Chapter

Technological Trajectories Studies of Sugarcane Ethanol Production Using Patent Citation

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Abstract

The production of ethanol from sugarcane has migrated from the first to the second-generation thanks to the biotechnological advancement in the production process. From the survey of patent documents in the area, it is possible to highlight the most relevant patents according to the impact index, measured by the number of citations, and to evaluate the technological trajectories involved in the production of ethanol using a patent citation as a methodology. In addition, it is possible to identify the main actors involved in the technological field, as well as the network of international collaborators. In this context, the study of patent citations will help better understand the main technological advances and global geopolitics in an environment of globalization of technological innovations.

Keywords: ethanol, sugarcane, patent, technological trajectories

1. Introduction

The recent growing demand for energy alternatives to fossil fuels has been a reality shared by many countries in the first few decades of the twenty first century. Economic and environmental issues, population growth, industrial consumption, energy insecurity as well as existing conflicts around the use of raw materials for the production of food types used in the making of fuels, are some of the factors driving governments, universities and multinational corporations to broaden the scalability of their biofuels, such as ethanol, using renewable sources such as lignocellulosic types.

Ethanol can be produced from various raw materials, which can be classified into three categories: (a) simple sugar sources; (b) starch sources; and; (c) lignocellulosic material sources.

As to the technological profile of such categories, when presented in a timeline, they form the technology trajectories representing the production of ethanol, each one related to a specific technological paradigm. Therefore, one considers first generation ethanol ethical alcohol whose production requires raw materials that are rich in saccharosis (sugar cane juice, saccharine sorghum, beetroot, etc.) and/or rich in starch (sweet potato, wheat, potato, corn, cassava, etc.). Regarding second generation ethanol, it is made from biomass that is rich in lignocellulosic materials, such as wood, straw, stems and grass leaves. Finally, third generation ethanol comes from the processing of microalgae biomass after the extraction of lipidic materials (this production modality does not have an industrial representativity yet).

Taking into account this theoretical basis and considering the raw materials that are suitable for ethanol production, as well as the three modalities of the technological trajectory of ethanol production, we conclude that ethanol produced from sugarcane is currently the bioenergy production with the highest yield per unit and higher total energy balance, when we consider the proportion of energy in the final product (ethanol and mechanical energy, thermal and electric) and the fossil energy needed for its production. Besides, sugarcane ethanol offers the possibility of two technology trajectories that are almost consecutive (first- and second-generation productions with the use of sugar cane juice and bagasse).

In this context and in the light of the current technological scenario, this chapter develops an innovative approach to the production of ethanol that comes from sugarcane, combining concepts of patent heuristics with studies of technology trajectories, dependence and paradigms [1]. The study uses technology prospection techniques with analyses of "Breakthrough Inventions," also applying "Forward citations" for an analysis of future technology affinity. Finally, it seeks to obtain a consolidated profile to forward the technology trajectory of sugarcane-based ethanol production.

The piece is divided into three sections: methodology, results and final conclusions. Results and discussions are, in their turn, subdivided into five subsections: general panorama, breakthrough inventions—geographic and current owner distribution analysis, breakthrough inventions—technology analysis, breakthrough inventions—forward citation analysis and recent innovations and technological advances in ethanol production.

2. Material and method

The methodology is based on the study of patent citation and is divided into two stages. In the first stage, patent documents were retrieved with bibliometric analysis carried out through the PatSeer® commercial patent database. It uses keywords such as: alcohol, bioalcohol, ethanol, bioethanol, saccharum, sugarcane, "sugar cane," bagasse, cellulose, biomass, lignocellulose and molasses. In the title and summary fields, it used the extend family filter. The study made use of Boolean operators "OR," "AND" and words truncated with asterisk (*). We covered the period between 2000 and 2018, according to the priority date. All the retrieved documents were classified according to the keywords in the title, summary and claim fields, which resulted in the following categories: (i) pretreatment with acid and enzymatic hydrolysis, (ii) fermentation with yeast, bacteria or non-yeast fungus, (iii) distillation and (iv) sugarcane.

The second step was the data analysis per se, composed by:

(1) Evolution over time of patent documents according to priority year, highlighting quoted documents (>5);

(2) Analysis of patent documents (heavily cited > 5) in different types of citations: patent literature—PL (backward and forward), non-patent literature—NPL (references), family size and documents made available. Calculation of self-citations (difference between forward citations (individual and non-self-citation));

(3) Calculation of the patent index citation of "breakthrough inventions" (CPR: citation patent ratio) [2, 3] according to the priority origin country:

$$CPR = \frac{\text{\%of a variable''s patents forward citation in the breakthrough inventions}}{\text{\%of all patents in the breakthrough inventions}} \quad (1)$$

A ratio of >1 is good, a ratio of <1 is relatively low.

(4) Analysis of the profile of main authors of "breakthrough inventions";

(5) Analysis of the interrelation of the technologies in the most cited "breakthrough documents" and the calculation of the technical impact index (TII) of the breakthrough inventions—the percent of patents in a period analyzed, which are in the most highly cited of all the breakthrough inventions. The expected value of the TII has been normalized to equal 1. "A TII below 1 indicates that patents are not especially highly cited" ([3], p. 272).

(6) Analysis of citations of the downstream of breakthrough inventions.

3. Results and discussion

3.1 Overview

As highlighted in the methodology section, the technology focus of the study is the production of ethanol from sugarcane in its various first-generation (ethanol) and second-generation (bioethanol) modalities. The search strategy used retrieved 223 patent documents in the 2000–2018 period according to the year of priority. Out of those 301 have more than five forward citations by patent family. An expressive range of data on first-generation (ethanol) and second-generation (bioethanol) production were observed positively that when stimulated and directed, there is a growing interest in the patent protection of the intellectual assets (in the form of patent depositories) coming from research and industrial developments (**Figure 1**).

It is worth highlighting again that, on industrial levels, ethanol is considered to be a very relevant biofuel for producer countries, and which can be obtained from various primary and secondary (lignocellulosic biomass types) sources, such as:

i. through the hydrolysis of starch of cereal grains (corn, sorghum, wheat, triticale, rye, malted barley, rice);

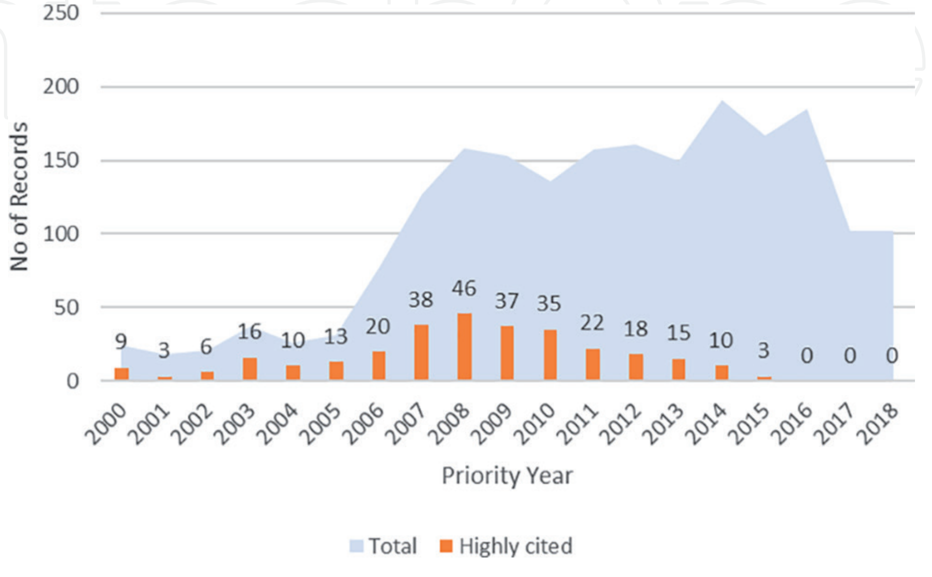

Figure 1.
Distribution over time of patent documents related to the production of sugarcane ethanol, highlighting 301 highly cited documents. Period: 2000–2018. N = 2023. Source: Compiled by the authors, PatSeer® database.

