8
Pharmaceuticals	73,701	71,276	102,790	4.1	3.4
Organic fine chemistry	57,323	54,253	63,603	2.5	1.0
Total	374,768	402,876	629,524	24.9	4.8

Table 8.1 illustrates the published patent applications worldwide by field of technology in chemistry, as adapted from the World Intellectual Property Indicators 2017 [3]. Among them, pharmaceuticals, basic materials chemistry, and organic fine chemistry are the most contributing fields between 2005 and 2015; while food chemistry, microstructural and nanotechnology, materials-metallurgy are the three chemistry-related fields with the highest average growth rates over a decade. Average growth rate of all chemistry-related fields between 2005 and 2015 is 4.8%.

of biomass. Herein, the technology scope of biomass refers to algal and lignocellulosic biomass resources; whereas catalytic upgrading refers to conversion of the aforementioned biomass resources by various processes using heterogeneous catalytic routes.

Nonpatent literature (NPL) publications were retrieved from Scopus, which is the largest abstract and citation database of peer-reviewed literature, with more than 69 million core records. Approximately 3 million new items are added to the database each year [4,5]. NPL publications addressed in this study consist of articles, reviews, conference proceedings, book chapters, and articles in the press, which are covered in the Scopus database, matched with the search criteria performed within the search fields of title, abstract, and keyword.

Patent literature (PL) publications were retrieved from the Enhanced Patent Data of Derwent World Patents Index (DWPI). DWPI is the

2 METHODOLOGY

This section provides a detailed explanation of the dataset comprising both patent (PL) and nonpatent literature (NPL) covered under this R&D landscape study on the catalytic upgrading

2. BIO-BASED PROCESSES AND BEYOND

most comprehensive database of enhanced patent information in the world. The database is produced by Derwent Innovation—Clarivate Analytics and it includes data from over 50 worldwide patent authorities covering 72.7 million patent records and 34.7 million patent families [6]. DWPI has been selected as a PL data-source in this study to have a more enhanced and accurate dataset because it offers rewritten patent data by subject experts, which provide speaking titles and abstracts summarizing the novelty of the invention, as well providing unique coding and indexing. The Derwent abstract is generally much richer than the original abstract, which is merely a copy of the first claim. PL publications in this study consist of patent-related records which are covered in the DWPI database and fulfill the criteria performed within the search fields of title, abstract, and independent claims.

p0050 The first step in preparing such an R&D landscape study is to determine the main objectives and the boundaries of the technology scope. This study was conducted not only to compare the patent literature with the nonpatent literature, which covers the records on upgrading algal and lignocellulosic biomass resources by heterogeneous catalytic routes, but also to understand the overall trends and the technical patterns of evolution in the field. The terminology used in this study covers the technical language used by experts who cross-functionally work in in several technical fields: IP, catalysis, and renewable biomass energy.

p0055 In order to retrieve the relevant technological information from the databases, three levels of combined information were searched:

- o0010 1. The feedstock; biomass descriptors;
- o0015 2. Conversion routes: heterogeneous catalysts descriptors while excluding homogeneous and enzymatic catalysts as much as possible;
- o0020 3. Use of product: general applications as fuels, monomers, polymers descriptors; and identified chemical products descriptors.

p0075 Initially, the necessary principal keywords for the creation of search strings (queries) were

obtained by screening the related topics by highly cited review publications. The obtained keywords were categorized and segmented into the sets of keywords, like pieces of a puzzle, addressing various technical subgroups such as feedstock, conversion processes, biofuels, and value-added chemicals, type of solid catalysts, etc. Numerous searches were iteratively carried out; the results of each generation of search queries were sampled and systematically reviewed for verification and further evaluation. Hence the spectrum for each set of keywords was enriched by the addition of further key terms of interest, the synonyms and their derivatives generated using truncation operators (such as?, and *). Several tailor-made search strategies were crafted by logically linking the keyword-set of each technical sub-group with the keyword-set of others using Boolean (AND, OR, NOT, AND NOT), and proximity (ADJ/PRE, NEAR, “”) operators. The sample query below corresponds to the set of keywords belonging to the subgroup for biofuels and value-added chemicals. This search query was performed to collect relevant NPL records from the Scopus database, which fulfill the request within the fields of title-abstract-keywords, published in English between 1998 and 2017. Likewise, similar strategies were improved and applied for the creation of PL collection. As a last step, refinement strategies were performed to remove irrelevant results and to decrease noise, particularly excluding fermentation, bacterial- and enzyme-related keywords, only within title, in order to obtain a reliable and manageable dataset for PL and NPL collections remaining within the boundaries of the technology scope of this R&D landscape study.

For the sample query:

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(((TITLE-ABS-KEY((green OR sustainable OR u0010
renewable OR value OR valuable OR platform)
PRE/1 (bioplastic OR biomonomer OR
biopolymer OR biodiesel OR biogasoline)))
AND ((PUBYEAR > 1997 AND PUBYEAR < 2018)))
OR ((TITLE-ABS-KEY ((green OR sustainable

2. BIO-BASED PROCESSES AND BEYOND

OR renewable OR value OR valuable OR platform OR biobased) PRE/1 ("building block"))) AND ((PUBYEAR > 1997 AND PUBYEAR < 2018))) OR ((TITLE-ABS-KEY (green OR sustainable OR renewable OR value OR valuable OR platform OR biobased) PRE/1 (*fuel*))) AND ((PUBYEAR > 1997 AND PUBYEAR < 2018)))) OR ((TITLE-ABS-KEY (ethanol OR glycerol OR lactic OR hydroxypropionic OR succinic OR fumaric OR malic OR aspartic OR butyrolactone OR itaconic OR levulinic OR glutamic OR xylitol OR arabitol OR arabinitol OR valerolactone OR gvl OR glucaric OR sorbitol OR fdca OR hmf OR *furan* OR *furfural*)) AND ((PUBYEAR > 1997 AND PUBYEAR < 2018)))) AND (LIMIT-TO (LANGUAGE , "English"))

the final dataset consists of an NPL collection of 7866 nonpatent documents and a PL collection of 6485 patent family documents (November 2017). A patent family is the set of interrelated patent applications filed in one or more countries to protect the same or a similar invention by a common inventor and linked by a common priority (or priorities) [7]. The 6485 documents of simple or extended patent families in this study cover 15,978 patent records. Each patent family is represented by the representative patent of the family.

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p0090

The dataset (so-called "the entire collection") consist of 14,351 of (6485) PL and (7866) NPL documents, retrieved from DWPI and Scopus, and exported onto the Questel Intellixir analytics platform, where the documents were further organized and indexed for a deeper analysis of the merged PL and NPL dataset. The Intellixir analytics platform is an analysis tool in which data originating from different sources can be loaded and blended, normalized, and categorized according to custom fields. Complex value strings were created to generate specified custom fields in various technical fields for further analysis. A custom field corresponds to segmentation and so its values correspond to sub-segments, the aim being to categorize the

study content with the competence of experts, helped by Intellixir's vocabulary statistics or other glossaries or thesauri [1]. Value strings were mainly created within the fields of title-abstract-descriptors and title-abstract-claims for NPL and PL documents, respectively. Custom field value searches were iteratively carried out; the results of each generation of search queries were sampled and systematically reviewed for verification and further evaluation.

It should be emphasized that the categorization of documents using complex queries is only based on text-mining semantic retrieval and that neither manual interpretation nor corrections have been applied. The assumption is that the document titles and abstracts or claims are sufficiently explicit to underpin the added value of the document and minimize noise (which would be very significant when using the introductions of scientific publications or the prior art description of patents, where reference is made to the general framework of the discussed topic).

