energies

MDPI

Review

Technology Evolution in Membrane-Based CCS

José Luis Míguez [1], Jacobo Porteiro [1], Raquel Pérez-Orozco [1,*] and Miguel Ángel Gómez [2]

[1] Industrial Engineering School, University of Vigo, Lagoas-Marcosende s/n, 36310 Vigo, Pontevedra, Spain; jmiguez@uvigo.es (J.L.M.); porteiro@uvigo.es (J.P.)
[2] Defense University Center, Spanish Naval Academy, Plaza de España s/n, 36900 Marín, Spain; miguelgr@cud.uvigo.es
* Correspondence: rporozco@uvigo.es; Tel.: +34-986-818624

Received: 17 October 2018; Accepted: 11 November 2018; Published: 14 November 2018

Abstract: In recent years, many CO_2 capture technologies have been developed due to growing awareness about the importance of reducing greenhouse gas emissions. In this paper, publications from the last decade addressing this topic were analyzed, paying special attention to patent status to provide useful information for policymakers, industry, and businesses and to help determine the direction of future research. To show the most current patent activity related to carbon capture using membrane technology, we collected 2749 patent documents and 572 scientific papers. The results demonstrated that membranes are a developing field, with the number of applications growing at a steady pace, exceeding 100 applications per year in 2013 and 2014. North American assignees were the main contributors, with the greatest number of patents owned by companies such as UOP LLC, Kilimanjaro Energy Inc., and Membrane Technology and Research Inc., making up 26% of the total number of published patents. Asian countries (China, Japan, and Korea) and international offices were also important knowledge sources, providing 29% and 24% of the documents, respectively. Furthermore, this paper highlights 10 more valuable patents regarding their degree of innovation and citations, classified as Y02C 10/10 according to the Cooperative Patent Classification (CPC) criteria.

Keywords: membrane-based technology; CO_2 capture and storage; patent; cooperative patent classification (CPC) code

1. Introduction

Anthropogenic greenhouse gas (GHG) emissions have been growing uninterrupted since the beginning of fossil fuel use, and they are expected to grow by approximately 30% by 2040 from 2016 levels, mainly due to contributions from industrial activity [1]. Carbon dioxide is the major causative agent of global climate change and currently reaches atmospheric concentrations above 400 ppm, which is an alarming and substantially higher value compared to the preindustrial period when the concentration was approximately 280 ppm [2,3]. Hence, future actuations have to be guided to reverse current trends, stabilize GHG concentrations in the atmosphere, and avoid a temperature increase of more than 2 °C in the present century.

As awareness of global warming grows, certain strategies are being studied in order to mitigate the consequences. The main ones focus on the following [4]: reducing energy intensity through energy efficiency, as several authors have explained [5–7]; reducing carbon intensity by means of renewable energy and use of less carbon-intensive fuels, as shown in many studies [8–12]; and promoting the implementation of carbon capture and storage (CCS) technologies [13]. Owing to the intrinsic GHG emissions of some industries and the fact that hydrocarbons are expected to be used as fuels for a long time yet, CCS techniques have become essential. According to the International Energy Agency, 95% of coal-fired plants and 40% of gas-fired plants are required to be equipped with CCS systems in order to curtail the rise in global temperature [1]. Industries such as natural gas, fertilizer manufacturing, and hydrogen production operate in a mature CO_2 separation market. However, carbon capture for large-scale power plants still remains to be implemented due to economic or technical viability [14].

In recent years, many researchers have studied CCS technologies. Zheng and Xu, Figueroa et al., Leung et al., Pires et al., and Tan et al. [15–19] all reviewed the current status of carbon capture technologies. Strazza et al. [20] provided key information related to the development of specific rules for the application of Life Cycle Assessment (LCA) to CCS. Carbon capture can be carried out in different phases of the combustion process. The available procedures are postcombustion systems, which have been studied by many authors such as Lior Rao [21,22] among others; precombustion systems, reviewed by Jansen et al. [23]; and oxy-fuel capture systems, shown in several studies [24–26]. The most common CO_2 separation techniques used to accomplish the previously mentioned procedures are absorption process [27–30], adsorption [31–47], gas separation membranes and cryogenic distillation [17,48–52], and biological separation [53–59].

Membranes, which are described more deeply in this paper, utilize differences in the diffusivity, solubility, absorption, and adsorption abilities of different gases on different materials for separation [60]. According to Ebner and Ritter [61], membranes are an attractive option for CO_2 separation because their molecular size is smaller than that of most gases. The performance of the membrane depends on the membrane material, thickness, structure, configuration as well as the design of the capture system [62], and they can obtain results up to 88% [16]. As the use of separating agents or phase changes is unnecessary, membranes have lower costs compared to other separation technologies [61]. In addition, they present high versatility in industrial applications because they have the possibility of being used in both postcombustion and particularly in precombustion modes [63]. Other advantages of membranes are low weight, low maintenance requirements, the possibility of being vertically or horizontally positioned, and scalability. However, the technique also has limitations, such as the requirement for low CO_2 concentration and pressure in waste gases, together with the loss of its separating properties [63], which requires the use of large flow volumes and low temperatures for some materials, such as polymers, in order to increase membrane durability [64].

Several authors, including Park et al., Bernardo et al., Brunetti et al., Ebner and Ritter, Khalilpour et al., Kotowicz et al., and Atsonios et al., have collected available information to show recent advances in membrane utilization for CO_2 separation [61,62,65–69]. Kotowicz et al., in several works [70,71], studied the impact of introducing membranes for CCS in coal power plants. Burdyny et al. studied the availability of hybrid separation using membrane and cryogenic systems together in oxy-fuel processes [72]. Luis et al. [73] established membrane classification based on the separation mechanism employed, obtaining performance indicators as a function of the materials used. Another classification based on the membrane material was made by D'Alessandro et al. [74].

Polymeric membranes are most common in commercial applications, and two types of polymeric membranes are defined according to their glass transition temperature [61,75,76]. Glassy polymers, such as polysulfones, polyimides, polyaramides, and polycarbonates, are more common in commercial applications. From the large variety of available polymers, polyethylene oxide (PEO, consisting of polar ether groups that can produce quadrupolar interactions with CO_2, being translated into remarkably high CO_2/H_2 solubility selectivity) [77] is one of the most selective polymers for CCS because it has a high affinity towards CO_2, as seen in several studies [78–80]. Hollow fibers are mainly used in membrane contactors as nonselective barriers between liquid (sorbent) and gas phases, with the possibility of operating in parallel flow or cross-flow modes [81,82]. Wang and Zhang [83] studied the influence of membrane wetting using an aqueous diethanolamine (DEA) solution as an absorbent and a polymeric-based membrane. Inorganic membranes have greater stability than the other previously mentioned ones and are able to resist high temperatures and hard work conditions. They can be nonporous (made of materials such as palladium or stainless steel) or porous [84] (commonly made of alumina, zeolites, or silicates), and they are widely treated by Pera-Titus [85]. Emerging materials in this field include metal–organic frameworks (MOFs, consisting of microporous crystalline solids composing a three-dimensional network of metallic ions to result in a porous structure), which are used in hybrid membranes [40,74]; and graphene [86,87]. Recently, mixed matrix membranes (MMMs)—also called hybrid membranes—have been developed by blending at least two materials with different properties. Three types of MMMs have been reported depending on the filler: solid, liquid, and solid–liquid [88,89]. Nafisi and Hägg [90] worked on solid–polymer membranes with nanoparticle fillers, creating a membrane with zeolite imidazolate framework-8 (ZIF-8, a member of the Zeolitic Imidazole Framework family characterized by a high internal surface area, high thermo-chemical stability, and highly selective sieving ability) nanoparticles as an inorganic filler in a Pebax-2533 polymer matrix (Pebax is the trade name of commercial products made of poly(ether amide) block copolymer materials). Other examples of hybrid membranes include three-component membranes such as Pebax, poly (ethylene glycol), and multiwalled carbon nanotubes, as studied by Wang et al. [91]; and graphene oxide (GO) nanosheets as fillers in polymeric matrix membranes, provided by Li et al. [92]. Another membrane type is a facilitated transport membrane in which carriers transport gas molecules through the membrane by means of a reversible reaction. Fixed carrier, solvent-swollen, and immobilized liquid membranes are distinguished according to their carrier mobility [93] and were studied by Sandru et al. [94,95] and Kasahara et al. [96] among others.

The study of the economic viability of carbon capture has also been the topic of some reviews. Lockwood [97], Markusson et al. [98,99], and Noureldein et al. studied different uncertainties about CCS, including economic and technological ones [98,99]. Melien et al. [100], Viebahn et al. [101], and Valentic et al. [102] focused on the cost of CCS in different locations. Other researchers have studied the feasibility of concrete CCS techniques. Abanades et al. [103] focused on sorbent costs, while Ho et al. [104,105] analyzed pressure swing adsorption and membrane costs.