ii. tubers (potatoes);

iii. through direct use of molasses sugar and juice from: (a) sugarcane; (b) saccharin sorghum; (c) saccharin beetroot;

iv. through the breakdown and decomposing of the lignocellulosic structure of biomass materials, followed by processes of saccharification and fermentation, which can happen through intervention with: (I) yeast; (II) bacteria and (III) non-yeast fungus; finally;

v. by implementation of algae crops, with the potential of a co-production of biodiesel and bioethanol.

The global ethanol production from various raw materials has grown year on year, mainly because of its usability as a fuel (or supplementary fuel), and also thanks to its availability from renewable sources as a result of incentives and social and environmentally friendly credentials. This growth in the global ethanol production noticeable from **Figure 2** takes place independently from the struggle between the use of its primary raw materials (grains and sugarcane juices/extracts, sorghum and saccharin beetroot) and food production for the global population.

From an economic point of view, when we compare **Figures 1** and **2**, we perceive a noticeable alignment of evolutions over time given that the patent system, as it reflects the advances of investments in R&D, reveals the bias that paired the economic development of a nation to its technological development thus highlighting the strong maintenance of interests in the technologies in question. It also important to emphasize that patent data analysis aids significantly to understand technology tendencies as well as forecast future technology perspectives.

This way, with a focus on studies of future technology perspectives, we applied here the analysis of "patent citation" (PC). The methodological effort made here is in line with what many researchers across the globe have been doing for decades, using methodologies based on "patent citation analysis." This methodology has gained traction and has been developed and adapted to increase access to valuable information among companies, researchers, research centers, universities and countries. The information contained in patent documents reveals the extent and conduction of applied technical research. Therefore, the use of this tool (patents) makes it possible to show that information available in those patent documents overcomes all barriers and can be used for the expansion

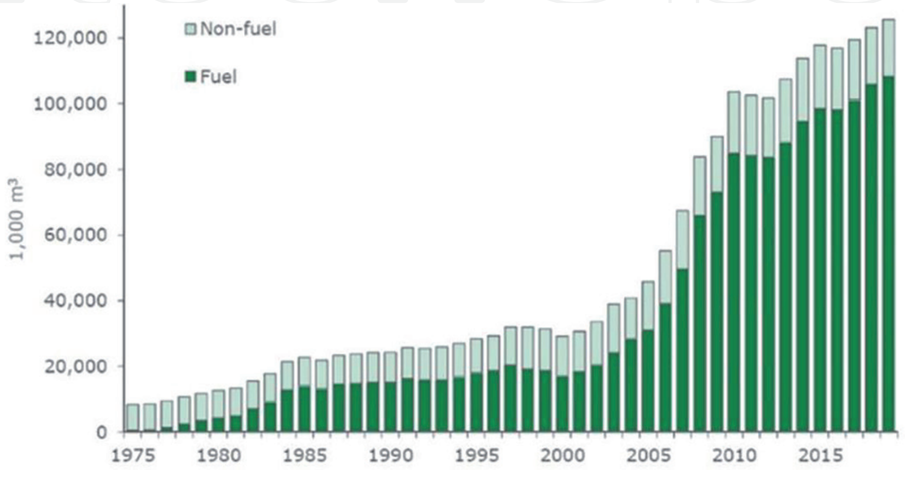

Figure 2.
World ethanol production. Source: KNect365 Energy, 2019.

Document quality indicators retrieved	Total	Most highly cited (>5) (Percentage of total)
No documents	2023	301 (14.9%)
No. of extended family members	5128	811 (15.8%)
NPL—non patent literature:		
No. of references	1612	642 (39.8%)
PL—patent literature:		
No. of backward citation	5585	1780 (31.9%)
No. of forward citations (individual)	6807	5280 (77.7%)
No. of non self citations (forward citation)	5054	3954 (78.2%)
Auto-citation	1753	1326 (21.8%)
Granted	685	137 (20%)
Average year	2011.4	2008.1

Source: Compiled by the authors, PatSeer® database.

Table 1.
Main quality indicators of retrieved documents.

of the technique and technology development. Therefore, "patent citation analysis" reveals the creation and propagation of information, as well as promotes its applicability in various technical fields which will be able to originate/spawn new technologies [4–6].

Figure 1 also shows the evolution of highly cited patent documents based on retrieved data (orange bars), whose extraction can be observed in **Table 1**, which shows a summary of the main quality indicators of the retrieved documents, comparing the total number of retrieved documents in comparison with the most cited ones.

We can see that around 78% of the individual forward citations concentrate in 15% of retrieved documents, denoting a high concentration around specific technology nuclei, while 25.1% of individual forward citations also refer to self-citations of patent documents.

Another very relevant information from **Table 1** refers to the relation between the values of "patent literature" (PL) and "non-patent literature" (NPL). According to Demet et al. [7], this relation (PL/NPL) infers a state of industrial maturity hoped to be reached. In other words, values below the first inferior quarter (>25%) suggest a favorable state for innovation and the commercialization of products/processes of a given technology sector. Therefore, it is possible to conclude there are well-established maturity nuclei in detriment of the possibility of the existence of nuclei that are not mature yet. A better definition of these maturity nuclei was set out by "breakthrough inventions" study of "patent citations" [8].

3.2 Breakthrough inventions: geographic and current owner distribution analysis

According to Yan et al. [9], "breakthrough inventions" can be understood as inventions that aspire to or serve as technology bases for the creation of subsequent inventions. They are inventions that are a relevant source of competitive edge and can be part of a viable strategy to boost a company" capacity to generate innovative inventions. They can help meeting the challenge to create radical/disruptive inventions through the recombination of non-redundant knowledge, mainly by using patent publications of industrial competitors' patent publications. In this case, the technology sector of first- and second-generation ethanol production.

Kerr [10] used "breakthrough inventions" to identify important areas for future research in the area. Similarly, Egli et al. [11] used "breakthrough inventions" to identify and induce applied technologies to climate change mitigation. This way, in this paper we used such studies as reference in the investigation of the efforts and technology maturity, patenting growth and the influence of patents in the technology development of first- and second-generation ethanol production. This way, this work presents "breakthrough inventions" through "patent citations" with an analysis of the main technology clusters within the ethanol production sector and its temporal and spatial migrations.

Before we continue with the present analysis, it important to understand the relevance of the study on geographic distribution and the owners of technologies in "breakthrough inventions." Therefore, the analysis of components of geographical distribution and the ownership of inventions is key as it provides information on the flow of knowledge of the analyzed technology [4]. For that matter, we drew from Kaki's study on citations performances ratio (CPR). CPR comes from a comparative study based on the presence of highly cited patents in a given patent database, a specific timeline and category. The values whose ratio are bigger than the unit (CPR > 1) indicate a good performance. According to Narin and Olivastro" study [12], any patent document cited 06 (six) or more times can be considered as very relevant for the "patent citation analysis." They can also be considered "breakthrough inventions."