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3 OVERALL TRENDS AND PATTERNS OF EVOLUTION

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This section provides detailed information about overall trends of the patent and nonpatent documents covered under the R&D landscape of catalytic upgrading of biomass over the last two decades.

p0100

Because patent rights generally last for 20 years from the priority date the application was filed, the time coverage for this landscape study was determined as 20 years. The complete set of information by years through this period allows evaluating trends in the PL of a related field of technologies. Similarly, the publication years of NPL documents also cover the timeline between 1998 and 2017, thus allowing the comparison of the PL and NPL collections. Fig. 8.1 illustrates the temporal distribution of PL and NPL publications included in the dataset, which

p0105

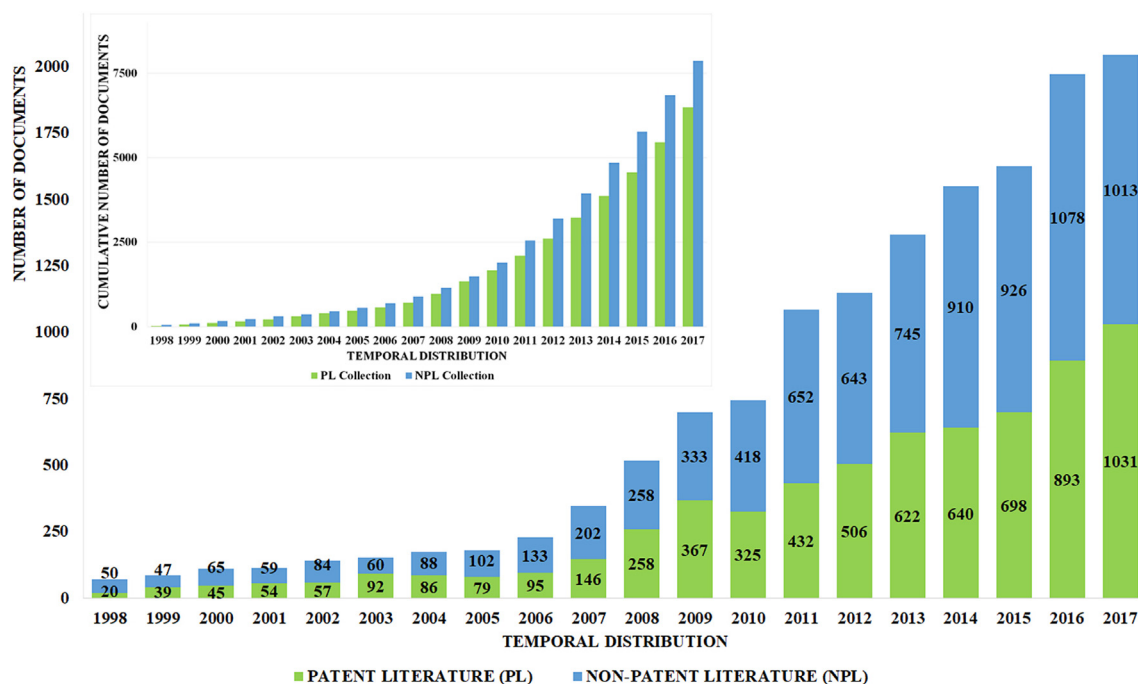


FIG. 8.1 Temporal distribution of the PL (green) and NPL (blue) publications in the R&D landscape study.

consists of 14,351 documents. Herein, PL documents correspond to patent families which are represented by the representative patent of the family. To be able to make a comparison with the NPL collection, the temporal distribution for PL documents was based on the first publication date instead of the priority date due to the delay between the filing of patents and the publication by patent offices, usually taking place 18 months later.

This temporal distribution demonstrates that the increase in the number of both PL and NPL documents, and the interest in catalytic upgrading of biomass have been continuously growing over the last two decades. There exist two distinct phases: a first phase between 1998 and 2007, (called “the previous decade”) and a second phase between 2008 and 2017, (called “the last decade”). The dataset of both PL and NPL for 2017 does not contain records from December 2017.

The increase in the number of PL and NPL documents on the second phase of this timeline is attention-drawing. Of the number of PL and NPL documents in this R&D landscape study, the average growth rate over the last decade corresponds to 14.8%, which is more than threefold the average growth rate of patent applications published worldwide in all chemistry related fields (see Table 8.1). Moreover, the growth rate of the number of documents in the PL collection (16.6%) is very similar to the growth rate of the number of documents in the NPL collection (16.4%). Despite this tiny difference, it can be expected that PL would contribute more documents than NPL to the entire collection in this technology scope. Indeed, the trend shows the primacy of NPL over PL in the contribution to the entire collection between 2004 and 2016 but eventually, in 2017, PL provided more documents than NPL to the entire collection.

2. BIO-BASED PROCESSES AND BEYOND

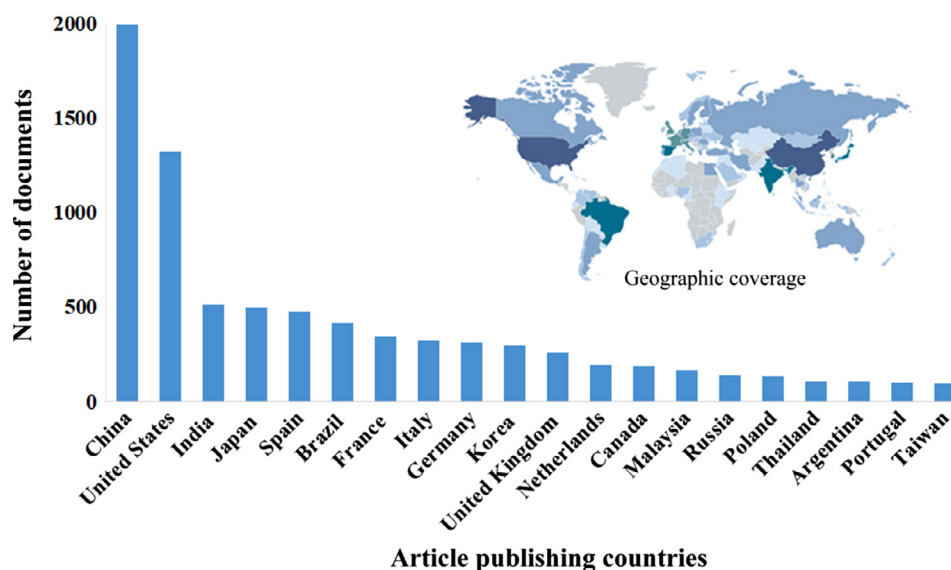


FIG. 8.2 The top 20 NPL countries and geographic coverage in the R&D landscape study.

Although it is recognized that the 2017 statistics collected are incomplete, as the dataset does not contain records of the entire year, the data suggest that 2017 is a trend-twist year in this R&D landscape. The 2017 data compared to the fraction of PL (45%) and NPL (55%) documents in the entire collection (the total number of PL and collections by years can be seen in the inset of Fig. 8.1), indicate an evolution in favor of patent literature. It is also expected that the growth of the entire collection will continue in the coming years. So far, there is no sign of reducing interest in catalytic conversion of biomass.

Fig. 8.2 shows the ranking of top 20 NPL countries and overall geographic coverage of 7866 nonpatent documents in this R&D landscape study. NPL documents were originated from 97 countries. China (20.6%) and the United States (13.6%) are the main contributing countries to the NPL collection. Thirteen of top 20 countries are in high-income economies; six are in upper middle-income countries (China, Brazil, Malaysia, Russia, Thailand and Argentina). The only country among the lower

middle-income economies is India, ranked third, with a 5.3% of the share. The remaining 17.4% NPL documents were produced by the rest of the world.

Fig. 8.3 represents the ranking of top 20 PL countries and the corresponding fraction of patent extension. The ranking is based on the geographical indications of all members of patent families in the PL collection of this landscape study: as mentioned earlier, the 6485 simple or extended patent family documents which cover 15,978 patent records. 6485 PL documents were first filed and identified by the priority number in 46 originating countries; the invention protection of 9494 PL documents has been expanded in 39 extended countries. Further details (number of patent applications, share, income level) of the top 20 patent-originating and extended countries are reported in Table 8.2.