Patent documents contain valuable research results that are useful for industries, businesses, and policymakers. Their main applications include analyzing competitors, tracking technology, and identifying trends in markets [106–108]. Hall et al. [109] assigned a measurement of company reputation from the number of patent citations. Patents are also used by some industries as a protection guarantee for trade secrets [110]. On average, approximately 13,500 scientific publications per year cite patents, which is 1.7% of the total publications indexed in the Science Citation Index (SCI) database. Nearly 70% of them are related to chemistry, followed distantly by physics [111]. Database digitalization has led to growth in this trend in recent years, with a 10-fold increase in patent citations in Google Scholar between 2010 and 2014 [112].

Unfortunately, few investigations about the most recent patent documents of membrane-based CCS were found within the reviewed literature in this study. An earlier work [113] gave a general review of the whole CCS patent process, also providing information from the point of view of knowledge-generating companies. A more recent study, developed by Qiu and Liu [114], was focused on the investigation of knowledge mapping of CCS technologies. Accordingly, the aim of this paper was to analyze the current status of patents related to specific CCS technology based on the use of membranes. The study of the status of CCS membrane technology focused on the most prominent scientific producers. Moreover, it was performed as a function of the geographical provenance of the documents and the number of assignees and in consideration of the classification of patents according to Cooperative Patent Classification (CPC) codes and the degree of innovation.

2. Methodology

More than 100 international databases comprising international patent offices, such as the European office (EPO) and the World Intellectual Property Office (WIPO), as well as the national offices of the United States, France, Germany, United Kingdom, China, Korea, and Japan among others, were consulted to provide more details for this study. Keywords and their variants combined with the CPC codes were used to design the search strategy following the method used in a previous work where a more generic CCS patent study was performed [113]. Moreover, the search was restricted to the last decade because only approximately 25% of documents related to CO_2 capture were published before that.

The main sources utilized were the Derwent World Patents Index (DWPI), a very complete database containing more than 28 million patent families from approximately 50 patent offices, created by Thomson Reuters; PatBase, the most used patent database developed by Minesoft and RNS Group which provides a tool offering very complete results; Patentscope, the WIPO's database; Espacenet, providing access to more than 80 million patent documents; and Web of Science, an online service for scientific information.

According to the CPC code, only documents classified as Y02C 10/10 (capture by membranes or diffusion) were collected, which was included as one of the six technologies for carbon dioxide separation, codified as B01D 2257/504. The most used terms in the 787 innovations found (2749 patent documents) were waste gas-related and gas stream-related terms, such as "gas steam", "separation device", "gas mixture", "preparation method", "CO_2", and "CH_4" in addition to membrane technology terms, such as "membrane module", "composite membrane", "hollow fiber", and "molecular sieve". The literature was also analyzed using the same keyword criteria, producing 572 scientific papers related to membrane separation.

Most of the patents were classified as the Y02 or B01 groups. However, activity in sections C (C01, C10, C08) and F (F25, F23) was observed to a lesser degree. Subgroups B01D 2257/504 and B01D 53/228 were the most dominant—assigned to 64% and 40% of patents, respectively—and were related to the CO_2 capture process and membrane usage for gas or vapor separation. Other relevant subgroups, although to a lesser extent, were Y02P20/152 and B01D53/22, which related to CO_2 emission reduction and waste gas purification and represented 30% and 27% of patents, respectively.

Prior knowledge related to each innovation is generally requested by international offices. Therefore, related patent documents and scientific papers have to be cited in patent texts by applicants and even by patent examiners if they are considered necessary. These references are shown by search tools such as Scopus or Google Scholar, allowing the analysis of innovations in a specific field. Patents that receive numerous citations indicate the introduction of an interesting innovation that must be further developed, whilst uncited patents represent the end of the line of development. Thus, a relationship can be defined between patent relevance and a high number of citations received [115].

Consequently, not every patent has the same level of quality but depends on the technical and economic value of the inventions, which can be inferred by the number of citations received [112,116]. An indicator (*i*), shown in Equation (1) below, was created to rank patents according to innovation and breakthrough. The indicator compared the citations provided and citations received and added a weighing criterion that depended on the time elapsed since the patent publishing date. A reasonable comparison was established among patents. Hence, recent patents with few issued references and many received citations had the highest *i* values and were therefore considered to have a better position.

$$i = \frac{Patent\ j\ received\ citations - Patent\ j\ issued\ citations}{Present\ year - \ Patent\ j\ pubication\ year} \quad (1)$$

3. Results and Discussion

3.1. Analysis of Scientific Literature

Scientific literature from the decade studied was analyzed due to the parallelism shown by patent activity. Figure 1 shows that the number of membrane-related papers started increasing from 2007, reaching a maximum in 2013 with almost 100 documents. The activity slowly diminished from then on.

As expected, most active publishers were research centers and universities; this is shown in Table 1 where the main scientific producers are listed. The list was topped by a French organization, the Centre National de la Recherche Scientifique, which contributed 5% of the total, followed by the US Department of Energy and the Norwegian University of Science & Technology. The scientific papers could be found in more than 150 scientific journals and publications, with the highest percentage

(11%) being published in the Journal of Membrane Science. Other top sources included International Journal of Greenhouse Gas Control and Industrial and Engineering Chemistry Research. In regard to sources of information, peer-reviewed journals prevailed above proceedings papers or other types of publications, such as reviews or book chapters, with 71% of total coming from peer-reviewed articles versus 19% and 10% from proceedings and other types of publications, respectively.

Table 1. Top 10 organizations producing scientific papers related to carbon capture using membranes.

ID	Organization	Documents	% Total
1	Centre National de la Recherche Scientifique (CNRS)	30	5%
2	United States Department of Energy	27	5%
3	Norwegian University of Science & Technology (NTNU)	24	4%
4	University of Lorraine	22	4%
5	Chinese Academy of Sciences	18	3%
6	SINTEF Mat & Chem	16	3%
7	University System of Georgia	16	3%
8	Zhejiang University	16	3%
9	Cooperative Research Centre for Greenhouse Gas Technologies (CO_2CRC)	15	3%
10	University of Melbourne	12	2%

Ebner and Ritter [61] had studied peer review manuscripts from several universities, research centers, and some companies published over an earlier period (1995–2005). In that study, the University of Texas and Georgia Institute of Technology had stood out, taking part in more than 40 studies each. The study evidenced considerable research activity at that time.

Differences between the scientific literature and patents could also be noted in our study. Contributing organizations had a more equal number of studies carried out than assignees with owned patents, and research centers outpaced companies in terms of published papers. Moreover, co-authorship was usual; therefore, most of the papers were written by investigators from more than one organization.

Citations are also important indicators of relevance, as are patent documents. Two papers could be highlighted in terms of received references, surpassing the thousand others. Sumida et al. from the University of California studied *Carbon dioxide capture in metal–organic frameworks* [117]. This research obtained more than 2300 citations since it was published in 2012. In this work, recent advances in MOFs were reviewed as well as their ability as adsorbents in different applications and combined with amines. The performance of MOF-containing membranes in CO_2/H_2 and H_2/CO_2 mixture separation was also studied, and selectivity and permeability properties were compared according to the MOF type used.

D'Alessandro et al. authored the second most-cited paper, *Carbon Dioxide Capture: Prospects for New Materials* [74], which received approximately 1600 citations since 2010. This publication addressed progress in CO_2 separation by chemical or physical adsorption, sorbent absorption, and membranes in natural gas sweetening, postcombustion, and precombustion applications.

3.2. Number of Patents and Assignees

According to the WIPO [118], a patent family is defined as "a collection of published patent documents relating to the same invention, or to several inventions sharing a common aspect, that are published at different times in the same country or published in different countries or regions".

Figure 1 illustrates the evolution of the collected membrane patent family (CPC Y02C 10/10) and the relationship between applications and publications. During the period between 2007 and 2013, the number of applications was growing yearly, starting from less than 50 in 2007 until reaching more than 100 in the years 2013 and 2014. From 2015 onwards, a pronounced decrease occurred in applications, while publications were still growing due to the delay that usually occurs following the application date.

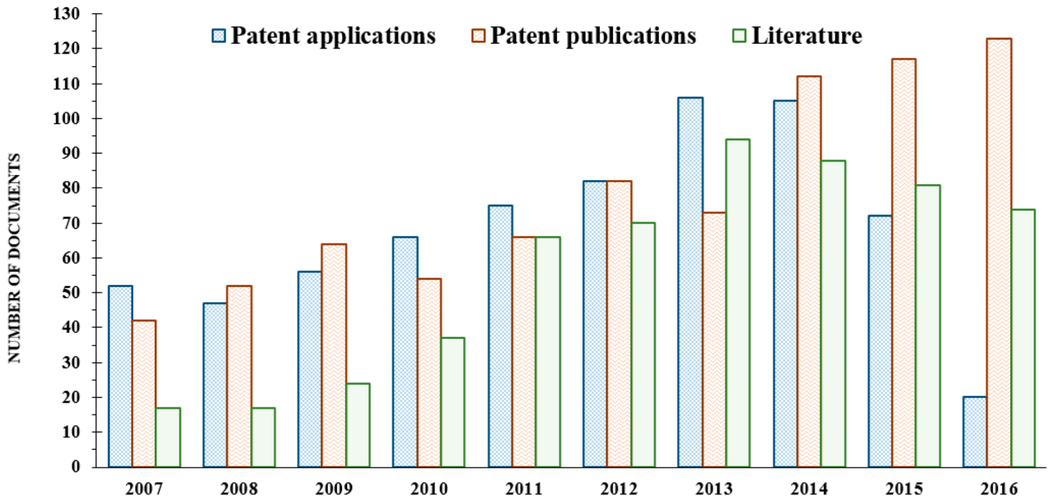

Figure 1. Evolution of the number of patent family applications and publications of Cooperative Patent Classification (CPC) Y02C 10/10 and scientific literature between 2007 and 2017.