In this sense, **Table 2** sums up the main indicators of patent quality according to the country of origin of the priority request. The importance of analyzing this parameter is to understand which countries dominate the technology. Only the USA, China and Japan have CPR numbers above 1, which are considered good. Other countries did not obtain a good performance during analysis.

When we analyze **Table 2**, we can see a strong performance by the United States as the conductor of technology within the analyzed setting. Therefore, even if it does not have its ethanol matrix focused on sugarcane crops, the United States present a relevant patent achievement in terms of "breakthrough inventions". This suggests technology leadership in related areas when a sugarcane matrix is used. Also relevant is the fact that the United States are the biggest ethanol producers in the world, followed by Brazil, EU, China and Canada (**Figure 3**) while the largest sugarcane producer are Brazil, India, China, Thailand and Pakistan [13].

Priority country	No. of records	CPR	% granted of the priority country	% of extended family members
United States	61	8.35	42.6	61.7
China	172	6.21	50.6	23.7
Japan	52	2.53	32.7	8.6
Germany	5	0.18	0.0	2.2
Korea	4	0.11	50.0	1.5
Czech Republic	2	0.06	50.0	0.9
Russian Federation	2	0.04	0.0	0.6
Brazil	1	0.02	100	0.5
France	1	0.02	100	0.2
United Kingdom	1	0.02	100	0.1
Total	301		45.2%	100%

Source: compiled by the authors, PatSeer database.

Table 2.
Country of origin profile analysis of "breakthrough inventions."

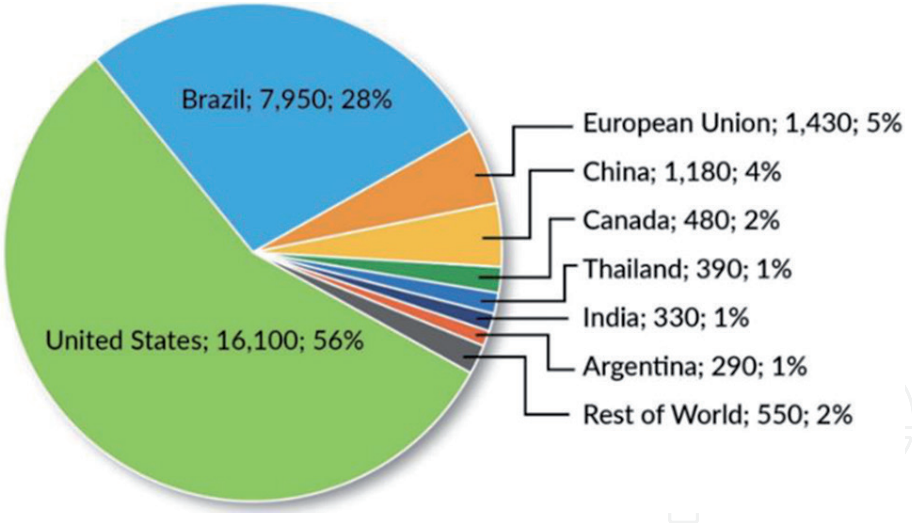

Figure 3.
Global ethanol production by country of 2018 (country; million gallons; share of global production). Source: RFA analysis of public and private data source.

Following the same logic, we can see that China plays an important role in the "breakthrough inventions" analyzed scenario, that is, it appears as one of the five global ethanol powers, as well as one of the five countries with the highest number of innovative inventions. We should highlight here that the Chinese government is planning the implementation of a policy of an E10 ethanol addition to gasoline across its territory by 2020. This will be very important for countries like the United States and Brazil, whose CPR of the latter is only 0.02. Such piece of information about Brazil (CPR = 0.02) may suggest a strong dependence and even propensity to the technology "colonization" in specific sub-sectors and the existence of "Patent Pools" [14, 15] and "Patent Trolls" [16, 17].

Regarding the profile of the main holders of "breakthrough inventions" retrieved during the CPR analysis, **Table 3** shows the importance of Chinese companies. This is a very important piece of information for this analysis of technology trajectory because it enables a clear visualization of the steps taken by companies and Chinese university research centers toward control and technology independence of methods of first- and second-generation ethanol production.

Although the companies listed in **Table 3** show low CPR (<0.5), an indicator they produce little impact with the dissemination of their technologies, their respective values often surpass by several times the CPR of countries like Germany (2.8×); Russia (12.5×); Brazil (25×); and France (25×).

Also relevant is the fact that the number of "breakthrough inventions" documents retrieved from these companies and Chinese universities present low statistical dispersion (average standard deviation = 1.88). This, however, suggests something positive. These figures can indicate a cohesive movement of technology ascension for the sector, cluster or grouping formation. We must also call attention to the high number of documents made available by these actors, except for Toshiba Corp, Institute of Process Engineering, and the Chinese Academy of Sciences, who until the time when the analysis was made did not have patents issued for the technologies herein studied.

The analysis of **Table 3** also reveals the absence of actors from other countries. For example, the presence of actors such as the United States and Japan merely indicates them to be countries with a considerable number of "breakthrough inventions" documents. However, it can be concluded there is great dispersion of patent document ownership, which in its turn suggests an open and competitive market, without business clusters. Regarding the technology aspect of ethanol production,

Current owner	No. records	CPR	No. granted	Sugarcane	Biomass Pretreatment		Fermentation			
					Acid hydrolysis	Enzymatic hydrolysis	Yeast	Bacterium	Fungus without yeast	Distillation
China petroleum & chem-sinopec	9	0.27	9	1	3	3	4	5	0	4
Univ tsinghua	8	0.32	8	4	3	3	4	3	1	4
Tsukishima kikai Co Ltd	7	0.32	2	0	2	2	1	0	0	0
Univ tianjin	7	0.29	5	2	0	1	4	1	1	5
Toshiba corp	5	0.12	0	0	0	1	2	0	0	0
Oji holding corp	5	0.20	4	0	0	0	1	0	0	2
Inst process Eng Cas	4	0.13	0	0	0	1	2	0	0	3
Hitachi group	3	0.10	1	0	0	0	0	0	0	1
Cofco Ltd	3	0.10	3	0	2	3	3	3	0	0
Dalian chem physics inst	3	0.08	3	0	0	0	0	0	0	0

N = 301. Source: Compiled by the authors, PatSeer® database.

Table 3.
Analysis of the profile of the main patent holders of "breakthrough inventions".