Eleven of the top 20 all-patent countries are in high-income economies, five are in upper middle-income countries (China, Brazil, Malaysia, Russia, Thailand and Argentina) and two are in the lower middle-income economies

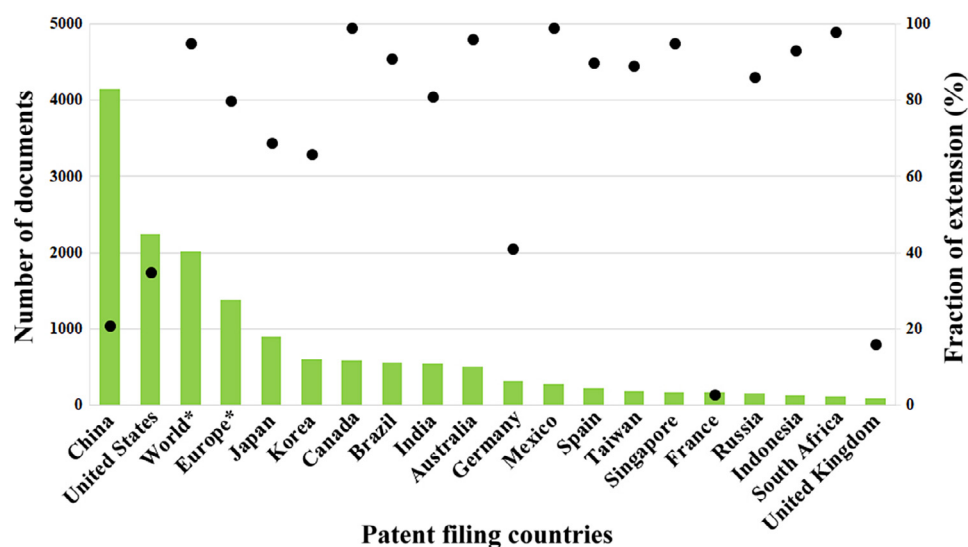


FIG. 8.3 The top 20 PL countries in the R&D landscape study. The number of filed patents and the fraction of extended patents are represented by green bars and black dots, respectively.

TABLE 8.2 The Top 20 Patent Originated and Patent Extended Countries in the R&D Landscape Study

Top 20 Originating Countries					Top 20 Extended Countries				
Ranking	Country	Patent	Share (%)	Income Level*	Ranking	Country	Patent	Share (%)	Income Level*
1	China	3280	50.6	Upper-middle	1	World*	1920	20.2	–
2	United States	1467	22.6	High	2	Europe*	1107	11.7	–
3	Japan	277	4.3	High	3	China	863	9.1	Upper-middle
4	Europe*	272	4.2	–	4	United States	777	8.2	High
5	Korea	202	3.1	High	5	Japan	620	6.5	High
6	Germany	191	2.9	High	6	Canada	579	6.1	High
7	France	165	2.5	High	7	Brazil	515	5.4	Upper-middle
8	India	101	1.6	Lower-middle	8	Australia	491	5.2	High
9	World*	100	1.5	–	9	India	443	4.7	Lower-middle

TABLE 8.2 The Top 20 Patent Originated and Patent Extended Countries in the R&D Landscape Study—cont'd

Top 20 Originating Countries					Top 20 Extended Countries				
Ranking	Country	Patent	Share (%)	Income Level*	Ranking	Country	Patent	Share (%)	Income Level*
10	United Kingdom	76	1.2	High	10	Korea	396	4.2	High
11	Brazil	50	0.8	Upper-middle	11	Mexico	278	2.9	Upper-middle
12	Italy	47	0.7	High	12	Spain	202	2.1	High
13	Russia	23	0.4	Upper-middle	13	Taiwan	169	1.8	High
14	Spain	23	0.4	High	14	Singapore	168	1.8	High
15	Taiwan	21	0.3	High	15	Russia	140	1.5	Upper-middle
16	Australia	19	0.3	High	16	Germany	134	1.4	High
17	Netherlands	18	0.3	High	17	Indonesia	128	1.3	Lower-middle
18	Finland	17	0.3	High	18	South Africa	115	1.2	Upper-middle
19	Denmark	15	0.2	High	19	Hong Kong	70	0.7	High
20	Sweden	14	0.2	High	20	Malaysia	65	0.7	Upper-middle

(India, Indonesia) and only 1.6% documents were produced in the rest of the world [8]. China (25.9%) and the United States (14%) are the leading countries of the PL collection in this R&D landscape study. Moreover, China and the United States are the main drivers of global growth in patent filings with 50.6 and 22.6% of share as shown in Table 8.2. “World” (12.6%) and “Europe” (8.6%), ranked as third and fourth, respectively, representing the patent records corresponding to the number of PCT and European patent applications. Applying PCT and European patents after the first filing is a mainstream strategy for the entities and attorneys due to several strategy- and cost-affecting factors such as maximizing delay in

the granting procedures, allowing postponing decision on where else to file. In this R&D landscape study, PCT (20.2%) and European patent (11.7%) extension applications were filed more than the national applications of other patent-extended countries.

The Patent Cooperation Treaty (PCT) is an international treaty under which a single international patent application can be filed for patent protection in up to 144 countries where patent protection is desired [7]. The filing of an international application will automatically constitute the designation of all contracting countries to the PCT on that filing date and the priority date will result in an extension of the period for entering the national stage to

30 months from the priority date [9]. Entering the national stage through European patent extends the priority date 31 months from the first filing date as the regulations and processes differ across national patent offices. The European patent is a patent which can be obtained for 38 contracting states of the European Patent Convention by filing a single application with the European Patent Office (EPO). European patents granted by the EPO have the same legal rights and are subject to the same conditions as national patents granted by the respective national patent office. A granted European patent is a bundle of national patents which becomes effective upon validation by the national patent offices of the countries selected by the applicant, after the official fees are paid [7,9].

p0140 In Fig. 8.3, the black dots represent the percentage of the extended patents on the sum of originated and extended patents in a specified country (called “fraction”). Because it is a preferable route for the entities to apply for a PCT or European patent after the national patent application, World and Europe have a high fraction ratio. The geographic coverage of a patent can be expanded in the countries in which protection of the invention is desired within a certain period of time. The fraction ratio corresponds the extended patents in a country to the sum of originated and extended patents in that specified country. A low fraction in a given country means that fewer countries are extending their originating patents to this country. The countries with the lower fraction ratio are France, the United Kingdom, China, the United States, Germany, Korea, Japan, and India; whereas the countries with the higher fraction ratio are Russia, Taiwan, Spain, Brazil, Indonesia, Singapore, Australia, South Africa, Canada, and Mexico. Higher fraction would be an indication of opportunities of deploying the patent-protected technology which can be linked to the fast development nature of the country or to its presence of large amounts of biomass. In Brazil, known as one of leading countries in biomass; only

50 patent applications have been filed, whereas 515 patent records were extended [10]. In other words, global entities extended the number of patents originated in Brazil more than tenfold. The trend in Brazil and Brazil-like countries highlights that these countries have potentially high amounts of assessable biomass resources, including where the new biomass-related technologies might be implemented.

Fig. 8.4 illustrates the intersections of top p0145 20 patent-originating countries and top 20 patent-extending countries for the patent records covered in the R&D landscape study. It is clearly seen that the United States is the major player as an overwhelming number of U.S.-originated patents not only extend through PCT or European applications but were filed throughout the world. China, Canada, and Brazil are the top three countries in where U.S.-originated patents extend the most. Contrarily, even though China is the first ranked country with 50.6% of the share and an important key player of global growth in patent filings (see Table 8.2), entities filing applications for Chinese patents follow a different behavior and rarely expand the geographical coverage of Chinese patent applications in other countries. This is undoubtedly due to the fact that China is a paramount production hub so most of the entities from other countries file by extending in China to protect their inventions. However, Chinese entities focus on protecting their technology which reflects that they stay local and have little intention of deploying their technology outside China.

4 TECHNICAL ANALYSIS OF CATALYTIC CONVERSION OF RENEWABLE BIOMASS

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This section provides detailed information p0150 and statistics that were obtained from the collections of PL and NPL in catalytic upgrading of biomass over the last two decades. The analysis not only allows making comparisons between

