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The relevance of thermochemical energy storage in the last two decades: The analysis of research evolution

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ABSTRACT

The research field on thermochemical energy storage (TCS) has shown consistent growth over the last decade. This study analysed over 1196 scientific publications in indexed journals and books from the last decades. What can we learn from analysing the evolution of research? There is no other study that has used bibliometrics to perform a detailed analysis of the TCS field, which has only been assessed from the perspective of the whole thermal energy storage field to date. The trends obtained in this study provide an important perspective of the field, indicating the strengths and weaknesses of the thermochemical materials and systems applied to energy storage. The main publication trend shows an exceptional increase in TCS research and in both defined research sub-areas (sorption and chemical reaction heat storage). The sub-category chemical reaction heat storage has fewer publications compared to sorption heat storage, indicating that it is a less explored field. In general, the evolution of the keywords in publications reflects technology maturity since the most recent terms are associated more with final use applications. Remarkably, there has been a change from a total dependence on funding for scientific output to a scenario in which a significant number of publications mention no specific funding, but this trend has changed in recent years.

1. Introduction

The mismatch between energy supply and energy demand is one of the key issues that has to be addressed to improve energy saving in the grid and in the more energy-intensive sectors [1]. Storage systems can improve the energy efficiency of clean energies and the security of energy supply in the short and/or long term.

Thermal energy storage (TES) systems are one of the most promising complementary systems to deal with this issue. These systems can decrease the peak consumption of the energy demand, switching this peak and improving energy efficiency in sectors such as industry [2], construction [3], transport [4] and cooling [5]. TES systems can store thermal energy through three different technologies. The first is through sensible heat thermal energy storage (SHTES), which is one of the most frequently used systems in the market at the utility scale, for example, in current state-of-the-art concentrating solar power (CSP) plants [6]. This is the easiest technology to store energy, but it has a lower energy density. The second technology is through latent heat thermal energy storage (LHTES), which has the highest potential since it is a midterm compromise between simplicity of the system and energy density. LHTES systems are implemented in several applications, but are most widely used in improving active [7] and passive [8] building systems through a variety of materials [3]. The third technology to store thermal energy is through the heat released during reversible chemical reaction and/or sorption processes of gases or vapor in solids and liquids [9]. The systems that use this technology are called thermochemical energy storage (TCS) systems. They have the highest storage density in comparison to the other two technologies. Despite the potential of TCS, it is less developed since it is more complex to achieve. However, novel concepts are currently being developed, such as consecutive reaction cycles [10] and hybrid TES systems [11]. The potential application of these systems is large, since these systems have several advantages that help them improve energy efficiency in a wide range of applications in construction, district heating and cooling [12], and transport [13]. These advantages include: TES at ambient temperatures that allow the long-term usage of TCS systems since there are no thermal losses [14,15]; storage at high temperatures for industrial or utility systems; and temperature stability during discharge/charging processes [16]. The high energy density potential allows compact systems and promotes the use of thermal batteries [17].

TCS technology can be classified into sorption heat storage (SHS) and

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Nomenclature

TES	Thermal Energy Storage
SHTES	Sensible Heat Thermal Energy Storage
LHTES	Latent Heat Thermal Energy Storage
TCS	Thermochemical Energy Storage
SHS	Sorption Heat Storage
CRHS	Chemical Reaction Heat Storage
WoS	Web of Science
CLab	Complexity Lab Barcelona
IRENA	International Renewable Energy Agency
KET	Key Enabling Technology
MOF	Metal-Oganic Framework
TCM	Thermochemical Material
CSP	Concentrating Solar Power
CaL	Calcium Looping
PCM	Phase Change Material
P	Performance ratio
P_5	Performance ratio over the last 5 years
USA	United States of America
UK	United Kingdom

chemical reaction heat storage (CRHS). Both technologies have the benefits such as follows: high thermal energy storage capacity, thermal energy storage at low temperature, low heat losses, compact storage systems, etc. [16]. The storage mechanism includes three processes: charging (reaction/sorption), storage (low temperature-open/close system), and discharging (reversible reaction/sorption).

SHS involves a reversible reaction with an absorption or adsorption reversible process. In the absorption process, a gas or liquid material (absorbate) is retained by another material (absorbent), while in the adsorption process, a concentration of gas (adsorbate) is retained on the surface of another material (adsorbent) [18]. CRHS involves a reversible reaction without a sorption process [19]. Regarding CRHS materials, there are exceptions. It is the case of $CaCl_2{\cdot}6H_2O$, for instance, which performs a deliquescence process [17].