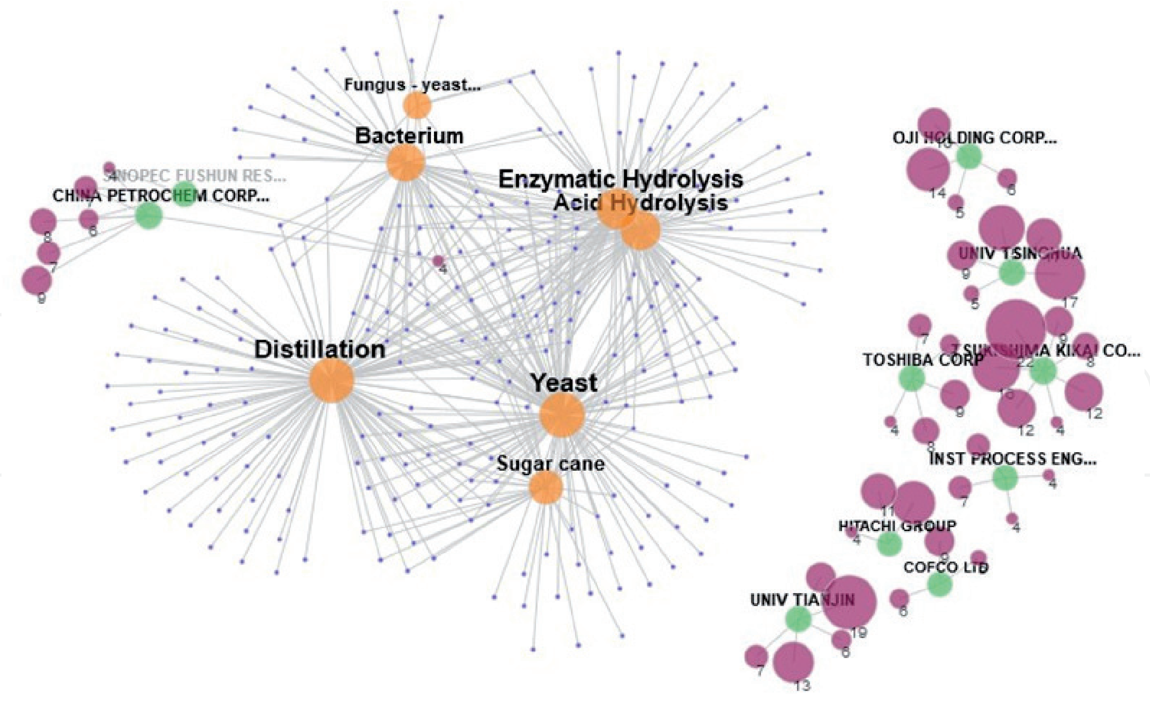

Figure 4.
Relationship network among the 10 main holders of technologies associated to the production of ethanol, "breakthrough inventions" and biomass categories (sugarcane), pretreatment (acid hydrolysis and enzymatic hydrolysis), fermentation (yeast, bacterium and yeast-free fungus) and distillation. N = 301. Source: Elaborated by the authors, PatSeer® database.

Table 3 reveals to readers that the great intellectual effort by Chinese companies is in areas such as: (i) pretreatment of raw materials (hydrolysis); (ii) fermentation; and, (iii) post-treatment (distillation); in that order.

From that point of view, **Figure 4**, created from 301 "breakthrough inventions" documents-corroborates previous understandings of **Table 3** analysis, showing a relationship between actors and technology areas in each category. Therefore, it is possible to verify a certain level of non-binding cohesion among the analyzed actors, there being no sharing of technology in those supposed partnerships.

China Petrochem Corp (Sinopec) appears as an exception to the block composed by all the other actors. The data suggests low adhesion by that company to the cluster formed by other companies and universities. There seems to be no apparent link between them and no effort of interaction among them.

In the case of technology associated to the production of ethanol, the "breakthrough inventions" and the analysis of biomass (sugarcane) analysis, pretreatment (acid hydrolysis and enzymatic hydrolysis), fermentation (yeast, bacterium and yeast-free fungus), post-treatment (distillation) indicates possible dispersion.

3.3 Breakthrough inventions: technology analysis

In 2016, the United Nations Conference on Trade and Development (UNCTAD) [18] launched a report where they laid out the main distinctions between first and second generation renewable fuels, based on their raw materials' features (**Table 4**). Therefore, **Table 4** shows that first generation biofuels are made from seeds, cereals and sugar types (from extracts and juices) while second generation biofuels are produced from the pretreatment of cellulosic and lignocellulosic biomass, such as: carbonaceous materials of renewable vegetable sources (wood, bagasse, straw, barks, grass, etc.).

In order to comply with the time-based interval adopted in this paper, it is necessary to highlight that the conversion of lignocellulosic biomass materials into

First-generation biofuels (from seeds, grain and sugar)	Second-generation biofuels (from lignocellulosic biomass, such as crop residues, woody crops or energy grasses)
Petroleum-gasoline substitutes • Ethanol or butanol by fermentation of starches of sugars	**Biochemically produced Petroleum-gasoline substitutes** • Ethanol or butanol by enzymatic hydrolysis
Petroleum-diesel substitutes • Biodiesel by transesterification of plant oils (FAME and FAEE) • Can be produced from various crops such as rapeseed (RME), soybeans (SME), sunflowers, coconut oil, palm oil, jatropha, recycled cooking oil and animal fats. • Pure plant oils (straight vegetable oil)	**Thermochemically produced Petroleum-gasoline substitutes** • Methanol • Fischer-Tropsch gasoline • Mixed alcohols **Thermochemically produced Petroleum-diesel substitutes** • Fischer-Tropsch diesel • Dimethyl ether (substitutes propane as well) • Green diesel

Source: UNCTAD [18].

Table 4.
Differences between the production of first- and second-generation biofuel according to raw materials.

biofuel was already viable in the mid-2000s and, on an industrial level, biofuels derived from this process involving enzymatic stages were not a common practice nor were they produced in great volumes for the market before the year 2005 [19]. Besides, it is possible to notice a significant change in the alcohol (ethanol) production from 2005 onwards (see **Figure 2**), the year when the Kyoto protocol was signed by most ethanol-producing countries and regions. At first, China and the United States did not agree to sign the protocol. However, after discussions that lasted more than half a decade, those countries ratified the protocol and started a global pact aimed at mitigating the production of greenhouse gases, in 2011 [20].

This global agreement directed, once and for all global efforts and interests in ethanol-producing technologies from lignocellulosic materials (biomass route: **Figure 5**). This way, it boosted their sustainability footprint and benefits for the

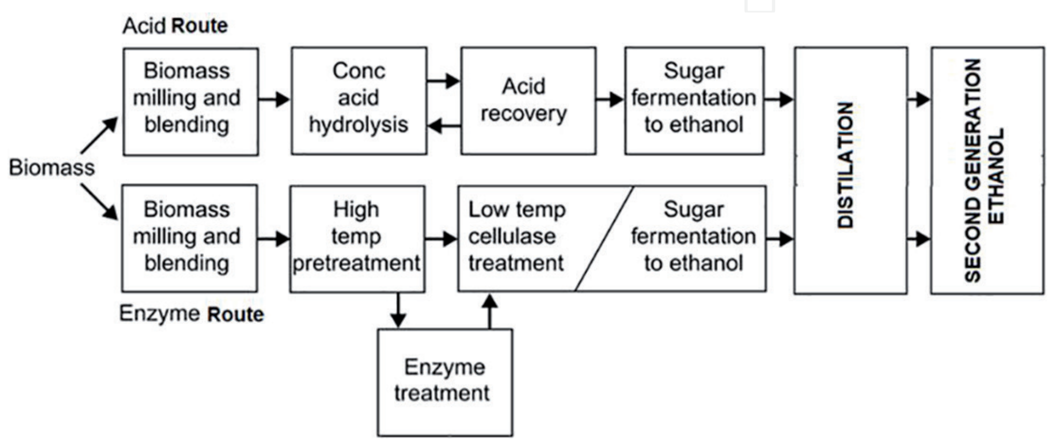

Figure 5.
Schematic representation of the stages of second-generation ethanol production. Source: Elaborated by authors.