2. BIO-BASED PROCESSES AND BEYOND

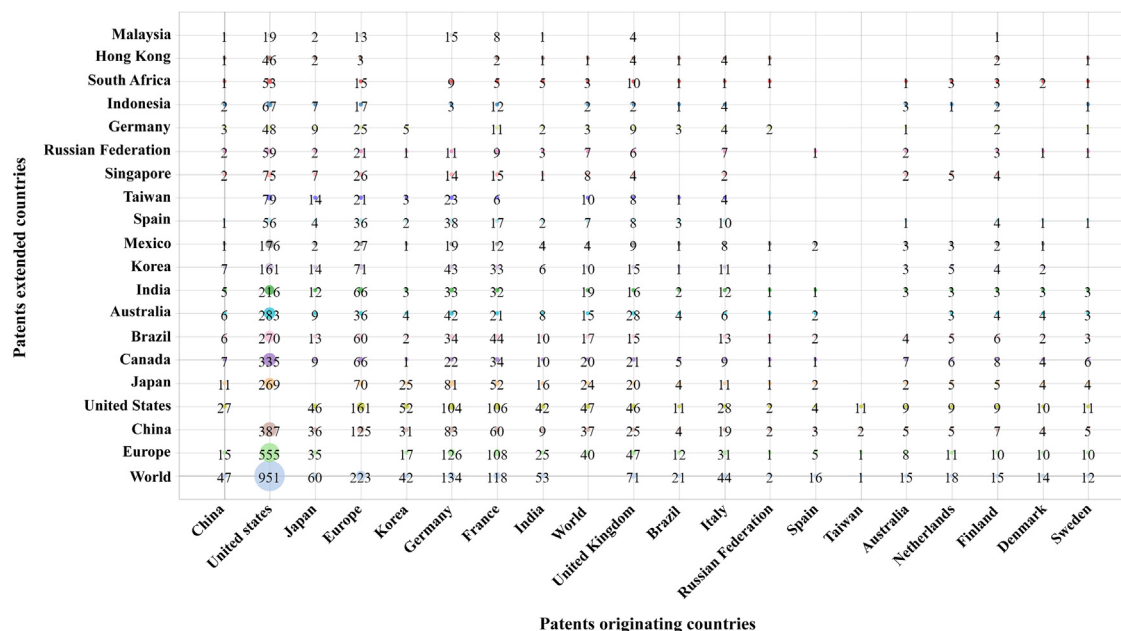


FIG. 8.4 The top 20 patent-originating and patent-extending countries for the patent documents covered in the R&D landscape study.

PL and NPL collections within the technology scope of the R&D landscape study, but also focuses on the patterns of evolution in various technical fields regarding heterogeneous catalysis, feedstock types, biomass conversion processes, and corresponding solid catalysts and biomass-derived chemicals. The technical field analyses were performed by counting the number of hits in the detailed, enriched, and verified custom fields on Intellixir.

Fig. 8.5 illustrates the temporal distribution of patent families and nonpatent literature publications associated with solid catalysis which are categorized in 4 main groups: metal, acid, base, and electro-catalysis with a distribution of 45.8%, 34.5%, 12.3%, and 7.4% respectively. This categorization is arbitrary but reflects the typical types of heterogeneous catalysis. Acid and base catalysis are related to clear distinguishable mechanism of catalysis, protonation (or electron withdrawal, generating intermediate cations),

and deprotonation (or electron donation, generating intermediate anions) linked to the nucleophilic or electrophilic nature of the substrate. Metal catalysis is still a broad field of catalysis characterized by many different mechanisms, but in general terms metal catalysis is about redox reactions like hydrogenation-dehydrogenation and reduction-oxidation. Electrocatalysis has been regarded as a particular class of catalysis as it is an emerging field, although it can be considered part of metal catalysis that implies electrochemical reactions. Where in other types of catalysis the reaction of or between chemicals is accelerated, electrocatalysts assist in the transfer of electrons from or to power sources between the electrodes and reactants or products, and hence accelerate the transformation into a selective product by an overall half-reaction. They are thermodynamically governed by the total energy available to do work (e.g., producing electricity instead of reaction heat like in a fuel cell or

2. BIO-BASED PROCESSES AND BEYOND

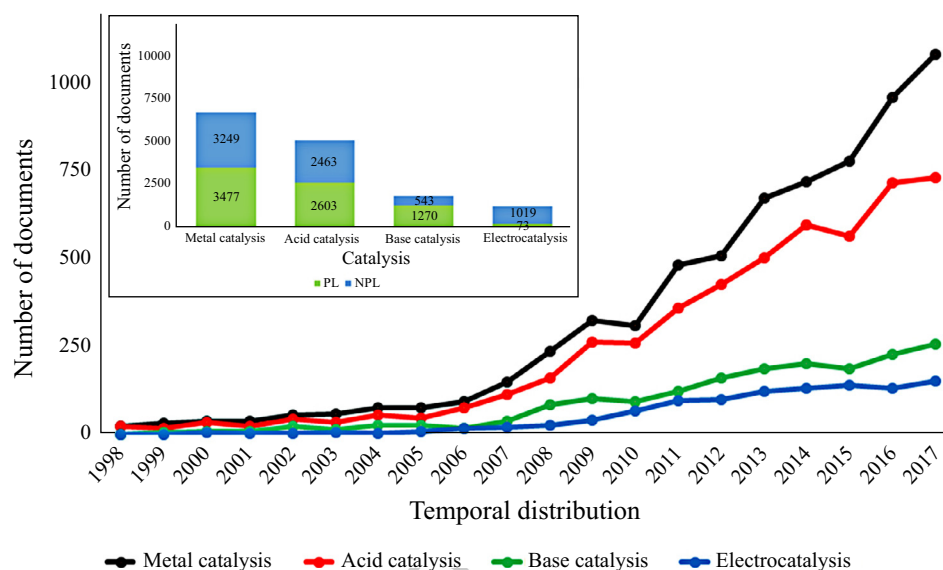


FIG. 8.5 Temporal distribution of heterogeneous catalysis-related documents within the PL and NPL collections of the R&D landscape study. Metal, acid, base and electrocatalysis are represented by black, red, green, and blue lines, respectively.

consuming electricity instead of high temperature heat for thermolysis/electrolysis of water).

It is notable that 50.5% of documents, which responded to the related custom field value strings used for the temporal distribution of catalysis, come from PL publications while 49.5% of them are among the NPL documents of the entire collection. The total number of documents categorized in the four fields of catalysis is significantly higher in case of PL (7423 [115%] categorized versus 6485 original documents), while lower in the case of NPL (7274 [92%] categorized versus 7866 original documents). No detailed explanation has been looked into for this but it may point to a less-specific nature of patents (a broader scope of claims in general) compared to scientific publications or eventually the use of multifunctional catalysts in PL, reflecting the industrial innovation purpose of patents where often a final marketable product is envisioned (requiring multifunctional conversions). But in a scientific publication, a precise catalytic composition or

reaction is elucidated. From 2007 onwards, rapid growth is observed in metal and acid catalysis-related publications covered in the R&D landscape study. Base catalysis and electrocatalysis seem not yet to have found a large place in biomass upgrading. However, it might be expected that the potential of electrocatalysis is high, as electrocatalysis allows the catalyzing of very specific reactions, in particular, for temperature-sensitive reactants or products, as they often occur at reasonably low temperatures. The use of electrons in reducing reactions is an appropriate way to convert highly oxygenated compounds (where carbon has a fairly high formal oxidation state, around 0 for sugars and around -1 for lignin) into hydrocarbon type compounds (where carbon has a low formal oxidation state, between -2 and -3). Reaction mechanisms, which require base catalysis (typically nucleophilic), are less appropriate as a highly oxygenated biomass is itself already rather nucleophilic and hence less prone to nucleophilic activation.

2. BIO-BASED PROCESSES AND BEYOND

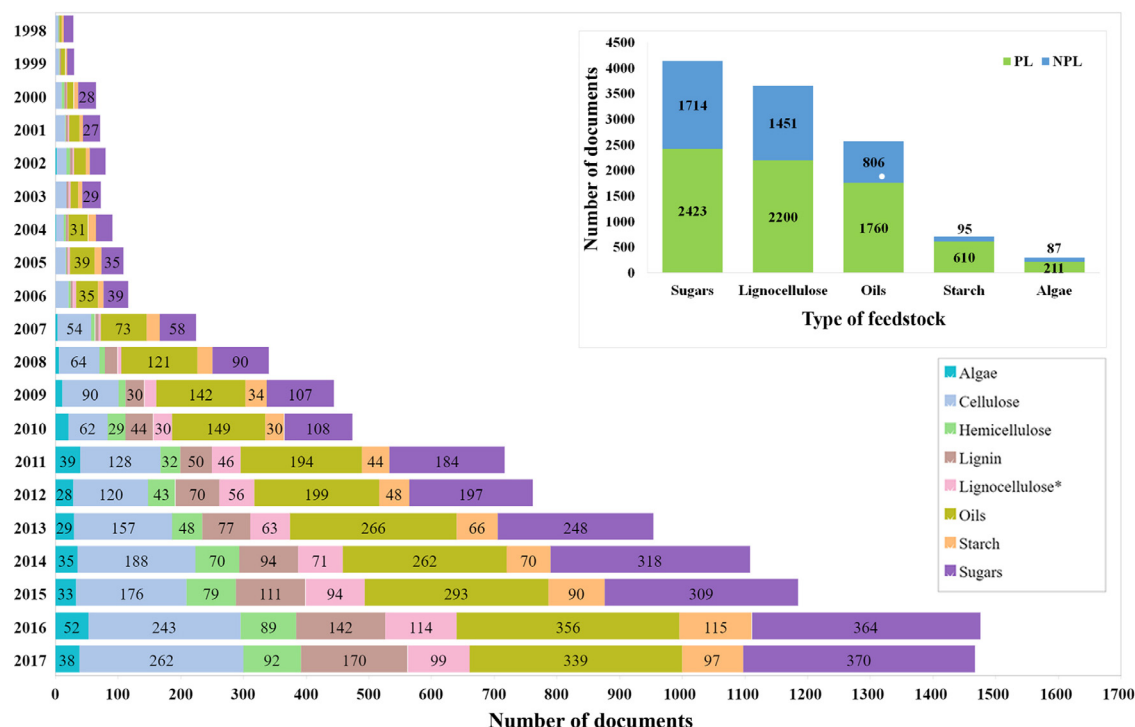


FIG. 8.6 Temporal distribution of feedstock-related documents within the PL and NPL collections of the R&D landscape study.