Patent information was analyzed to see the relevance of the patent. It was found that 67% of the patent families did not receive any citation, whereas less than 1% of documents had been referenced more than 50 times. The amount of received citations is an indicator of patent relevance, and the results demonstrated that only a small percentage of published documents had high value.

3.3. Analysis by Country/Office and Assignee Nationality

Geographical analysis of patents based on publishing country or international office can help determines the extension of patent generation areas and potential markets for that technology. Figure 2 depicts the distribution of patents from the last decade showing their provenance, both published and generated. The USA appeared as the main receiving market of CO_2 capture technology innovations, with 714 publications in the last 10 years (27%). Asian countries, especially China, Japan, and Korea, and international offices were also important publishers, with 29% and 24% patents, respectively. However, among the countries generating patents, the USA clearly stood out as the primary knowledge generator, with 42% of the total. The fact that only six countries/offices generated 90% of patents worldwide was also remarkable; publications were slightly more geographically distributed.

Considering the type of applicants can reveal the ownership of the membrane technology. It was observed that 27% of patents were generated by companies. Furthermore, 14% of patents came from research centers and universities, while the rest (59%) were owned by individual inventors. Although membrane technologies have entered the market, market implementation will not be strong if the high percentage of patents from individuals continues. US policy on this field involves the inventor's identity often prevailing over the institution to which they belong, indicating that there was probably a greater number of patents from companies or governmental academic institutions than those accounted for in this study.

Moreover, there are competitive barriers or obstacles to introducing new products in the market, which are caused by a high technological concentration of innovations. Indeed, our results showed that a few applicants generated more than half of the patent families. These were considered the reference group and are summarized in Table 2. In contrast, 88% of applicants had generated only one or two patent families, and 9% of them possessed between three and seven innovations.

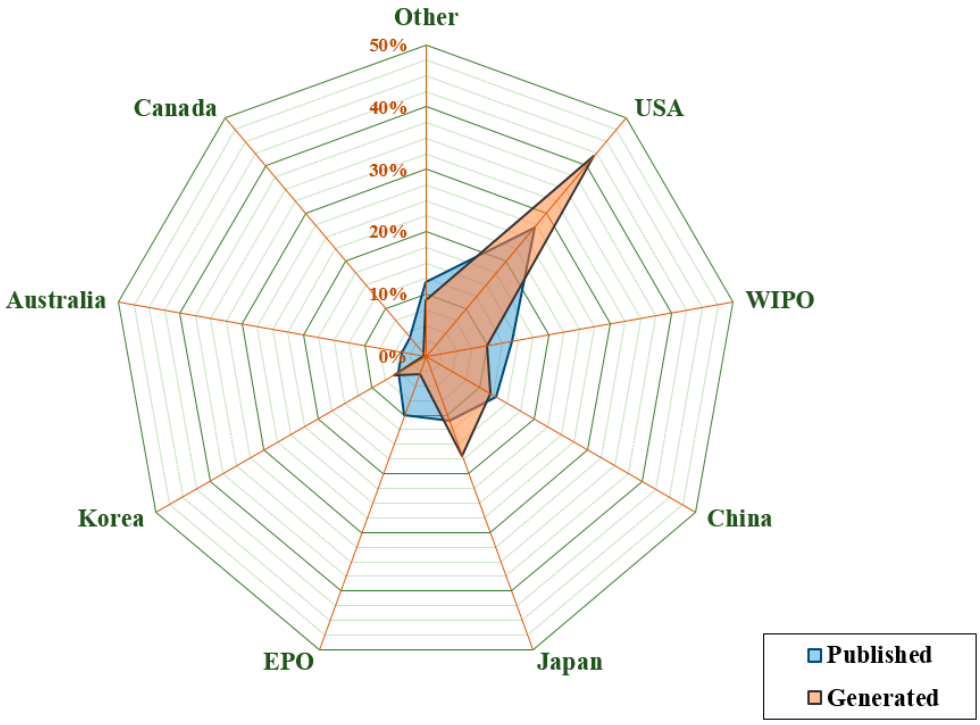

Figure 2. Patents of CPC Y02C 10/10 as a function of their provenance.

Companies from different CO_2 emitting sectors, such as oil and gas, power generation, and cement and steel production, along with research centers investigated the technology presented in this paper. Multinational UOP LLC, which is a provider of technological solutions to oil and petrochemical companies, led the reference group list with 7% of total patent production. This company is the owner of processes and technologies for gas separation, including the UOP Separex™ Membrane System designed for natural gas sweetening and Selexol Process for carbon dioxide and acid gas separation through the use of a high pressure solvent. The second-highest applicant was General Electric Co., followed by Kilimanjaro Energy Inc. and Fuji Film Corp. In fifth place was Shell Internationale Research Maatschappij BV, a company that has developed different CO_2 capture technologies on an industrial scale. The biggest CCS project worldwide, which is located in Australia and led by Chevron with participation from ExxonMobil, was included in this study, and it is expected to capture between 3 and 4 million tons of carbon dioxide per year.

Figure 3 represents patent evolution of the top five companies in Table 2, including data from the previously mentioned research by Ebner and Ritter [61]. From the graph, it can be seen that these companies emerged in the membrane technology field in this decade, especially from 2007 onwards. Two tendencies can be distinguished: UOP LLC and Fuji Film Corp. continued increasing their efforts. By contrast, General Electric Co. and Kilimanjaro Energy Inc. decelerated their patent production. Shell Internationale Research Maatschappij maintained almost stable activity throughout the studied period.

Table 2. Number of published patent families and individual patents according to the main assignees (Y02C 10/10).

ID	Applicant	Pcatent Families	% Total	Patent Documents	% Total
1	UOP LLC	56	7%	203	7%
2	General Electric Co.	29	4%	145	5%
3	Kilimanjaro Energy Inc.	19	2%	136	5%
4	Fuji Film Corp.	39	5%	123	4%
5	Shell Internationale Research Maatschappij	19	2%	120	4%
6	Air Liquide SA	27	3%	97	4%
7	Membrane Technology & Res. Inc.	28	4%	89	3%
8	Mitsubishi Hitachi Power Systems Euro GM	25	3%	81	3%
9	Chevron Corp.	23	3%	79	3%
10	University of Colorado	14	2%	74	3%
11	Renaissance Energy Res. Corp.	12	2%	57	2%
12	Nippon Steel & Sumitomo Metal Corp.	13	2%	54	2%
13	ExxonMobil Res & Eng Co.	8	1%	53	2%
14	Nippon Oil Co. Ltd.	10	1%	47	2%
15	Evonik Degussa GMBH	3	<1%	42	2%
16	Georgia Tech Res. Corp.	11	1%	42	2%
17	University of Tianjin	27	3%	41	1%
18	Samsung Electronics Co. Ltd.	8	1%	40	1%
19	JFE Steel Corp.	2	<1%	38	1%
20	University of Hanyang IUCF-HYU	8	1%	37	1%
21	Saudi Arabian Oil Co.	6	1%	32	1%
22	Aramco Services Co.	4	1%	29	1%
23	Gas Technology Institute	10	1%	27	1%
	Total	**401**	**51%**	**1686**	**61%**

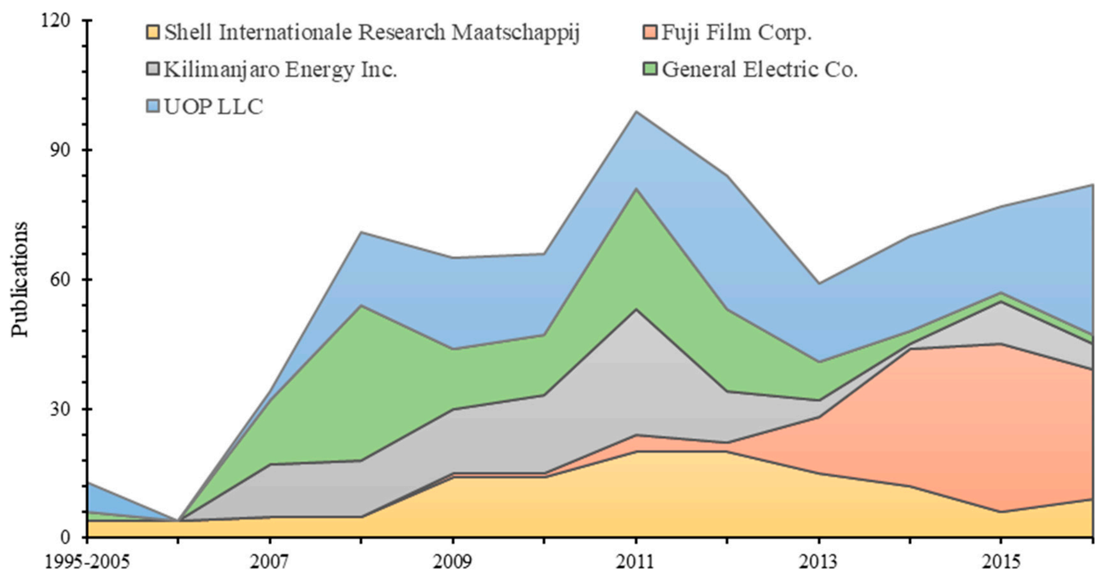

Figure 3. Evolution of the current top five patent-generator companies.