Biofuel type and production capacity (millions of liters per year)								
Fuel	2009	2010	2011	2012	2013	2014	2015	2016
Advanced Ethanol	27.71	42.36	46.52	922.62	2.522.22	4.770.26	8.538.41	8.848.82
Cellulosic Sugars Ethanol	0.00	0.04	0.08	0.08	3.82	3.82	102.21	102.21

Source: Biofuels digest, 2011. Note: 2012–2016 data represents 2011 estimates.

Table 5.
Biofuel type and production capacity.

environment and also appeased disputing parts regarding sources of raw materials to be used to produce energy in detriment of food for people, as is the case of sugarcane in Brazil and China [21].

In this sense, after 2013 the whole political debate about the implementation of second-generation fuels became a new reality of technological-industrial trajectory, while for example, ethanol coming from lignocellulosic materials (vegetable biomass and cellulosic residue) began to be produced at industrial/commercial scale (**Table 5**), representing an opportunity for a number of countries to be inserted technologically and take part of the emerging industry of second generation biofuels [18].

As we can see from **Table 5**, the advanced route of ethanol production, similarly to biomass route (cellulose), gains momentum from 2013, when several new technologies started to be implemented in the industrial field. This way, using studies on clusters of the topic-based documents of "breakthrough inventions" as a departing point, a series of more detailed analysis was carried out about the technology profile of the main routes of ethanol production (**Figure 6**).

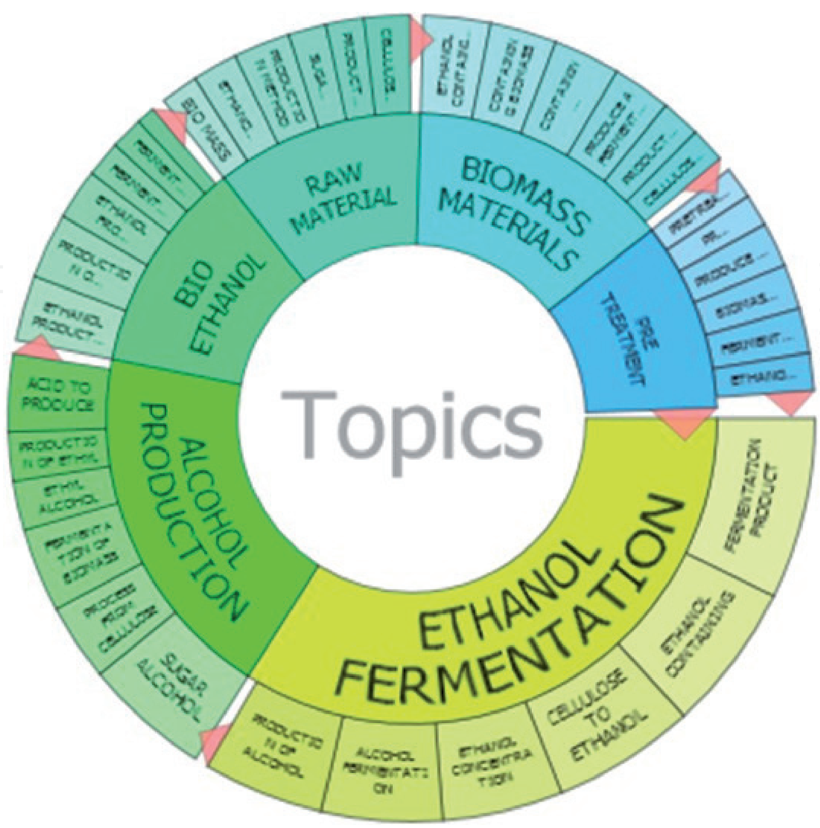

Figure 6.
Graphic representation of the topics in documents of patents of "breakthrough inventions". Source: Compiled by the authors, PatSeer® database.

By reading **Figure 6**, we can see that technology linked to the Ethanol Fermentation phase and pre-treatment (Alcohol Production) are the base of new technology trajectories in the production of ethanol. The image allows us to see subsections related to the conversion of cellulose into ethanol, as well as the treatments with the use of acids and enzymes for the preparation of sugars that will be consumed by microorganisms during fermentation. Regarding the raw materials the analysis in **Figure 6** comprises, it is possible to see the technological inclination toward the use of biomass material (lignocellulosic) as a pillar for the technology trajectory in the production of fuel alcohol that will continue into coming years. The greater emphasis is on the biomass material that is not consumable by humans and animals, especially the waste from the lignocellulosic base.

As a way to corroborate this timely analysis, **Table 6** shows the relation of the 10 main international classifications of patents with the biomass categories (sugarcane), pre-treatment (acid and enzymatic hydrolysis), fermentation (yeast, bacterium, yeast-free fungus) and post-treatment (distillation). We noticed the main classification is C12P (fermentation or enzyme-using processes to synthesize a desired chemical compound or composition or to separate optical isomers from a racemic mixture), with a TII higher than one (3.67), proving to be a relevant technology field for the production of ethanol. The most representative categories were related to yeast and distillation, because during the ethanol production process, both first and second generation, fermentation and distillation are crucial. However, TII for both was low (0.37).

Based on the data in **Table 6**, it must be highlighted that the classification code C12P, (Fermentation or enzyme-using processes to synthesize a desired chemical compound or composition or to separate optical isomers from a racemic mixture) was the main classification for the analysis, using a TII above one (3.67), a technology field

IPC	No. records	TII	Biomass	Pretreatment		Fermentation			Posttreatment
			Sugarcane	Acid hydrolysis	Enzymatic hydrolysis	Yeast	Bacterium	Fungus (without yeast)	Distillation
C12P	1105	**3.67**	130	322	363	562	264	35	379
C12R	370	**1.23**	50	139	151	261	135	15	125
C12N	260	**0.86**	23	47	56	151	80	17	54
C07C	200	**0.66**	17	20	14	18	4	1	71
C02F	126	**0.42**	7	2	2	11	16	4	25
C12M	110	**0.37**	13	16	19	35	16	3	47
C10L	107	**0.36**	10	17	19	20	16	2	42
C08L	99	**0.33**	1	8	1	2	12	0	18
B01J	78	**0.26**	0	7	2	0	0	0	8
B01D	63	**0.21**	6	4	5	3	1	0	32
TII			**0.11**	**0.23**	**0.25**	**0.37**	**0.18**	**0.03**	**0.37**

N = 301. C12P: Fermentation or enzyme-using processes to synthesize a desired chemical compound or composition or to separate optical isomers from a racemic mixture; C12R: Indexing scheme associated with subclasses; C12N: Microorganisms or enzymes; compositions thereof; C07C: Acyclic or carbocyclic compounds; C02F: Treatment of water, waste water, sewage or sludge; C12M: Apparatus for enzymology or microbiology; C10L: Fuels not otherwise provided for; natural gas; synthetic natural gas obtained by processes; C08L: Compositions of macromolecular compounds; B01J: Chemical or physical processes; B01D: Separation. Source: Compiled by the authors, PatSeer® database.

Table 6.
List of the top 10 IPC main class with document classification according to "breakthrough inventions" patent technology process, and technical impact index–TII.