Fig. 8.6 illustrates the temporal distribution of patent families and nonpatent literature publications associated with different types of biomass feedstock used in the catalytic transformation. In principle, they all originate from biomass, but such categorization reflects the need for isolated and purified components of it in order to use heterogeneous catalysts for the transformation. As shown in the inner Fig. 8.6, the types of biomass feedstock are clustered in five main groups: sugars (glucose, fructose, sucrose, xylose, lactose, and arabinose), lignocellulose (lignocellulose, cellulose, hemicellulose, and lignin), oils, starch, and algae with a distribution of 36%, 32%, 23%, 6%, and 3%, respectively. Sixty-three percent of documents, which responded the related custom field value strings used for the temporal distribution of biomass feedstock type, come from PL

publications, while 37% of them are among the NPL documents of the entire collection. This distribution of responses is in line with the documents on types of catalysis, again reflecting the dominance of PL. As mentioned earlier, the increase over the last decade in PL and NPL publications on biomass conversion is striking, as seen on the main graph in Fig. 8.6. Here, the occurrence of different subclasses of biomass reported in the document's title, abstract, or keywords have been counted against time. 2007 was the pivotal year, with a nearly exponential growth in publications. A twofold-or-more increase of publication numbers between 2011 and 2017 was observed for all types of feedstock with exception of algae. The stagnation in the number of algae-related documents can be explained by their complex nature (typically the

2. BIO-BASED PROCESSES AND BEYOND

order of components occurrence is: proteins >carbohydrates>lipids) but certainly by their still-lower availability compared to lignocellulosic materials like wood and agricultural crops or wastes (rich in carbohydrates and lignin but with very little proteins). However, it should be considered that fermentation-like processes (enzymatic, microbial, and bacterial) and thermal conversion processes (pyrolysis and hydrothermal conversion, typically employed as first process step to upgrade algae) were out of the technology scope of this R&D study. Moreover, lignin, seen as a byproduct/waste from lignocelluloses fractionation to obtain carbohydrates, receives enhanced attention for catalytic conversion. A similar trend is seen for hemicelluloses, another fraction of lignocelluloses obtained as waste of cellulose extraction.

Fig. 8.7 shows the top 25 biomass conversion processes (reflecting the type of chemical transformation) and the corresponding solid acid, base, metal, or electrocatalysts within the PL

and NPL collections of the R&D landscape study. The occurrence numbers, at the intersections of conversion processes and type of catalysis, corresponds to the number of documents that fulfill the retrieval criteria for the associated values of the custom fields generated on Intellixir.

The subset of metal catalysts has been expanded according to the most reported types of metals. The rationale is that often each metal has a particular catalytic effect and hence catalyzes a given reaction with the appropriate selectivity for a given product. This means that the mechanisms of metal-catalyzed reactions are in general very different from one metal to another. In the case of acid and base catalysts, the reaction mechanism is, in general, less differentiated—acid catalysts have the ability to deliver protons, whereas basic catalysts abstract protons. Electrocatalysis is essentially linked to oxidation reactions. Most publications deal with fuel cell applications, where electrons are transferred

Processes	Acid catalysis	Base catalysis	Electrocatalysis	(Ni)	(Pd)	(Cu)	(Pt)	(Fe)	(Co)	(Ru)	(Zn)	(Mo)	(Au)	(Rh)	(W)	(Mn)	(Cr)	(Ag)	(V)	(Re)	(Ir)
Amination	34	31	2	27	19	20	12	14	17	12	13	10	8	9	6	10	7	9	10	8	7
Saccharification	35	20	1	4	2	4	2	3	1	3	2	1	1	2	1	2	1	2	1	1	1
Hydrocracking	52	28	1	33	8	16	12	12	21	12	10	19	2	6	16	6	8	2	5	5	4
Oligomerisation	60	23	2	19	14	10	10	4	10	7	7	3	1	5	3	3	6	4	3	4	2
Decarbonylation	45	19	3	17	18	11	13	6	12	5	13	7	1	3	6	7	10	2	9	1	1
Fischer-Tropsch	36	33	2	22	10	18	10	23	25	19	12	16	5	10	9	8	16	5	8	14	6
Decarboxylation	57	35	2	19	15	12	15	5	13	4	16	12	2	3	11	7	7	5	5	1	2
Aldol condensation	65	51		12	12	11	11	5	7	7	3	2	2	3	3	3	3	4	4	3	4
Depolymerization	84	56	3	25	20	12	17	14	13	17	14	22	2	6	15	7	9	2	6	4	6
Deoxygenation	84	38	7	34	30	22	27	14	19	19	15	36	6	11	22	8	11	7	10	14	9
Liquefaction	93	49	3	29	19	11	18	21	19	14	15	17	3	13	11	4	9	6	5	5	11
Etherification	169	71		15	12	16	12	7	14	8	18	8	3	5	10	9	7	3	2	5	5
Alkylation	164	67	2	31	26	22	18	20	16	15	26	12	7	11	10	12	11	8	8	9	8
Hydrodeoxygenation	130	51	9	68	53	30	48	30	42	37	14	50	9	16	29	4	15	9	8	15	22
Isomerisation	204	86	4	41	35	20	32	10	23	30	16	24	5	11	18	11	16	4	15	15	5
Cracking	188	80	6	65	37	31	29	40	41	20	29	38	4	17	30	12	17	10	8	11	9
Hydrogenolysis	144	82	9	81	54	54	33	34	34	70	28	20	7	30	34	11	15	12	7	30	27
Pyrolysis	256	106	34	89	43	36	49	59	52	36	27	52	7	27	38	14	20	7	12	13	14
Polymerisation	331	310	40	48	40	59	18	45	41	28	96	33	12	13	29	29	23	18	24	10	7
Esterification	665	405	11	31	37	53	21	40	42	22	83	25	24	15	34	30	15	10	18	4	4
Condensation	560	452	20	125	113	122	104	95	89	69	126	63	36	60	48	54	57	38	35	39	35
Hydrolysis	727	436	35	150	99	126	93	109	77	115	89	57	31	45	52	34	41	34	27	32	42
Dehydration	1196	440	23	152	111	147	103	111	104	85	129	60	34	60	73	55	63	32	65	37	29
Hydrogenation	716	474	45	514	460	414	369	222	280	437	209	214	118	215	167	106	153	88	67	180	159
Oxidation	647	619	1068	249	316	233	351	210	206	190	147	139	282	115	106	160	91	107	139	74	72

FIG. 8.7 The top 25 biomass conversion processes and corresponding solid catalysts (the group of metal catalysts has been expanded according to metal type) within the PL and NPL collections of the R&D landscape study.