It can be seen that the first patents of UOP LLC originated from the period between 1995 and 2005, but production frequency increased from 2007 onwards; this was also the case for General Electric Co. Fuji Film Corp. was mostly known for image- and document-related activity but started membrane investigations later as a means of business diversification. Their contribution is remarkable considering the number of recent publications (over 50% in only two years) and collaboration with other organizations in membrane development for industrial applications. Kilimanjaro Energy Inc. did not have any innovation before 2007 as it is a new company founded in 2004. The organization was born with the purpose of researching and developing CO_2 capture technology. Indeed, it is focused on a system called ACCESS for carbon dioxide capture from the atmosphere.

A similar study of patent assignees was carried out by Ebner and Ritter [61], who collected information about the main companies creating membrane, adsorption, and absorption patents. Most of the innovations at that time were related to adsorption, followed by absorption, with membrane technology in the last place. According to them, the first commercial PRISM membrane was developed in the 1980s by Monsanto. This product uses asymmetric hollow fibers to perform selective permeation and to separate nitrogen from air [119]. PRISM membranes are still commercialized currently by Air Products and Chemicals, which was part of Monsanto when this technology appeared. Other companies started to develop their own systems for natural gas purification. Thus, Cynara, Selexol, and Grace Membrane Systems took part in the membrane business, being acquired in the 1990s by Natco, UOP, and Kvaerner, respectively, as mentioned by Baker and Drioli [120,121]. Later, the improvement in membrane properties allowed them to be used in other applications, diversifying the market and encouraging the appearance of new companies.

The abovementioned study separated patent assignees into two categories: companies and research groups. It encompassed the years between 1995 and 2005, adding up to a total of 154 published patents by companies over the entire period. In addition, almost half came from a short period from 2002 to 2005. Most active organizations in that decade were Membrane Technology and Research and Praxair Technology, tied at first place with 23 patents each, followed by Air Products and Chemicals Inc. and Air Liquide. Table 3 compares the 10 most active companies at the time with their current activity. Most of the summarized companies have increased their activity, except Praxair Technology, Engelhard Corp. and Norsk Hydro ASA. The last two have halted innovations in the membrane field. These results reveal a big increase in patent production and a change in membrane technology leadership.

Table 3. Evolution of published patents of the 10 most active companies between 1995 and 2005 according to Ebner and Ritter [61].

Company	1995–2005	2007–2017
Praxair Technology, Inc., USA	23	6
Membrane Tech. & Research, Inc., USA	23	89
Air Products and Chemicals, Inc., USA	11	24
Air Liquide, France	11	97
Exxon Mobil, USA	10	53
Chevron USA Inc., USA	9	79
UOP LLC, USA	7	203
Engelhard Corporation, USA	6	0
Norsk hydro ASA, Norway	6	0
E.I. Du Pont de Nemours and Company, USA	5	13

3.4. Analysis by Innovation Index

According to the innovation index mentioned in the Methodology section, we carried out a classification of membrane patents for carbon capture. Table 4 presents a list of the 10 most valuable patents organized by their degree of innovation as well as their assignee, date, and number of issued/received references.

In the first place was patent US20080127632A1 *Carbon dioxide capture systems and methods* [122], which had the highest *i* value; it was published in 2008 by General Electric Co. This innovation protects a CO_2 capture system based on a membrane, whose selective permeability of carbon dioxide allows separation from a gas stream. This system includes a compressor to heighten the pressure of the exhaust gas and a separator, with the membrane located in the middle. The separator produces a CO_2 lean stream, which is carried to an expander in order to generate power and optimize this process, and a CO_2-rich stream, which will be stored. This patent only cited 11 documents, whilst it was widely cited by patents from SustainX Inc., ExxonMobil, and General Electric Co. related to emission control, carbon capture, and compressed gas energy.

The abovementioned company is the current assignee of patent US20070072949A1 *Methods and apparatus for hydrogen gas production* [123] as well, which is related to a method and reactor for syngas conversion and hydrogen purification. This reactor contains a catalyst combined with a membrane and integrates a heat exchanger for cooling the catalyst.

Kilimanjaro Energy Inc. possessed two valuable patents. US20080087165A1 *Method and apparatus for extracting carbon dioxide from air* [124] describes different techniques with a common foundation: extraction of CO_2 using conventional methods and subsequent release of a portion of extracted gas in controlled environments, with the purpose of improving the growth of vegetal species. This was the most cited document in the list and was referenced by 154 other patents. Citations were made since the publication date, reaching the highest amount in 2011 with a total of 32 citing documents, but decreasing from then on. Approximately 60% of new patents citing this addressed the CCS topic not only through membranes but also using biological capture, adsorption, or absorption. Assignees were analyzed, and the results showed that half of them were companies, 38% were particular inventors, and the remaining 10% were research centers. SustainX Inc. turned out to be the company with the highest number of citing patents (26%), mostly related to energy storage using compressed gas. Kilimanjaro Energy Inc. had 9% of references in other carbon capture patents, making it the second most-cited company; however, it was found that 15% of citations were from patents of individual inventors belonging to this company.

WO2007016271A2 *Removal of carbon dioxide from air* [125] was also patented by Kilimanjaro Energy Inc. It proposes a method and apparatus for CO_2 removal that exposes the gas stream to sorbent-covered surfaces. Then, the captured gas is extracted from the sorbent using an ionic exchange resin. This resin is exposed to a second sorbent, which is cleaned by a thermal or pressure swing, recovering a CO_2-rich stream on one side and recirculating the sorbent on the other side.

Fuji Film Corp., the most active company during the last two years, owns two of the patents included in the previous list. WO2012096055A1 *Composition for formation of carbon dioxide separation membrane, carbon dioxide separation membrane and process for production thereof, and carbon dioxide separation apparatus* [126] is a patent in which two other companies have contributed as developers to a lesser extent. The document discloses a high efficiency membrane made of water-absorbable polymer cooled at 0 °C and the method for its production. WO2013018538A1 *Carbon dioxide separation member, method for producing same, and carbon dioxide separation module* [127] presents a separation method consisting of a hydrophobic porous membrane that can resist temperatures above 100 °C. The membrane is surrounded by a polymeric layer and contains an alkali metal carbonate working as a carrier, allowing carbon dioxide from a CO_2/H_2 mixture to permeate at temperatures between 100 °C and 250 °C.

Renaissance Energy Corp., in collaboration with Kobe University, created a facilitated transport membrane that is able to work under temperatures above 100 °C and in different pressure ranges, as documented in JP2009195900A *Carbon dioxide separation apparatus* [128]. This system is designed to carry out hydrogen purification and consists of a hydrophilic porous membrane surrounded by a gel layer made of a mixture of caesium carbonate and polyvinyl alcohol–polyacrylic acid copolymer. The membrane is fed with a gas stream containing carbon dioxide, steam, and other gas impurities, with CO_2 permeation to the other side.

Another carbon capture system was patented in 2010 by Innosepra LLC. It is designed to be implanted in a refinery, a natural gas-fired power plant, or a coal-fired power plant. The system is able to process feed gas containing impurities and water vapor using temperature and pressure swing adsorption. Approximately 80% of the moisture and other impurities from the CO_2-rich stream is eliminated by membrane separation, pressure swing adsorption, or temperature swing adsorption, as explained in patent US20100251887A1 *Carbon dioxide recovery* [129].

Table 4. Main innovations according to the CPC field Y02C 10/10 and innovation degree.