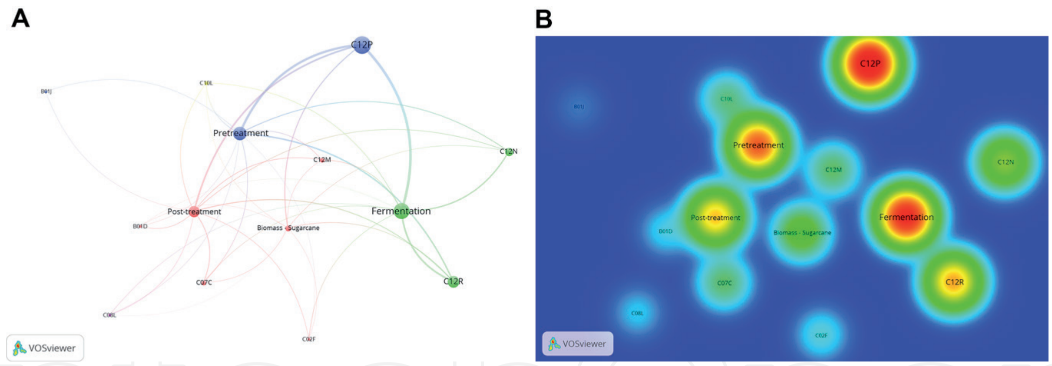

Figure 7.
Networking of the top 10 IPC Main class and the categories (pre-treatment = acid hydrolysis, enzymatic hydrolysis; fermentation = yeast, bacterium, fungus without yeast; distillation), (A) and density graph of the same networking (B). Source: Compiled by the authors, PatSeer® database and VOS viewer visualization [22].

that is essential for ethanol production. Meanwhile, the other technology categories (IPCs) involved in the ethanol process have proven to be statistically with TII impacts but without major discrepancies or significant dispersion (average TII = 0.434; Average deviation = 0.163). They are hierarchically ranked in the relevance sequence that follows: (1st): Fermentation technologies (Yeast, Bacterium and Yeast-free Fungus), because both in first and second generation, fermentation is a crucial stage to obtain ethanol. (2nd) pre-treatment technologies (Acid and enzymatic hydrolysis- slight tendency toward the latter); finally (3rd) Post-treatment technologies (Distillation). This hierarchical configuration can be confirmed in **Figure 7**, which shows the relation between all networks of relationship between technology clusters.

Still looking at **Figure 7A** and **B** it is possible to see strong and direct relations between the stages of the ethanol production process, especially between the pre-treatment and fermentation stages, which are interrelated and form a network of weak knots. But when isolated, they are intense. We can observe that, together, such stages make up the central technology focus of ethanol production.

In the sequence, we present some of the most highly cited patent documents of "breakthrough inventions" within the context of previous analysis.

WO2003078644-A2 (25 September 2003): Conversion of cellulose to glucose involves treating a pre-treated lignocellulosic substrate with cellulase.

WO2006007691-A1 (26 January 2006): Obtaining a product sugar stream from cellulosic biomass, involves hydrolyzing a neutralized cellulosic biomass with cellulase enzymes.

WO2006110900-A2 (19 October 2006): Production (P1) of ethanol comprising biomass with aqueous solution containing ammonia, a saccharification enzyme consortium to produce fermentable sugars, and a fermentation conditions with a suitable biocatalyst to produce ethanol.

JP4522797-B2 (11 August 2010): Pre-processing of lignocellulose-containing raw material for use in ethanol production.

JP5233452-B2 (10 July 2013): System for saccharification and fermentation of woody biomass raw material, by adding cellulose degrading enzyme, hemicellulolytic enzyme and alcohol fermentation microorganism.

BR200100762-A (06 November 2001): The method involves grinding lignocellulosic biomass (LB) followed by steam-explosion pre-treatment.

3.4 Breakthrough inventions: forward citation analysis

Currently, the analysis of "Forward Citation" is often used by authors of non-patent literature when the objective is a better understanding of patterns, for example, of formation of a portfolio of patent documents for a systematic analysis of the international codes of patent classification. Carpenter, Narin and Woolf [23] and Trajtenberg [8], in their respective works, managed to measure the relationship between "Forward Citation" and the future value of an invention, therefore the "Forward Citation" number that a given patent document receives, and which accumulates over time, is related to the significant technology impact of the technical content of those documents (that is, "breakthrough inventions"). That suggests that patents with a high number of citations have a relevant technology impact and contribute significantly to the advance of technology [24].

Keeping that in mind, it was necessary for the present analysis of investigation of the technology trajectory for the field of first and second generation ethanol production sector to use "Forward Citation" analysis as a "proxy" for the measurement of intangible added value that those "breakthrough inventions" documents really have. This way, under the prism adopted by this study, it was noted that: the more valuable a patented technology, the newer the incentives are created from past learnings; this way, looking at it from an economic point o view, "Forward Citation" results in the measurement of the valuing of those documents of "breakthrough inventions".

This way, the "Forward Citation" analysis of the 301 documents of "breakthrough inventions" was carried out by taking into account the codes of international classification of patents retrieved in previous analyses (**Figure 8**). From that analysis it was possible to identify: (i) 3506 patent documents in "forward citation"; and, (ii) 1524 patent documents in "backward citation"; the main classifications in the documents in (i) were: (a) C12P7 (count-1337); (b) C12P19 (count-532); (c) C07C29 (count-434); and, (d) C12M1 (count-359).

Still looking at **Figure 8**, it is possible to note that the ratio between the quantity of retrieved documents to (i) "forward citation" and (ii) "backward citation" outnumbers the unit by 2.3 times, thus indicating that the 301 "breakthrough inventions" documents analyzed in this study presented a strong impact on subsequent technology generations [25].

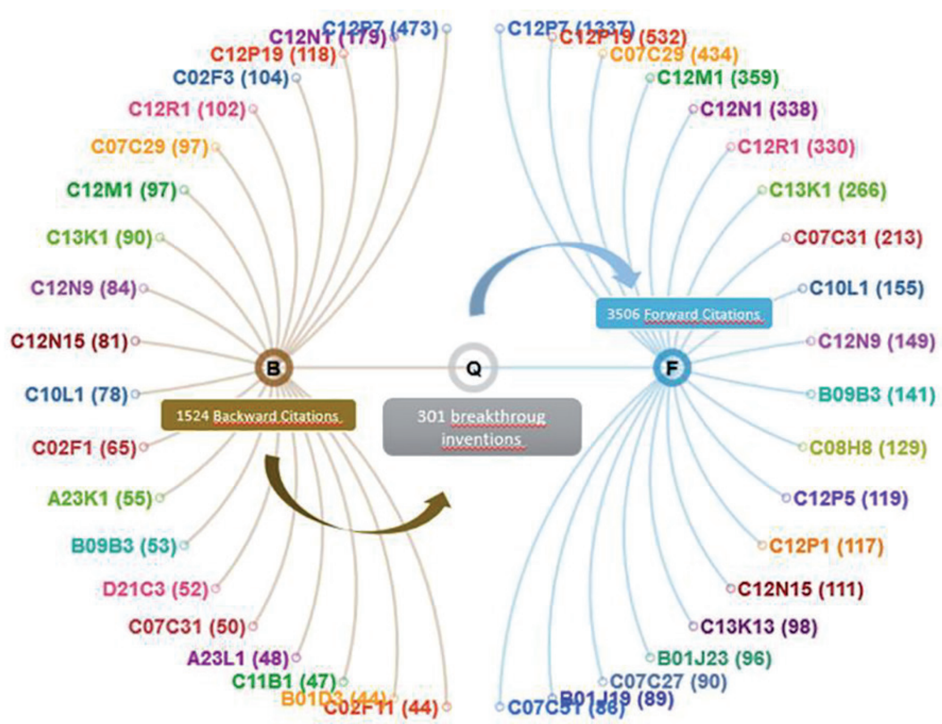

Figure 8.
Analysis of citations of breakthrough inventions. Source: Compiled by the authors, PatSeer® data.