2. BIO-BASED PROCESSES AND BEYOND

from fuels to molecular oxygen. Acid catalysts are essentially linked to types of reactions like dehydration, hydrolysis, condensation, cracking, isomerization, esterification, and polymerization. The significant intersection between hydrogenation and oxidation with acid catalysis is explained by bifunctional catalysts requiring both an acid and a metal function, or by a combination of different kinds of consecutive reactions and hence catalytic functions. A typical example is the synthesis of FDCA from sugars, requiring acid-catalyzed isomerization of glucose into fructose, acid-catalyzed dehydration into HMF, and several further oxidation steps using metal-type catalysts. Basic catalysis is in particular important for condensation (carbon-carbon bond formation) and esterification (e.g., biodiesel synthesis from triglycerides to methyl-esters). Moreover, the basic nature of the supports for hydrogenation and oxidation metal-catalyzed reactions explains the significant amount of intersection hits matching for these processes with basic catalysis. Base-catalyzed dehydration is presumably related to several condensation reactions including a dehydration step making enones or enals (conjugated ketons/aldehydes).

p0180 In 2004, the US Department of Energy (DOE) identified the top 12 most-relevant compounds derived from biorefinery carbohydrates [11]. Twelve building block chemicals (molecules with multiple functional groups, which can be transformed into other marketable derivatives and which can be produced from carbohydrates via biological or chemical conversions, were described in detail. The 12 sugar-based building blocks are 1,4-diacids (succinic, fumaric, and malic), 2,5-furan dicarboxylic acid, 3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinitol. The selection was based on the potential of such molecules for further development in commercially valuable products. The intent of the report was to catalyze research

efforts to develop industrial applications and identify the common challenges and barriers of associated production technologies. In 2010, Bozell et al. reported on the considerable progress made in the use of carbohydrates as starting materials for chemical production [12].

Fig. 8.8 displays the temporal distribution of the top 25 biomass-derived chemicals within the PL and NPL collections of the R&D landscape study over the last two decades. The selection of the top 25 is merely based on the occurrence of documents reporting them. The feedstock is now not limited to carbohydrates but includes all lignocellulosic biomass. The custom field-value string for each biomass-based chemical was based on a search within title, abstract, and keywords for NPL documents; and within title, abstract, and claims for PL documents among the entire collection and on retrieval of the matching documents. The only exception was performed for ethanol, due to unacceptable high noise in the results. Although a decrease in the actual number of ethanol-related documents was expected, the value string was limited to the title for PL and NPL documents in order to have more sensible results. The general trend for biomass-derived chemicals is a steady growth over time. However, the activity on given molecules and their growth rates vary from one to another. In order to better monitor their patterns of evolution, compound annual growth rates (CAGR) of the top 25 biomass-derived chemicals were evaluated between 1998 and 2007, 2008 and 2017, and 1998 and 2017, as reported in Table 8.3, which also summarizes the percentage of PL documents with the total number of PL and NPL documents for each biochemical. The color-ranking was applied to each column to illustrate the numeric comparison. Each cell of a column has a shade of color, shifting from dark green for the highest numeric value, to lighter colors, and ultimately dark red for the lowest numeric value in the column. The highest growth rates through the whole 1998-to-2017

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2. BIO-BASED PROCESSES AND BEYOND

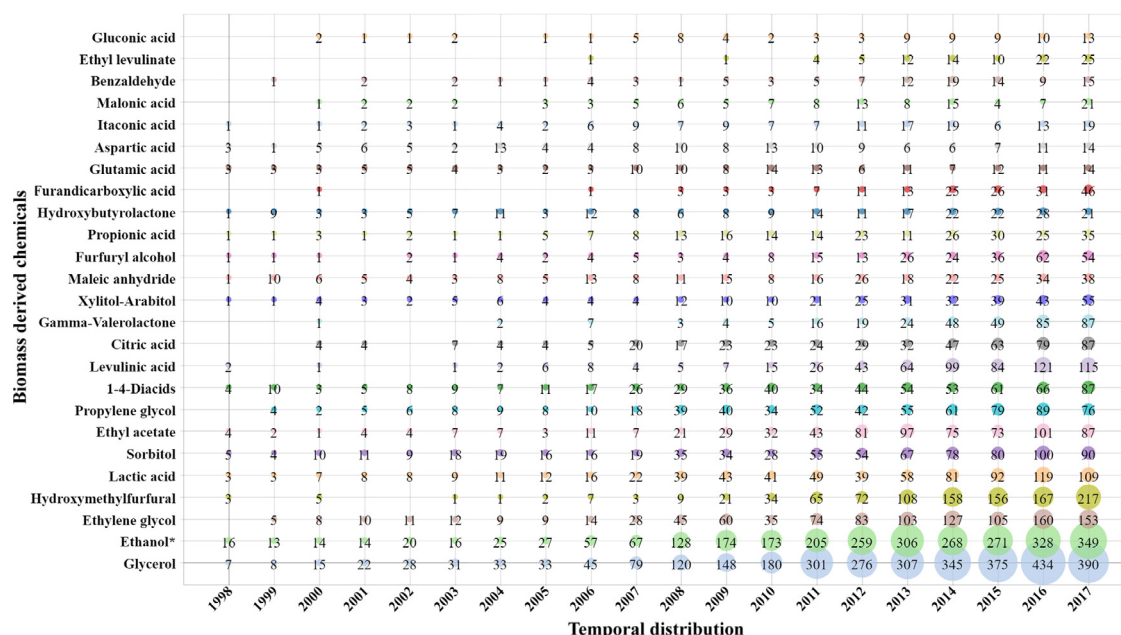


FIG. 8.8 Temporal distribution of the top 25 biomass-derived chemicals within the PL and NPL collections of the R&D landscape study.

period, among these 25 biochemicals are observed for glycerol, ethanol, ethylene glycol, and 5-hydroxymethylfurfural. Their green-shaded cells indicate where the CAGR is well above the average. The presentation of the data of the decades 1998–2007 and 2008–2017 in two separate columns allows to identify some tendencies of evolution of the compound growth rate. The CAGR of maleic anhydride, hydroxybutyrolactone, and some organic acids (propionic, malonic, itaconic, gluconic, glutamic, and aspartic acid) are lower in the last of the two decades, with lower publication activity. Their white-colored cells indicated that there was an attention for them over the previous decade; whereas the color change of the cells to red, where the CAGR is below the average, indicates that attention on those chemicals decreased over the last decade. In particular the latter organic acids, which were considered in the top 12 in 2004, are not presently receiving the expected

attention. Contrarily, 5-hydroxymethylfurfural (HMF), levulinic acid, gamma-valerolactone, furfuryl alcohol, and 2,5-furandicarboxylic acid (FDCA), follow an opposite trend. These promising compounds have a negligible number of records belonging to the previous decade (low CAGR between 1998 and 2007, represented by the red cells) in comparison to the last decade (high CAGR between 2008 and 2017, represented by green cells), in which the number of patent and nonpatent literature publications has boosted dramatically. Explicitly, HMF and levulinic acid are the most attention-drawing molecules with 1029 and 603 PL and NPL records, respectively.

The number of hits of conversion processes and type of catalyst corresponding to each of the top 25 biomass-derived chemicals within the PL and NPL collections of the R&D landscape study are shown in Figs. 8.9 and 8.10. It should be remembered that computer-based

TABLE 8.3 Evaluation of the Top 25 Biomass-Derived Chemicals Within the PL and NPL Collections of the R&D Landscape Study

Biomass derived chemical	Cagr (%) (1998–2007)	Cagr (%) (2008–2017)	Cagr (%) (1998–2017)	PL (%)	# of PL and NPL documents
Glycerol	61.1	81.7	36.8	44	3177
Ethanol*	58.9	78.9	35.8	29	2730
Ethylene glycol	46.0	65.0	30.3	79	1051
Propylene glycol	42.3	50.1	25.6	27	637
Lactic acid	41.7	58.3	27.8	58	769
1-4-Diacids	39.4	53.7	26.2	64	604
Sorbitol	38.5	54.7	26.3	85	748
Citric acid	36.0	56.0	26.5	84	472
Ethyl acetate	27.4	57.1	26.2	82	689
Xylitol-arabitol	22.7	50.0	23.4	33	312
Maleic anhydride	25.3	42.3	20.9	90	276
Propionic acid	26.7	40.0	20.4	31	237
Malonic acid	19.7	33.4	17.4	71	112
Hydroxybutyrolactone	20.8	32.0	17.1	90	220
Itaconic acid	22.7	28.7	16.4	37	144
Gluconic acid	21.8	21.8	14.5	89	83
Glutamic acid	22.7	15.7	13.5	68	147
Aspartic acid	20.8	18.5	13.5	48	145
Hydroxymethylfurfural	12.3	75.7	32.6	56	1029
Levulinic acid	10.1	64.1	28.2	57	603
Gamma-valerolactone	4.4	59.7	26.5	85	350
Furfuryl alcohol	12.3	51.0	23.2	95	266
Furandicarboxylic acid	4.4	49.1	22.3	65	170
Ethyl levulinate	0.0	40.3	18.5	21	94
Benzaldehyde	7.6	31.0	15.3	73	104

text-mining does not differentiate between bio-chemicals, which are reactant, intermediate, or products. Hence the intersections merely refer to the link between each chemical and conversion process or type of catalyst.