ID	Publication Number	Title	Assignee	Year	Cited Documents	Received Citations	Innovation deg. "I"
1	US20080127632A1 [111]	Carbon dioxide capture systems and methods	General Electric Co.	2008	11	107	10.7
2	US20070004023A1 [115]	Methods, apparatuses, and reactors for gas separations	Trachtenberg, M.	2007	8	114	10.6
3	US20080087165A1 [113]	Method and apparatus for extracting carbon dioxide from air	Kilimanjaro Energy Inc.	2008	71	154	9.2
4	WO2007016271A2 [114]	Removal of carbon dioxide from air	Kilimanjaro Energy Inc.	2007	11	87	7.6
5	US20070022877A1 [116]	Ordered mesopore silica mixed matrix membranes and production methods for making ordered mesopore silica mixed matrix membranes	Kim, S. and Marand, E.	2007	18	90	7.2
6	JP2009195900A [117]	Carbon dioxide separation apparatus	Renaissance Energy Res. Corp.	2009	6	60	6.8
7	US20100251887A1 [118]	Carbon dioxide recovery	University of Kobe Innosepra LLC	2010	7	50	6.0
8	WO2012096055A1 [119]	Composition for formation of carbon dioxide separation membrane, carbon dioxide separation membrane and process for production thereof, and carbon dioxide separation apparatus	Jain Ravi Fuji Film Corp.	2012	8	35	5.6

Moreover, individual inventors also held positions in the list of top 10 patents. Trachtenberg's phase-conversion membrane, US20070004023A1 *Methods, apparatuses and reactors for gas separation* [130], occupied second place in the ranking. Here, several systems are presented, common among them being a membrane that is able to interact chemically with mixed gas streams, turning one component into a second phase and releasing it into the purified form. The designed apparatus comprises a spiral body reactor with a membrane reactor bag in liquid contact with a hollow fiber, with the phase-conversion membrane settled in the middle. Furthermore, this is a versatile system because operating temperatures oscillate from 4 °C to 140 °C and feed streams can be gases from the combustion of natural gas. Marand and Kim studied MMMs in US20070022877A1 *Ordered mesopore silica mixed matrix membranes and production methods for making ordered mesopore silica mixed matrix membranes* [131]. The membrane, made by adding mesoporous silica in a polymeric matrix, commonly polysulfone, has improved selectivity and permeability compared to simple polymeric membranes.

4. Summary

Although absorption continues to be the most used method for carbon capture, membrane separation has high potential in the field of carbon capture as a less energy-intensive and more affordable technique. Many types of membranes can be prepared depending on the separation method or the fabrication material, including polymeric, hollow fiber, or mixed matrix membranes among others. In fact, this diversity allows membranes to be adapted to feed gas features depending on the temperature, pressure, and carbon dioxide concentration.

This study collected 572 scientific papers and 2749 membrane-related patents from the last decade and analyzed them according to their geographical distribution, assignee, and innovation degree. The results showed that the number of patents had been increasing every year, starting from less than 50 applications in 2007 to more than 100 in the most recent years (2013 and 2014).

The USA was the main source of knowledge in this field, with many patents from companies such as UOP LLC, the main worldwide patent producer, Kilimanjaro Energy Inc., and Membrane Technology & Research Inc., including innovations created by particular inventors or research centers and universities. The USA was also the target market for membranes in terms of publication countries.

The results, together with some advantages such as versatility and lower cost, demonstrate that the state-of-the-art membrane technology is an emerging and attractive CCS system. Its benefits are more evident when the feed gas has an acceptable partial pressure of CO_2 and the purity requirements of the output stream are not too high, providing high potential for its industrial implementation.

Author Contributions: Conceptualization, J.L.M. and J.P.; Investigation, J.P., R.P.-O. and M.Á.G.; Resources, R.P.-O. and M.Á.G.; Writing—original draft preparation, R.P.-O.; Writing—review and editing, J.P. and J.L.M.; Supervision, J.L.M.

Acknowledgments: The authors would like to acknowledge financial support from the project Biomasa-AP, approved by the programme INTERREG V-A España-Portugal 2014-2020 (POCTEP) and co-financed by the European Regional Development Fund (FEDER). The work of Raquel Pérez-Orozco has been supported by the grant FPU-15/02430 of the Ministry of Education, Culture and Sports (Spain).

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this article

CCS	carbon capture and storage
CNRS	Centre National de la Recherche Scientifique
Co.	company
CO2CRC	Cooperative Research Centre for Greenhouse Gas Technologies
Corp.	corporation
CPC	Cooperative Patent Classification
DEA	diethanolamine

DWPI	Derwent World Patents Index
EPO	European Patent Office
GHG	greeenhouse gas
GO	graphene oxide
IEA	International Energy Agency
Inc.	incorporation
LCA	Life Cycle Assessment
LLC	limited liability company
MMMs	mixed matrix membranes
MOF	metal–organic frameworks
NTNU	Norwegian University of Science & Technology
PEBAX	polyether block amide
PEO	polyethilene oxide
SCI	Science Citation Index
US/A	United States of America
WIPO	World Intellectual Property Office
ZIF	zeolitic imidazolate framework

References

1. International Energy Agency. *World Energy Outlook: 2016*; OECD/IEA: Paris, France, 2016.
2. Aaron-Morrison, A.P.; Ackerman, S.A.; Adams, N.G. State of the climate in 2015. *Bull. Am. Meteorol. Soc.* **2016**, *97*, S12–S75. [CrossRef]
3. Oeschger, H. CO_2 and the greenhouse effect: Present assessment and perspectives. *Ciba Found. Symp.* **1993**, *175*, 2–17, discussion 17. [PubMed]
4. Yang, H.; Xu, Z.; Fan, M.; Gupta, R.; Slimane, R.B.; Bland, A.E.; Wright, I. Progress in carbon dioxide separation and capture: A review. *J. Environ. Sci.* **2008**, *20*, 14–27. [CrossRef]
5. Brown, M.A.; Kim, G.; Smith, A.M.; Southworth, K. Exploring the impact of energy efficiency as a carbon mitigation strategy in the U.S. *Energy Policy* **2017**, *109*, 249–259. [CrossRef]
6. Herring, H. Energy efficiency—A critical view. *Energy* **2006**, *31*, 10–20. [CrossRef]
7. Palm, J.; Thollander, P. An interdisciplinary perspective on industrial energy efficiency. *Appl. Energy* **2010**, *87*, 3255–3261. [CrossRef]
8. Alfonsin, V.; Suarez, A.; Urrejola, S.; Miguez, J.; Sanchez, A. Integration of several renewable energies for internal combustion engine substitution in a commercial sailboat. *Int. J. Hydrogen Energy* **2015**, *40*, 6689–6701. [CrossRef]
9. Cai, Y.P.; Huang, G.H.; Yeh, S.C.; Liu, L.; Li, G.C. A modeling approach for investigating climate change impacts on renewable energy utilization. *Int. J. Energy Res.* **2012**, *36*, 764–777. [CrossRef]
10. de Vries, B.J.M.; van Vuuren, D.P.; Hoogwijk, M.M. Renewable energy sources: Their global potential for the first-half of the 21st century at a global level: An integrated approach. *Energy Policy* **2007**, *35*, 2590–2610. [CrossRef]
11. Krozer, Y. Energy markets: Changes toward decarbonization and valorization. *Curr. Opin. Chem. Eng.* **2017**, *17*, 61–67. [CrossRef]
12. Murillo, S.; Míguez, J.L.; Porteiro, J.; Hernández, J.J.; López-González, L.M. Viability of LPG use in low-power outboard engines for reduction in consumption and pollutant emissions. *Int. J. Energy Res.* **2003**, *27*, 467–480. [CrossRef]
13. MacDowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C.S.; Williams, C.K.; Shah, N.; Fennell, P. An overview of CO_2 capture technologies. *Energy Environ. Sci.* **2010**, *3*, 1645–1669. [CrossRef]
14. Rubin, E.; De Coninck, H. *IPCC Special Report on Carbon Dioxide Capture and Storage*; TNO (2004): Cost Curves for CO_2 Storage, Part 2; Cambridge University Press: Cambridge, UK, 2005.
15. Figueroa, J.D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R.D. Advances in CO_2 capture technology—The U.S. Department of Energy's Carbon Sequestration Program. *Int. J. Greenh. Gas Control.* **2008**, *2*, 9–20. [CrossRef]