Moving on, the 3506 patent documents in "forward citation" were treated and filtered through extended family, resulting in 2406 original documents of patent family (no document doubling). These were equally stratified and analyzed according to technology categories and international codes of patent classification (IPC), which resulted in **Table 7**.

Analyzing **Table 7** in relation to **Figure 7A** and **B**, it is possible to see there is a prevalence of subclass C12P in detriments to other classification codes (IPC). This highlights that the technology trajectory in analysis is clearly directed to the production of second generation ethanol, through the use of cellulosic waste (biomass).

IPC full class	No. records	Biomass	Pretreatment		Fermentation			Post-treatment
		Sugarcane	Acid hydrolysis	Enzymatic hydrolysis	Yeast	Bacterium	Fungus (without yeast)	Distillation
C12P7/10: Substrate containing cellulosic material	460	56	165	192	179	59	0	95
C12P7/06: Ethanol	362	50	61	75	147	57	0	75
C12P19/14: Produced by the action of a carbohydrase	262	38	95	133	64	29	0	41
C12M1/00: Apparatus for enzymology or microbiology	167	24	29	33	32	12	0	45
C12P19/02: Monosaccharides	161	21	61	72	22	11	0	10
C12R1/865: *Saccharomyces cerevisiae*	149	22	47	63	112	47	0	31
C13K1/02: By saccharification of cellulosic materials	148	18	50	33	10	6	0	10
C12P7/16: Butanol	114	23	39	32	25	17	0	27
B09B3/00: Destroying solid waste or transforming solid waste into something useful or harmless	113	8	14	19	16	6	0	23
C12P7/08: Produced as by-product or from waste or cellulosic material substrate	113	11	26	29	42	12	0	39

N = 2406. Source: Compiled by the authors, PatSeer® database.

Table 7.
List of top 10 IPC full class with document classification according to the technology process of forward citation of "breakthrough inventions" patents.

This information can be inferred by the sequenced information of the main classifications, as follows: (i) C12P7/10: Substrate containing cellulosic material; (ii) C12P7/06: Ethanol; (iii) C12P19/14: Produced by the action of a carbohydrase (set of enzymes that catalyzes 5 types of breakdown during carbohydrates into simple sugars); (iv) C12M1/00: Apparatus for enzymology or microbiology; (v) C12P19/02: Monosaccharides; (vi) C12R1/865: Saccharomyces cerevisiae; (vii) C13K1/02: By saccharification of cellulosic materials; (viii) C12P7/08: Produced as by-product or from waste or cellulosic material substrate. Besides, there is emphasis on the use of enzymes during the initial stage of pre-treatment of raw materials through enzymatic hydrolysis.

This way, it is clear that the stages of pre-treatment and fermentation are the strongest and most relevant technology nuclei for the sector in the near future.

3.5 Recent innovations and technological advances in ethanol production

The theory of trajectory and technology paradigm that we use these days were laid out and drafted by Dosi [1]. In his study, the researcher adopted similarities in the process of innovation to incremental innovation and disruptive innovation, to the assessment of process of diffusion between science and technology, taking into account heuristics methodology, well-structured in the form of a strategy of search that directed toward the solution of problems under the existing paradigms. The heuristics sustained by the author, in thesis, boosts incremental innovation in the context of a given technology trajectory, like a driving force that unleashes changes for new trajectories or technology paradigms through the disruptive or radical innovation [1, 26]. Therefore, the heuristics seems to be essential for a better comprehension of the dynamics of the technology involved in ethanol production.

In this analytical context, a new heuristic context was created for the final part of this study, which enable the making of data profiling, on various levels: (i) geographical; (ii) temporal; and, (iii) technological; employing the same data on the family documents of the "forward citation" in a scenario of recent deposits—between 2017 and 2018. This led to **Figure 9** and **Table 8** as shown in sequence.

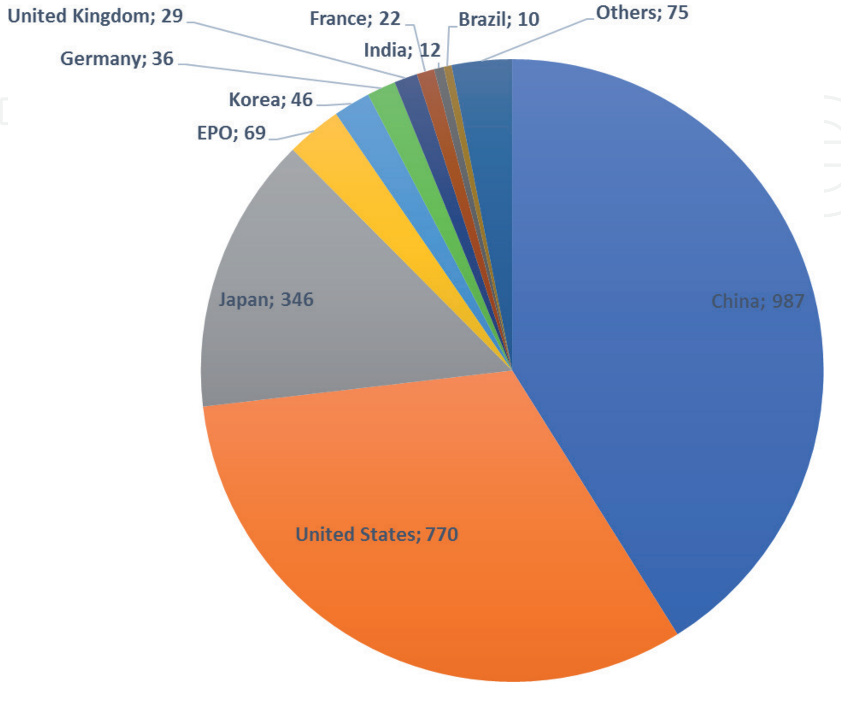

Figure 9.
Country of origin of "forward citations" for 2017 and 2018. Source: Compiled by the authors, PatSeer®.

IPC main	Sugarcane	Pretreatment	Fermentation	Post-treatment
C08L		2		
C10L			1	
C12N		1	4	
C12P	1	2	3	
C11C				1
D21B	1	1		
D21C		1	1	
Total Geral	2	7	9	1

Source: Compiled by the authors, PatSeer®.

Table 8.
Main IPC related to categories.

By analyzing the data set in **Figure 8** and **Table 8**, it is possible to infer that the technology trajectory from the data mined points to China as the country with the biggest technology power to rise in the future and replace the United States as the leader of ethanol-producing technologies, mainly in technologies related to the enzymatic pre-treatment and the fermentation stage. It is worth highlighting the presence of patent documents on the technologies that use modified bacteria and/or yeast-free fungus, which process the raw cellulosic material, and alternately absorb the stages of pre-treatment and fermentation of sugars resulting from the saccharification of lignocellulosic matter in one stage only (see: CN105154416-B, 2018; CN108603186-A, 2018; CN106755011-A, 2017; IN201741014528-A, 2018; IN201831041905-A, 2018; US2018230420-A1, 2018; BR102016030305-A2, 2018).