Some specific examples illustrate the richness of information which can be drawn from open NPL and PL. Fig. 8.11 displays a schematic illustration of the relationship between the most promising biomass-derived chemicals of the last decade: 5-hydroxymethylfurfural (HMF), levulinic acid, gamma-valerolactone, furfuryl alcohol, 2,5-furandicarboxylic acid, and ethyl levulinate.

HMF, an important bio-based platform molecule for the production of liquid fuels and fine chemicals, is a dehydration product of monosaccharides. Various effective and reusable heterogeneous catalysts are utilized, instead of homogeneous acids, for the selective dehydration of glucose and/or fructose to HMF, such as Amberlyst-15 [13], mesoporous tantalum phosphate or tantalum oxide [14,15], binderless zirconium phosphate coating on aluminum foam [16], Zr containing mesoporous MCM-41 silica [17], H-, Fe- and Cu-ZSM-5 [18], layered zirconosilicate [19], zirconium phosphate [20], phosphotungstic acid encapsulated in

2. BIO-BASED PROCESSES AND BEYOND

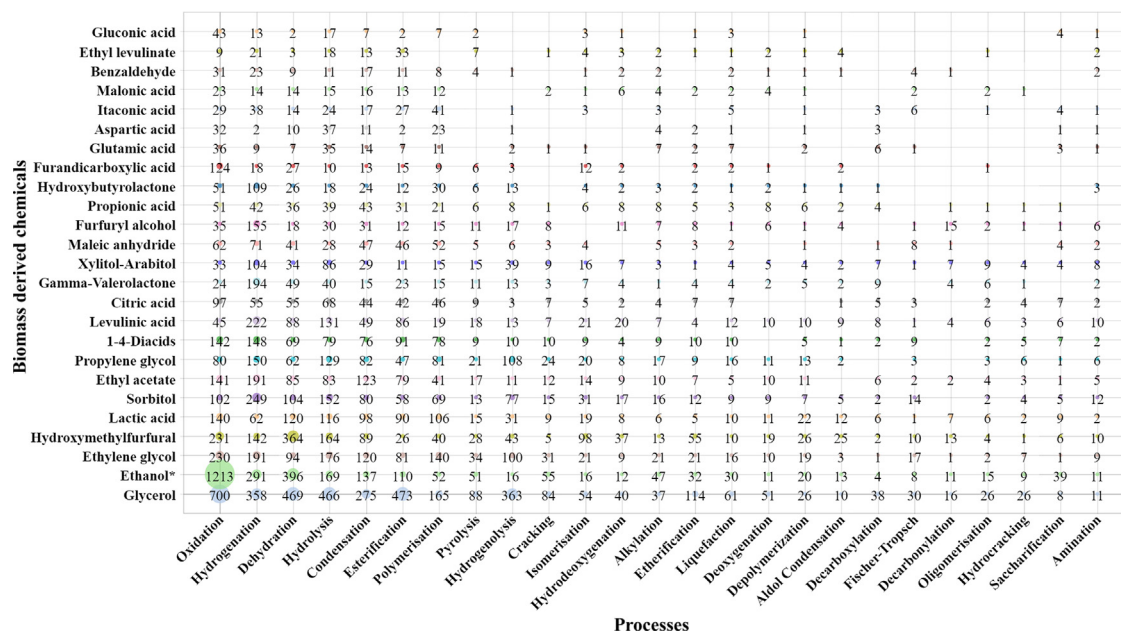


FIG. 8.9 The top 25 biomass-derived chemicals and corresponding conversion processes within the PL and NPL collections of the R&D landscape study.

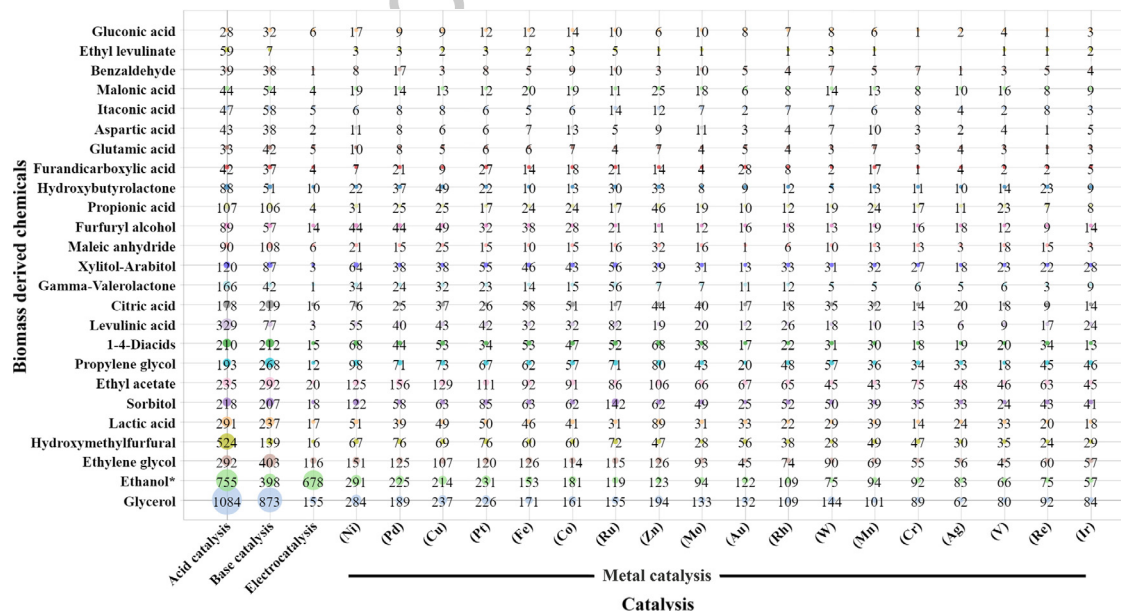


FIG. 8.10 The top 25 biomass-derived chemicals and corresponding solid catalysts within the PL and NPL collections of the R&D landscape study.

2. BIO-BASED PROCESSES AND BEYOND

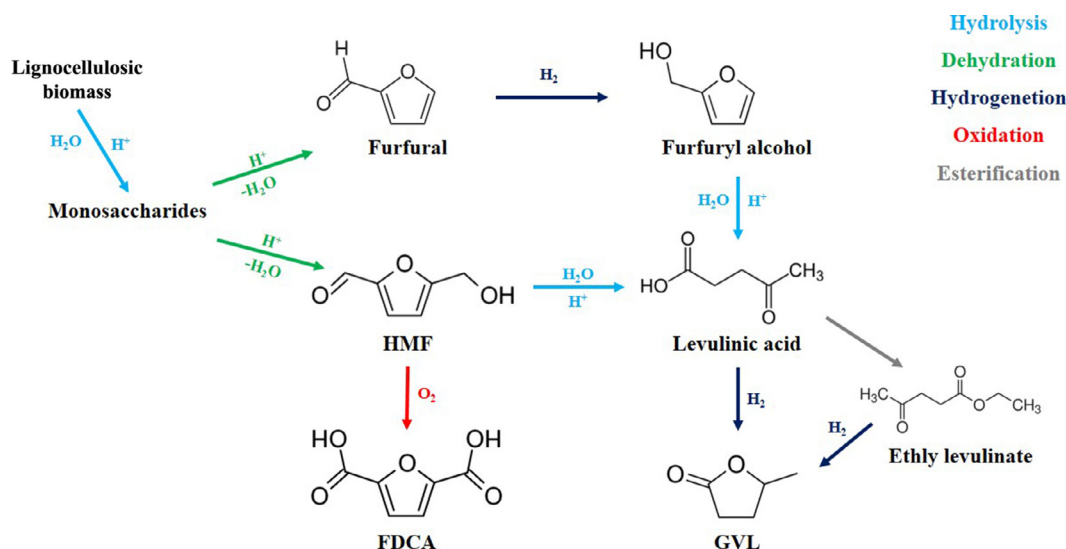


FIG. 8.11 The schematic illustration of the relations between the most attractive value-added biomass-derived chemicals over the last decade.

metal-organic framework [21], mesoporous niobium phosphate [22], sulfated ZrO_2 hollow [23], Cr-based heteropoly acid ionic crystal [24], and phosphorylated mesoporous carbons [25].