16. Leung, D.Y.C.; Caramanna, G.; Maroto-Valer, M.M. An overview of current status of carbon dioxide capture and storage technologies. *Renew. Sustain. Energy Rev.* **2014**, *39*, 426–443. [CrossRef]
17. Pires, J.C.M.; Martins, F.G.; Alvim-Ferraz, M.C.M.; Simões, M. Recent developments on carbon capture and storage: An overview. *Chem. Eng. Res. Des.* **2011**, *89*, 1446–1460. [CrossRef]
18. Zheng, B.; Xu, J. Carbon capture and storage development trends from a techno-paradigm perspective. *Energies* **2014**, *7*, 5221–5250. [CrossRef]
19. Tan, Y.; Nookuea, W.; Li, H.; Thorin, E.; Yan, J. Property impacts on Carbon Capture and Storage (CCS) processes: A review. *Energy Convers. Manag.* **2016**, *118*, 204–222. [CrossRef]
20. Strazza, C.; Del Borghi, A.; Gallo, M. Development of specific rules for the application of life cycle assessment to carbon capture and storage. *Energies* **2013**, *6*, 1250–1265. [CrossRef]
21. Li, Y.; Wang, Q.M.; Wang, P.B. Evaluation of post-combustion CO_2 capture technologies. *Adv. Mater. Res.* **2013**, *734–737*, 1881–1886.
22. Rao, A.B.; Rubin, E.S. A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. *Environ. Sci. Technol.* **2002**, *36*, 4467–4475. [CrossRef] [PubMed]
23. Jansen, D.; Gazzani, M.; Manzolini, G.; Dijk, E.V.; Carbo, M. Pre-combustion CO_2 capture. *Int. J. Greenh. Gas Control* **2015**, *40*, 167–187. [CrossRef]
24. Buhre, B.J.P.; Elliott, L.K.; Sheng, C.D.; Gupta, R.P.; Wall, T.F. Oxy-fuel combustion technology for coal-fired power generation. *Prog. Energy Combust. Sci.* **2005**, *31*, 283–307. [CrossRef]
25. Li, H.; Yan, J. Preliminary study on CO_2 processing in CO_2 capture from oxy-fuel combustion. In Proceedings of the ASME Turbo Expo, Montreal, QC, Canada, 14–17 May 2007; pp. 353–361.
26. Cormos, C.-C. Chemical Looping with Oxygen Uncoupling (CLOU) concepts for high energy efficient power generation with near total fuel decarbonisation. *Appl. Therm. Eng.* **2017**, *112*, 924–931. [CrossRef]
27. Alie, C.; Backham, L.; Croiset, E.; Douglas, P.L. Simulation of CO_2 capture using MEA scrubbing: A flowsheet decomposition method. *Energy Convers. Manag.* **2005**, *46*, 475–487. [CrossRef]
28. Gomes, J.; Santos, S.; Bordado, J. Choosing amine-based absorbents for CO_2 capture. *Environ. Technol.* **2015**, *36*, 19–25. [CrossRef] [PubMed]
29. Kwak, N.S.; Lee, J.H.; Lee, I.Y.; Jang, K.R.; Shim, J.G. A study of the CO_2 capture pilot plant by amine absorption. *Energy* **2012**, *47*, 41–46. [CrossRef]
30. Vega, F.; Sanna, A.; Navarrete, B.; Maroto-Valer, M.M.; Cortés, V.J. Degradation of amine-based solvents in CO_2 capture process by chemical absorption. *Greenh. Gases Sci. Technol.* **2014**, *4*, 707–733. [CrossRef]
31. Pellerano, M.; Pré, P.; Kacem, M.; Delebarre, A. CO_2 capture by adsorption on activated carbons using pressure modulation. *Energy Procedia* **2009**, *1*, 647–653. [CrossRef]
32. Siriwardane, R.V.; Shen, M.S.; Fisher, E.P.; Poston, J.A. Adsorption of CO_2 on molecular sieves and activated carbon. *Energy Fuels* **2001**, *15*, 279–284. [CrossRef]
33. Hu, H.; Li, X.; Fang, Z.; Wei, N.; Li, Q. Small-molecule gas sorption and diffusion in coal: Molecular simulation. *Energy* **2010**, *35*, 2939–2944. [CrossRef]
34. Duan, Y.; Pfeiffer, H.; Li, B.; Romero-Ibarra, I.C.; Sorescu, D.C.; Luebke, D.R.; Halley, J.W. CO_2 capture properties of lithium silicates with different ratios of Li_2O/SiO_2: An ab initio thermodynamic and experimental approach. *Phys. Chem. Chem. Phys.* **2013**, *15*, 13538–13558. [CrossRef] [PubMed]
35. Jiang, B.; Wang, X.; Gray, M.L.; Duan, Y.; Luebke, D.; Li, B. Development of amino acid and amino acid-complex based solid sorbents for CO_2 capture. *Appl. Energy* **2013**, *109*, 112–118. [CrossRef]
36. Singh, R.; Ram Reddy, M.K.; Wilson, S.; Joshi, K.; Diniz da Costa, J.C.; Webley, P. High temperature materials for CO_2 capture. *Energy Procedia* **2009**, *1*, 623–630. [CrossRef]
37. Yong, Z.; Mata, V.; Rodrigues, A.r.E. Adsorption of carbon dioxide at high temperature—A review. *Sep. Purif. Technol.* **2002**, *26*, 195–205. [CrossRef]
38. Ben-Mansour, R.; Qasem, N.A.A. An efficient temperature swing adsorption (TSA) process for separating CO_2 from CO_2/N_2 mixture using Mg-MOF-74. *Energy Convers. Manag.* **2018**, *156*, 10–24. [CrossRef]
39. Alonso, A.; Moral-Vico, J.; Abo Markeb, A.; Busquets-Fité, M.; Komilis, D.; Puntes, V.; Sánchez, A.; Font, X. Critical review of existing nanomaterial adsorbents to capture carbon dioxide and methane. *Sci. Total. Environ.* **2017**, *595*, 51–62. [CrossRef] [PubMed]
40. Li, J.R.; Kuppler, R.J.; Zhou, H.C. Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504. [CrossRef] [PubMed]

41. Wu, H.; Reali, R.S.; Smith, D.A.; Trachtenberg, M.C.; Li, J. Highly selective CO_2 capture by a flexible microporous metal-organic framework (MMOF) material. *Chem. A Eur. J.* **2010**, *16*, 13951–13954. [CrossRef] [PubMed]
42. Zhou, H.C.; Long, J.R.; Yaghi, O.M. Introduction to metal-organic frameworks. *Chem. Rev.* **2012**, *112*, 673–674. [CrossRef] [PubMed]
43. Bonalumi, D.; Lillia, S.; Manzolini, G.; Grande, C. Innovative Process Cycle with Zeolite (MS13X) for Post Combustion Adsorption. *Energy Procedia* **2017**, *114*, 2211–2218. [CrossRef]
44. Chen, C.; Park, D.W.; Ahn, W.S. CO_2 capture using zeolite 13X prepared from bentonite. *Appl. Surf. Sci.* **2014**, *292*, 63–67. [CrossRef]
45. Hauchhum, L.; Mahanta, P. CO_2 capture onto zeolite 13X and zeolite 4A by pressure swing adsorption in a fixed bed. *Appl. Mech. Mater.* **2014**, *592–594*, 1456–1460. [CrossRef]
46. Yu, L.; Gong, J.; Zeng, C.; Zhang, L. Synthesis of binderless zeolite X microspheres and their CO_2 adsorption properties. *Sep. Purif. Technol.* **2013**, *118*, 188–195. [CrossRef]
47. Delgado, M.R.; Arean, C.O. Carbon monoxide, dinitrogen and carbon dioxide adsorption on zeolite H-Beta: IR spectroscopic and thermodynamic studies. *Energy* **2011**, *36*, 5286–5291. [CrossRef]
48. Xu, G.; Liang, F.; Yang, Y.; Hu, Y.; Zhang, K.; Liu, W. An improved CO_2 separation and purification system based on cryogenic separation and distillation theory. *Energies* **2014**, *7*, 3484–3502. [CrossRef]
49. Tuinier, M.J.; van Sint Annaland, M.; Kramer, G.J.; Kuipers, J.A.M. Cryogenic CO_2 capture using dynamically operated packed beds. *Chem. Eng. Sci.* **2010**, *65*, 114–119. [CrossRef]
50. Tuinier, M.J.; van Sint Annaland, M.; Kuipers, J.A.M. A novel process for cryogenic CO_2 capture using dynamically operated packed beds—An experimental and numerical study. *Int. J. Greenh. Gas Control* **2011**, *5*, 694–701. [CrossRef]
51. Tuinier, M.J.; Hamers, H.P.; Van Sint Annaland, M. Techno-economic evaluation of cryogenic CO_2 capture-A comparison with absorption and membrane technology. *Int. J. Greenh. Gas Control* **2011**, *5*, 1559–1565. [CrossRef]
52. Tan, Y.; Nookuea, W.; Li, H.; Thorin, E.; Yan, J. Evaluation of viscosity and thermal conductivity models for CO_2 mixtures applied in CO_2 cryogenic process in carbon capture and storage (CCS). *Appl. Therm. Eng.* **2017**, *123*, 721–733. [CrossRef]
53. Goli, A.; Shamiri, A.; Talaiekhozani, A.; Eshtiaghi, N.; Aghamohammadi, N.; Aroua, M.K. An overview of biological processes and their potential for CO_2 capture. *J. Environ. Manag.* **2016**, *183*, 41–58. [CrossRef] [PubMed]
54. Yadav, G.; Sen, R. Microalgal green refinery concept for biosequestration of carbon-dioxide vis-à-vis wastewater remediation and bioenergy production: Recent technological advances in climate research. *J. CO_2 Util.* **2017**, *17*, 188–206. [CrossRef]
55. Van Duc Long, N.; Lee, J.; Koo, K.K.; Luis, P.; Lee, M. Recent progress and novel applications in enzymatic conversion of carbon dioxide. *Energies* **2017**, *10*, 473. [CrossRef]
56. Bond, G.M.; Stringer, J.; Brandvold, D.K.; Simsek, F.A.; Medina, M.-G.; Egeland, G. Development of integrated system for biomimetic CO_2 sequestration using the enzyme carbonic anhydrase. *Energy Fuels* **2001**, *15*, 309–316. [CrossRef]
57. Cowan, R.M.; Ge, J.J.; Qin, Y.J.; McGregor, M.L.; Trachtenberg, M.C. CO_2 capture by means of an enzyme-based reactor. *Ann. N. Y. Acad. Sci.* **2003**, *984*, 453–469. [CrossRef] [PubMed]
58. Eriksen, N.T. The technology of microalgal culturing. *Biotechnol. Lett.* **2008**, *30*, 1525–1536. [CrossRef] [PubMed]
59. Sadeghizadeh, A.; Farhad dad, F.; Moghaddasi, L.; Rahimi, R. CO_2 capture from air by *Chlorella vulgaris* microalgae in an airlift photobioreactor. *Bioresour. Technol.* **2017**, *243*, 441–447. [CrossRef] [PubMed]
60. Sreedhar, I.; Vaidhiswaran, R.; Kamani, B.M.; Venugopal, A. Process and engineering trends in membrane based carbon capture. *Renew. Sustain. Energy Rev.* **2017**, *68*, 659–684. [CrossRef]
61. Ebner, A.D.; Ritter, J.A. State-of-the-art adsorption and membrane separation processes for carbon dioxide production from carbon dioxide emitting industries. *Sep. Sci. Technol.* **2009**, *44*, 1273–1421. [CrossRef]
62. Bernardo, P.; Drioli, E.; Golemme, G. Membrane Gas Separation: A Review/State of the Art. *Ind. Eng. Chem. Res.* **2009**, *48*, 4638–4663. [CrossRef]