4. Final remarks

The study highlights some considerations to be taken up in a broader research agenda in sugarcane ethanol's production chain.

The first point is that the strategy of patent data retrieval used by the authors in this and other works and for a smaller spatial dimension proved totally valid to characterize technological advances in the aforementioned production chain at the global level. This reveals that the methodology experimented by the authors involving the use of the technological information contained in the patent documents consorted to the specific study of patent citations are very adequate to identify and understand the technology trajectories resulting from investment decisions, research and public policies related to the study of industrial sectors.

A second point to be considered concerns the dynamism of research on second generation technologies for ethanol production from sugarcane in the early years of the twenty-first century. However, what stands out is the prominence of the Chinese research system and its articulation with companies in areas of extremely high complexity, such as biotechnology, especially in the areas of fermentation and enzymatic processes.

Finally, looking at the Brazilian ethanol research and production system, the study indicates routes to be followed and bridges to be built in case the country should want to retake the leading role it has played in this sector in the twentieth century. And this is an important feature of the methodology used in this study that, in prospecting and extracting data and information from the patent system, stripped relevant sources of technological knowledge and research and development networks with which it will be essential to establish partnerships for the development of a collaborative work.

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References

[1] Dosi G. Technological paradigms and technological trajectories: A suggested interpretation of the determinants and directions of technical change. Research Policy. 1982;**11**:147-162

[2] Ahuja G, Lampert CM. Entrepreneurship in the large corporation: A longitudinal study of how established firms create breakthrough inventions. Strategic Management Journal. 2001;**22**(6-7 Special Issue on Strategic Entrepreneurship: Entrepreneurial Strategies for Wealth Creation):521-543

[3] Karki MMS, Krishnam KS. Patent citation analysis: A policy analysis tool. World Patent Information. 1997;**19**(4):269-272

[4] Sharma P, Tripathi RC. Patent citation: A technique for measuring the knowledge flow of information and innovation. World Patent Information. 2017;**51**:31-42

[5] Lee M, Kim Y, Woncheol J. Patent citation network analysis. Korean Journal of Applied Statistics. 2016;**29**:613-625

[6] Hasner C, de Lima AA, Winter E. Technology advances in sugarcane propagation: A patent citation study. World Patent Information. 2019;**56**:9-16

[7] Demet AE, Tanchoux N, Centi G, De Luca R, Di Renzo F, Vermeiren W. Chapter 8: On the R&D landscape evolution in catalytic upgrading of biomass. In: Studies in Surface Science and Catalysis. Elsevier; Vol. 178. 2019. pp. 149-171

[8] Trajtenberg M. A penny for your quotes: Patent citations and the value of innovations. The Rand Journal of Economics. 1990;**21**(1):172-187

[9] Yan Y, Dong JQ, Faems D. Not every coopetitor is the same: The impact of technological, market and geographical overlap with coopetitors on firms' breakthrough inventions. Long Range Planning. In Press. 2019. Available from: https://www.sciencedirect.com/science/article/abs/pii/S0024630118301031 [cited: 02 June 2019]

[10] Kerr WR. Breakthrough inventions and migrating clusters of innovation. Journal of Urban Economics. 2010;**67**(1):46-60

[11] Egli F, Johnstone N, Menon C. Identifying and inducing breakthrough inventions: An application related to climate change mitigation. OECD Science, Technology and Industry Working Papers. Paris: OECD Publishing; 2015. http://dx.doi.org/10.1787/5js03zd40n37-en

[12] Narin F, Olivastro D. Technology indicators based on patents and patent citations. In: Handbook of Quantitative Studies of Science and Technology. Elsevier; 1988. pp. 465-507. Available from: https://linkinghub.elsevier.com/retrieve/pii/B9780444705372500209 [cited: 02 June 2019]

[13] Food and Agriculture Organization of the United Nations—FAO. FAOSTAT—Statistics of Sugarcane Crop [Internet]. 2019. Available from: http://www.fao.org/faostat/en/#data/QC [cited: 02 June 2019]

[14] Ishihara A, Yanagawa N. Dark sides of patent pools with compulsory independent licensing. SSRN Electronic Journal. 2016. pp. 1-59. Available from: http://www.ssrn.com/abstract=2885620 [cited: 02 June 2019]

[15] Dequiedt V, Versaevel B. Patent pools and dynamic R&D incentives. International Review of Law and Economics. 2013;**36**:59-69

[16] Appel I, Farre-Mensa J, Simintzi E. Patent trolls and small

business employment. SSRN Electronic Journal. 2016. pp.1-68. Available from: http://www.ssrn.com/abstract=2887104 [cited: 02 June 2019]

[17] Turner JL. Patent thickets, trolls and unproductive entrepreneurship. SSRN Electronic Journal. 2011. Available from: http://www.ssrn.com/abstract=1916798 [cited: 02 June 2019]

[18] UNCTAD. Second generation biofuel markets: Satet of play, trade and developing country perspectives. In: United Nations Conf Trade Dev [Internet]. 2016. p. 69. Available from: http://unctad.org/en/PublicationsLibrary/ditcted2015d8_en.pdf

[19] Hamelinck CN, Faaij APC. Outlook for advanced biofuels. Energy Policy. 2006;**34**(17):3268-3283

[20] Ferreira L. Em decisão histórica, EUA e China comprometem-se a cortar gases estufa em pacto global: 11/12/2011-UOL Notícias. UOL Ciência e Saúde, em Durban [Internet]. 2011. Available from: https://noticias.uol.com.br/ciencia/ultimas-noticias/redacao/2011/12/11/em-decisao-historica-eua-e-china-comprometem-se-a-cortar-gases-estufa-em-pacto-global.htm [cited: 02 June 2019]

[21] Tomei J, Helliwell R. Food versus fuel? Going beyond biofuels. Land use policy [Internet]. 1 Nov 2016;**56**: 320-326. Available from: https://www.sciencedirect.com/science/article/abs/pii/S0264837715003579 [cited: 02 June 2019]

[22] Van Eck NJ, Waltman L. VOS viewer: Visualizing scientific landscapes [Internet]. 2016. Available from: http://www.vosviewer.com/ [cited: 12 April 2017]

[23] World Intellectual Property Organization. MP, Commission of the European Communities. F, Woolf P, Carpenter MP, Narin F, Woolf P. World patent information [Internet]. WIPO jointly with the Commission of European Communities, Vol. 3; 1979. pp. 160-163. Available from: https://econpapers.repec.org/article/eeeworpat/v_3a3_3ay_3a1981_3ai_3a4_3ap_3a160-163.htm [cited: 02 June 2019]

[24] Wagner RP, Parchomovsky G. Patent portfolios. SSRN Electronic Journal. 2004. Available from: http://www.ssrn.com/abstract=582201 [cited: 02 June 2019]

[25] Aristodemou L, Tietze F. Citations as a measure of technological impact: A review of forward citation-based measures. World Patent Information. 2018;**53**:39-44

[26] Martinelli A. An emerging paradigm or just another trajectory? Understanding the nature of technological changes using engineering heuristics in the telecommunications switching industry. Research Policy. 2012;**41**(2):414-429