The cascade oxidation process of HMF, involving several intermediates in parallel or successive reactions, allows synthesizing 2,5-furandicarboxylic acid. FDCA is one of the most attractive reactions for establishing biomass-based sustainable chemical processes. It is a promising renewable alternative to petroleum-derived terephthalic acid as a polymer precursor to produce recyclable biobased polymers, similar to PET. Pd-modified Au on carbon [26], carbon nanotube supported Au–Pd alloy [27], gold nanoparticles supported on nanoparticulate ceria and on titania [28], Pt-loaded reduced graphene oxide [29], Pt/ $\gamma\text{-Al}_2\text{O}_3$ [30], MnCo_2O_4 spinel supported Ru catalyst [31], nano- $\text{Fe}_3\text{O}_4\text{-CoO}_x$ [32], $\text{MnO}_x\text{-CeO}_2$ mixed oxides [33], and MnO_2 [34] have been proposed as selective oxidation catalysts.

Levulinic acid is considered as a versatile building block because it can be used for the

synthesis of several organic chemicals. Levulinic acid is formed by dehydration in acidic media of sugars to HMF which, upon subsequent hydration, produces levulinic acid, along with equimolar amounts of formic acid. Bimetallic oxide catalysts, such as $\text{WO}_3\text{-Ta}_2\text{O}_5$, are promising to simplify the process of converting saccharides into HMF and levulinic acid in one-pot reactions [35]. The alternative process involves the dehydration of saccharides to furfural, subsequent hydrogenation to furfuryl alcohol which is finally hydrolyzed to levulinic acid. Cu-doped niobium phosphate catalysts could catalyze furfural conversion to levulinic acid through a one pot single-step process. [36] The one-pot reactions are attractive due to exempting the separation and purification processes of the intermediates.

Ethyl levulinate, a biofuel additive, can be produced through the esterification reaction of levulinic acid with ethanol catalyzed by amberlyst-15 and sulfated SnO_2 [37], both ZrO_2 -supported phosphotungstic acid catalysts [38,39]. Furthermore, zirconium-based MOFs [40] using

2. BIO-BASED PROCESSES AND BEYOND

isopropanol as a hydrogen donor could be applied for catalytic transfer hydrogenation of ethyl levulinate to form gamma-Valerolactone (GVL), which is one of the paramount building blocks for the production of fuels and chemicals based on renewable feedstocks. As an alternative route, GVL can be obtained directly by the hydrogenation of levulinic acid, can be catalyzed by a ruthenium-supported catalyst in combination with a heterogeneous acid cocatalyst, such as the ion exchange resins Amberlyst A70 or A15, niobium phosphate, or oxides [41,42]. Additionally, Ru, Pt, and Pd noble metals supported on carbon [43], Ru-P/SiO₂ [44], Ni/SiO₂ [45], RuSn bimetallic catalysts [46], iridium nanoparticles supported on carbon nanotubes [47] and Ru/Mg-LaO-mixed oxide [48] have been proposed as selective hydrogenation catalysts of levulinic acid to GVL.

p0220 Heterogeneous catalysis have been employed for the conversion of well-defined reactants aiming a high selectivity for one given chemical. In the field of biomass upgrading, heterogeneous catalysis has been pushed further to its potential. Three examples are worth mentioning as they intend to convert raw biomass and lignocelluloses into intermediates or marketable products.

p0225 The concept of lignin-first biorefining of lignocelluloses using a supported ruthenium catalyst in the presence of hydrogen has been reported in 2015 [49,50] and is being taken up by many other researchers [51,52]. By using an appropriate solvent, like methanol, lignocellulose can be solvolyzed and hydrogenolyzed in one step into valuable carbohydrate pulp and liquid lignin oil. The lignin oil is composed of monomeric phenolic compounds next to some phenolic oligomers. This unconventional deconstruction of lignocellulose, lignin is simultaneously detached from the polysaccharide fibers, depolymerized and passivated by reductive conversion in the presence of a heterogeneous catalyst and hydrogen.

p0230 Another direct lignocelluloses catalytic conversion process is that developed by Gas Technology Institute, IH² being an integrated

hydropyrolysis of raw biomass in a two-reactor process [53]. Whereas pyrolysis of biomass results in very oxygenated compounds (>30 wt% resulting in low pH) next to significant amounts of soluble water (~20 wt%), requiring complex post-treatment [54,55], the IH² process can directly convert biomass to hydrocarbon transportation fuels through the use of hydropyrolysis or integrated hydropyrolysis plus hydroconversion. The first catalytic step of hydropyrolysis is carried out in a fast fluidized bed under 14–35 bar of hydrogen pressure with an effective deoxygenation catalyst, similar to hydrotreatment catalysts (sulfide CoMo or NiMo catalysts, [56,57]). It directly produces fungible hydrocarbons with a TAN (Total Acid Number) of less than 1, which can either be directly fed to a refinery for coprocessing or polished in an integrated hydroconversion reactor to produce gasoline and diesel with less than 1% oxygen.

Carlson et al. recognized that pyrolysis and catalytic conversion can be done in the same reactor vessel which was the basis of the start-up company, Anellotech [58]. The catalytic fast pyrolysis (CFP) process directly converts solid biomass to gasoline-range aromatics rich in BTX: benzene, toluene, and xylenes. CFP involves the rapid heating of biomass (500°C/s) in an inert atmosphere to intermediate temperatures (400–600°C) in the presence of zeolite catalysts. In addition to aromatics, some valuable light olefins, such as ethylene and propylene, are produced. The understanding is that the biomass pyrolyses into furan-type intermediates, small enough to enter in the zeolite pores, where they are converted into aromatics and light olefins. The oxygen in the biomass is expelled as carbon oxides and water.

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
p0240

5 CONCLUSIONS

In this chapter, R&D landscape on the catalytic upgrading of biomass over the last two decades is monitored by data-mining. More

2. BIO-BASED PROCESSES AND BEYOND

than 14 thousand patent and nonpatent literature documents, covered within the boundaries of the determined technology scope and published between 1998 and 2017, were retrieved from Scopus and DWPI then multidimensionally analyzed using Intellixir by the experts who cross-functionally work in catalysis, renewable biomass energy, intellectual property, and technology intelligence. The continuous growth in the number of PL and NPL records over the last two decades explicitly demonstrates the increase of the global attention on the catalytic conversion of renewable resources. The various types of proposed solid catalysts indicate the importance of the heterogeneous catalysis on the biomass upgrading. The number and growth of PL and NPL documents is very similar, reflecting that both the academic community and the industrial potential developers have similar interests.

 p0245 ~~Green and red cells, respectively, illustrate whether the numeric value is above the average or below the average value of the cells of columns, which report~~ compound annual growth rate (CAGR) between 1998–2007, 2008–2017, and 1998–2017; the percentage of PL documents; and the cumulative number of PL and NPL of the top 25 biomass derived chemicals.

st0045 Acknowledgments

p0250 This work received the support of the ENSCM (Ecole Nationale Supérieure de Chimie de Montpellier) and of SINCEM (Sustainable INdustrial CHEMistry), a joint doctorate programme selected under the Erasmus Mundus Action 1 Programme (FPA 2013-0037).

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2. BIO-BASED PROCESSES AND BEYOND

Non-Print Items

Abstract

For the last decade, the scientific community and industrial developers have been searching for improved methods to convert biomass into valuable products in order to respond to enhanced sustainability considerations. In this development, catalysts play an essential role at the core of the many technological routes to convert complex biomass into fuels or chemicals, which can be used in our daily lives. This chapter reports on the evolution of catalytic conversion of biomass by exploring databases on scientific literature and on patents retrieved from Scopus and DWPI. The trend analysis of more than 14,000 patent and nonpatent documents on renewable biological feedstock conversion by catalytic route has been carried out by using Intellixir, a statistical tool to analyze a large number of data for scientific intelligence.

The scope of this chapter is to not only display a comprehensive study on patent and nonpatent literature in the catalytic upgrading (value creation) of biomass, but to increase the awareness in the use of patent literature as a tool to reach the rich and open-source treasure of knowledge in various technological fields.

Keywords: Patent and nonpatent literature, Renewable feedstock, Biomass conversion, Heterogeneous catalysis, Intellectual property, Metadata, Data-mining