63. Kanniche, M.; Gros-Bonnivard, R.; Jaud, P.; Valle-Marcos, J.; Amann, J.-M.; Bouallou, C. Pre-combustion, post-combustion and oxy-combustion in thermal power plant for CO_2 capture. *Appl. Therm. Eng.* **2010**, *30*, 53–62. [CrossRef]
64. Merkel, T.C.; Lin, H.; Wei, X.; Baker, R. Power plant post-combustion carbon dioxide capture: An opportunity for membranes. *J. Membr. Sci.* **2010**, *359*, 126–139. [CrossRef]
65. Brunetti, A.; Scura, F.; Barbieri, G.; Drioli, E. Membrane technologies for CO_2 separation. *J. Membr. Sci.* **2010**, *359*, 115–125. [CrossRef]
66. Khalilpour, R.; Mumford, K.; Zhai, H.; Abbas, A.; Stevens, G.; Rubin, E.S. Membrane-based carbon capture from flue gas: A review. *J. Clean. Prod.* **2015**, *103*, 286–300. [CrossRef]
67. Kotowicz, J.; Balicki, A. Enhancing the overall efficiency of a lignite-fired oxyfuel power plant with CFB boiler and membrane-based air separation unit. *Energy Convers. Manag.* **2014**, *80*, 20–31. [CrossRef]
68. Atsonios, K.; Panopoulos, K.D.; Doukelis, A.; Koumanakos, A.; Kakaras, E. Exergy analysis of a hydrogen fired combined cycle with natural gas reforming and membrane assisted shift reactors for CO_2 capture. *Energy Convers. Manag.* **2012**, *60*, 196–203. [CrossRef]
69. Park, H.S.; Lee, J.S.; Han, J.; Park, S.; Park, J.; Min, B.R. CO_2 fixation by membrane separated NaCl electrolysis. *Energies* **2015**, *8*, 8704–8715. [CrossRef]
70. Kotowicz, J.; Chmielniak, T.; Janusz-Szymańska, K. The influence of membrane CO_2 separation on the efficiency of a coal-fired power plant. *Energy* **2010**, *35*, 841–850. [CrossRef]
71. Kotowicz, J.; Bartela, T. Optimisation of the connection of membrane CCS installation with a supercritical coal-fired power plant. *Energy* **2012**, *38*, 118–127. [CrossRef]
72. Burdyny, T.; Struchtrup, H. Hybrid membrane/cryogenic separation of oxygen from air for use in the oxy-fuel process. *Energy* **2010**, *35*, 1884–1897. [CrossRef]
73. Luis, P.; Van Gerven, T.; Van der Bruggen, B. Recent developments in membrane-based technologies for CO_2 capture. *Prog. Energy Combust. Sci.* **2012**, *38*, 419–448. [CrossRef]
74. D'Alessandro, D.M.; Smit, B.; Long, J.R. Carbon dioxide capture: Prospects for new materials. *Angew. Chem. Int. Ed.* **2010**, *49*, 6058–6082. [CrossRef] [PubMed]
75. Freeman, B.D. Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes. *Macromolecules* **1999**, *32*, 375–380. [CrossRef]
76. Wang, S.; Han, X. Application of Polymeric Membrane in CO_2 Capture from Post Combustion. *Adv. Chem. Eng. Sci.* **2012**, *2*, 7. [CrossRef]
77. Kazarian, S.G.; Vincent, M.F.; Bright, F.V.; Liotta, C.L.; Eckert, C.A. Specific Intermolecular Interaction of Carbon Dioxide with Polymers. *J. Am. Chem. Soc.* **1996**, *118*, 1729–1736. [CrossRef]
78. Liu, S.L.; Shao, L.; Chua, M.L.; Lau, C.H.; Wang, H.; Quan, S. Recent progress in the design of advanced PEO-containing membranes for CO_2 removal. *Prog. Polym. Sci.* **2013**, *38*, 1089–1120. [CrossRef]
79. Reijerkerk, S.R.; Arun, A.; Gaymans, R.J.; Nijmeijer, K.; Wessling, M. Tuning of mass transport properties of multi-block copolymers for CO_2 capture applications. *J. Membr. Sci.* **2010**, *359*, 54–63. [CrossRef]
80. Lin, H.; Freeman, B.D. Gas solubility, diffusivity and permeability in poly(ethylene oxide). *J. Membr. Sci.* **2004**, *239*, 105–117. [CrossRef]
81. Gabelman, A.; Hwang, S.-T. Hollow fiber membrane contactors. *J. Membr. Sci.* **1999**, *159*, 61–106. [CrossRef]
82. Dindore, V.Y.; Brilman, D.W.F.; Versteeg, G.F. Modelling of cross-flow membrane contactors: Physical mass transfer processes. *J. Membr. Sci.* **2005**, *251*, 209–222. [CrossRef]
83. Wang, R.; Zhang, H.Y.; Feron, P.H.M.; Liang, D.T. Influence of membrane wetting on CO_2 capture in microporous hollow fiber membrane contactors. *Sep. Purif. Technol.* **2005**, *46*, 33–40. [CrossRef]
84. Basu, A.; Akhtar, J.; Rahman, M.H.; Islam, M.R. A Review of Separation of Gases Using Membrane Systems. *Pet. Sci. Technol.* **2004**, *22*, 1343–1368. [CrossRef]
85. Pera-Titus, M. Porous inorganic membranes for CO_2 capture: Present and prospects. *Chem. Rev.* **2014**, *114*, 1413–1492. [CrossRef] [PubMed]
86. Yoo, B.M.; Shin, J.E.; Lee, H.D.; Park, H.B. Graphene and graphene oxide membranes for gas separation applications. *Curr. Opin. Chem. Eng.* **2017**, *16*, 39–47. [CrossRef]
87. Chi, C.; Wang, X.; Peng, Y.; Qian, Y.; Hu, Z.; Dong, J.; Zhao, D. Facile Preparation of Graphene Oxide Membranes for Gas Separation. *Chem. Mater.* **2016**, *28*, 2921–2927. [CrossRef]

88. Liu, C.; Kulprathipanja, S.; Hillock, A.M.W.; Husain, S.; Koros, W.J. Recent Progress in Mixed-Matrix Membranes. In *Advanced Membrane Technology and Applications*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2008; pp. 787–819.
89. Rezakazemi, M.; Ebadi Amooghin, A.; Mehdi Montazer-Rahmati, M.; Ismail, A.; Matsuura, T. State-of-the-art membrane based CO_2 separation using mixed matrix membranes (MMMs): An overview on current status and future directions. *Prog. Polym. Sci.* **2014**, *39*, 817–861. [CrossRef]
90. Nafisi, V.; Hägg, M.-B. Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO_2 capture. *J. Membr. Sci.* **2014**, *459*, 244–255. [CrossRef]
91. Wang, S.; Liu, Y.; Huang, S.; Wu, H.; Li, Y.; Tian, Z.; Jiang, Z. Pebax–PEG–MWCNT hybrid membranes with enhanced CO_2 capture properties. *J. Membr. Sci.* **2014**, *460*, 62–70. [CrossRef]
92. Li, X.; Cheng, Y.; Zhang, H.; Wang, S.; Jiang, Z.; Guo, R.; Wu, H. Efficient CO_2 capture by functionalized graphene oxide nanosheets as fillers to fabricate multi-permselective mixed matrix membranes. *ACS Appl. Mater. Interfaces* **2015**, *7*, 5528–5537. [CrossRef] [PubMed]
93. Shekhawat, D.; Luebke, D.R.; Pennline, H.W. *A Review of Carbon Dioxide Selective Membranes: A Topical Report*; National Energy Technology Lab.: Pittsburgh, PA, USA; Morgantown, WV, USA, 2003.
94. Sandru, M.; Kim, T.J.; HÄGG, M.B. Gas Separation Membrane. US20120067209A1, 22 March 2012.
95. Kim, T.-J.; Vrålstad, H.; Sandru, M.; Hägg, M.-B. Separation performance of PVAm composite membrane for CO_2 capture at various pH levels. *J. Membr. Sci.* **2013**, *428*, 218–224. [CrossRef]
96. Kasahara, S.; Kamio, E.; Ishigami, T.; Matsuyama, H. Effect of water in ionic liquids on CO_2 permeability in amino acid ionic liquid-based facilitated transport membranes. *J. Membr. Sci.* **2012**, *415–416*, 168–175. [CrossRef]
97. Lockwood, T. A Compararitive Review of Next-generation Carbon Capture Technologies for Coal-fired Power Plant. *Energy Procedia* **2017**, *114*, 2658–2670. [CrossRef]
98. Markusson, N.; Kern, F.; Watson, J. Assessing CCS viability—A socio-technical framework. *Energy Procedia* **2011**, *4*, 5744–5751. [CrossRef]
99. Noureldin, M.; Allinson, W.G.; Cinar, Y.; Baz, H. Coupling risk of storage and economic metrics for CCS projects. *Int. J. Greenh. Gas Control.* **2017**, *60*, 59–73. [CrossRef]
100. Melien, T. Economic and Cost Analysis for CO_2 Capture Costs in the CO_2 Capture Project Scenarios. In *Carbon Dioxide Capture for Storage in Deep Geologic Formations*; Elsevier Science: Amsterdam, The Netherlands, 2005; pp. 47–87.
101. Viebahn, P.; Vallentin, D.; Höller, S. Integrated assessment of carbon capture and storage (CCS) in South Africa's power sector. *Energies* **2015**, *8*, 14380–14406. [CrossRef]
102. Valentić, V.; Žiković, S.; Višković, A. Can CCS save coal fired power plants—The European perspective. *Int. J. Greenh. Gas Control* **2016**, *47*, 266–278. [CrossRef]
103. Abanades, J.C.; Rubin, E.S.; Anthony, E.J. Sorbent Cost and Performance in CO_2 Capture Systems. *Ind. Eng. Chem. Res.* **2004**, *43*, 3462–3466. [CrossRef]
104. Ho, M.T.; Allinson, G.W.; Wiley, D.E. Reducing the Cost of CO_2 Capture from Flue Gases Using Pressure Swing Adsorption. *Ind. Eng. Chem. Res.* **2008**, *47*, 4883–4890. [CrossRef]
105. Ho, M.T.; Allinson, G.W.; Wiley, D.E. Reducing the Cost of CO_2 Capture from Flue Gases Using Membrane Technology. *Ind. Eng. Chem. Res.* **2008**, *47*, 1562–1568. [CrossRef]
106. Fu, B.-R.; Hsu, S.-W.; Liu, C.-H.; Liu, Y.-C. Statistical analysis of patent data relating to the organic Rankine cycle. *Renew. Sustain. Energy Rev.* **2014**, *39*, 986–994. [CrossRef]
107. Mogee, M.E. Using Patent Data for Technology Analysis and Planning. *Res. Technol. Manag.* **1991**, *34*, 43–49. [CrossRef]
108. Mogee, M.E. Patent analysis for strategic advantage: Using international patent records. *Compet. Intell. Rev.* **1994**, *5*, 27–35. [CrossRef]
109. Hall, B.H.; Jaffe, A.; Trajtenberg, M. Market Value and Patent Citations. *RAND J. Econ.* **2005**, *36*, 16–38.
110. Linton, K. The Importance of Trade Secrets: New Directions in International Trade Policy Making and Empirical Research. *J. Int. Commer. Econ.* **2015**, *7*, 1.
111. Glänzel, W.; Meyer, M. Patents cited in the scientific literature: An exploratory study of 'reverse citation' relations. *Scientometrics* **2003**, *58*, 415–428. [CrossRef]
112. Jaffe, A.B.; de Rassenfosse, G. Patent citation data in social science research: Overview and best practices. *J. Assoc. Inf. Sci. Technol.* **2017**, *68*, 1360–1374. [CrossRef]

113. Luis Míguez, J.; Porteiro, J.; Pérez-Orozco, R.; Patiño, D.; Rodríguez, S. Evolution of CO_2 capture technology between 2007 and 2017 through the study of patent activity. *Appl. Energy* **2018**, *211*, 1282–1296. [CrossRef]
114. Qiu, H.H.; Liu, L.G. A study on the evolution of carbon capture and storage technology based on knowledge mapping. *Energies* **2018**, *11*. [CrossRef]
115. Harhoff, D.; Narin, F.; Scherer, F.M.; Vopel, K. Citation Frequency and the Value of Patented Inventions. *Rev. Econ. Stat.* **1999**, *81*, 511–515. [CrossRef]
116. Choe, H.; Lee, D.H.; Seo, I.W.; Kim, H.D. Patent citation network analysis for the domain of organic photovoltaic cells: Country, institution, and technology field. *Renew. Sustain. Energy Rev.* **2013**, *26*, 492–505. [CrossRef]
117. Sumida, K.; Rogow, D.L.; Mason, J.A.; McDonald, T.M.; Bloch, E.D.; Herm, Z.R.; Bae, T.H.; Long, J.R. Carbon dioxide capture in metal-organic frameworks. *Chem. Rev.* **2012**, *112*, 724–781. [CrossRef] [PubMed]
118. WIPO. Terms and Abbreviations. In *Handbook on Industrial Property Information and Documentation*; WIPO: Geneva, Switzerland, 2013; pp. 1–41.
119. PRISM® Membranes. Available online: http://www.airproducts.com/Products/Gases/supply-options/prism-membranes.aspx (accessed on 15 October 2018).
120. Baker, R.W. *Membrane Technology and Applications*; Wiley: Hoboken, NJ, USA, 2004.
121. Drioli, E.; Barbieri, G. *Membrane Engineering for the Treatment of Gases: Gas-Separation Problems with Membranes*; Royal Society of Chemistry: London, UK, 2011.
122. Finkenrath, M.; Bartlett, M.A.; Hoffmann, S.M.-N.; Ruud, J.A. Carbon Dioxide Capture Systems and Methods. U.S. Patent 20080127632A1, 5 June 2008.
123. Ruud, J.; Molaison, J.; Schick, L.; Ku, A.Y.-C.; Liu, K.; Kulkarni, P.; Rizeq, R. Methods and Apparatus for Hydrogen Gas Production. U.S. Patent Application 11/263,269, 31 October 2005.
124. Wright, A.; Lackner, K. Method and Apparatus for Extracting Carbon Dioxide from Air. US Patent 20080087165A1, 17 April 2008.
125. Wright, A.B.; Lackner, K.S.; Wright, B.; Wallen, M.; Ginster, U.; Peters, E.J. Removal of Carbon Dioxide from Air. U.S. Patent WO2007016271A2, 8 February 2007.
126. Hiraki, D.; Mochizuki, Y.; Yamazaki, K. Composition for Formation of Carbon Dioxide Separation Membrane, Carbon Dioxide Separation Membrane and Process for Production Thereof, and Carbon Dioxide Separation Apparatus. U.S. Patent WO2012096055A1, 20 October 2015.
127. Aburaya, Y.; Yamazaki, K. Carbon Dioxide Separation Member, Method for Producing Same, and Carbon Dioxide Separation Module. WO2013018538A1, 20 February 2013.
128. Kuzushita, K.; Matsuyama, H.; Okada, O.; Shimada, K.; Teramoto, M.; Yegani, R. Carbon Dioxide Separation Apparatus. JP2009195900A, 3 September 2009.
129. Jain, R. Carbon Dioxide Recovery. U.S. Patent 20100251887A1, 7 October 2010.
130. Trachtenberg, M. Methods, Apparatuses, and Reactors for Gas Separation. U.S. Patent 20070004023A1, 19 May 2004.
131. Marand, E.; Kim, S. Ordered Mesopore Silica Mixed Matrix Membranes, and Production Methods for Making Ordered Mesopore Silica Mixed Matric Membranes. U.S. Patent 20070022877A1, 5 July 2006.