Bibliometrics involve the study of publication outputs in a specific research area using statistical methods [21]. Bibliometric studies are becoming important tools for strategic decision making and for identifying the most relevant stakeholders in a research area. They have been used in several fields such as management, econometrics, marketing, entrepreneurship, data sciences, innovations, renewable energies and energy storage [22–24].

Calderon et al. presented a bibliometric analysis of TES systems that provided relevant information for this field [23]. Since then, different bibliometric analyses have been published in the TES field. Mustapha et al. [25] presented a bibliometric analysis on LHTES, Borri et al. [26] published a bibliometric study on the applications of TES in building environments, Ding et al. [27] produced a bibliometric analysis of advanced/hybrid TES technology, Boquera et al. [28] presented a bibliometric study on the use of concrete as a TES material, while Tarragona et al. [29] provided a bibliometric analysis of smart control applications in TES systems [30–34]. Cabeza et al. [35] published the most recent bibliometric study on TES in 2021, providing a statistical perspective on TES technologies and a general view of the research performed to date as well as the research gaps in the TCS field. To our knowledge, there is no bibliometric analysis in the literature focusing on TCS.

The main goal of this study was to perform a systematic analysis and review of the literature in order to understand the progress made in the TCS research field over the last two decades and highlight the relevance of this field in the world energy scenario. The trends obtained in this study will provide an important status of the field in order to understand the strengths and weaknesses of thermochemical materials and systems. Finally, the main advances in this field will be highlighted in relation to time in the most active regions around the world.

2. Methodology

The current study followed a methodology previously established for a bibliometric analysis of TES and CSP [23,24,36]. Fig. 1 shows the different stages of this method.

The first stage of this method is the selection of the research field. For the present study, the research field selected was TCS. A keyword map was then determined to obtain the appropriate bibliometric data in terms of the published papers collected in a database. The main keywords selected were: "Thermal Energy", "Energy Storage", "Heat Storage", "Thermochemical" and "Sorption".

Notice that the "Absorption" and "Adsorption" keywords were not included directly in this study due to their wide usage in terms that are not related to thermochemical heat storage. Their usage can induce analysis error because this keyword is part of many search drivers, leading to the inclusion of many articles that do not fall in the defined field. However, it was included indirectly in the search. This is the reason why, both words, which are very remarkable in the field, are included in an indirect manner, as part of the sub-area classification.

The next stage is the selection of an appropriate data source to perform the literature search. Web of Science (WoS), Google Scholar and Scopus are the most important sources of scientific publications. However, in this study, the WoS Core Collection was used due to the quality of the metadata and the high quality of the publications included in this source [37]. The most relevant publication articles, reviews, books and book chapters were included in the final search.

Two different query strings were used to obtain the bibliometric data. Several restrictions were applied to obtain thermochemical publications dedicated to TES (see Table 1). It should be noted that hydrogen production with thermochemical reactions and other terms were excluded from the search.

Once the bibliometric data were obtained with the query strings, statistical calculations as well as database extraction and processing were undertaken with Python. Moreover, the Python software allowed the division of the database into two research sub-areas: SHS and CRHS. To do so, search phrases and exception phrases were defined as shown in Table 2, where at least one of the search phrases had to be included in the abstract, title or keywords (either the ones defined by the authors or by Keywords Plus® of the Web of Science Core Collection). Furthermore, if any exception phrase was found in the mentioned metadata, the publications were discarded from the sub-area classification. This Python coding has been developed and used by researchers from the University of Barcelona.

After the bibliometric data were processed, Python coding, OriginLab Pro, MS Excel, VOS Viewer and Complexity Lab Barcelona (CLab) were used to perform the bibliometric analysis and obtain the different metrics for the main TCS research field and the research sub-areas. CLab from the University of Barcelona was used for obtaining clusters of the top authors. Five basic metrics were analysed: publications, keywords, countries, authorship and journals. The metrics used to perform the analysis were: author's name, publication title, journals, type of document, keywords, citations, publication year, research areas, affiliation, countries and funding agencies.

During data acquisition, 1196 documents were imported into the TCS database, considering the restrictions on the authors applied to produce the database. 520 publications were classified into the SHS sub-area, and 499 into the CRHS sub-area. There are inherent limitations in performing a bibliometric analysis that need to be considered. It is possible that not all the documents in the TCS field may have been collected by WoS because of the restrictions required for specialised content. Moreover, it can be assumed that a small proportion of the documents might be out of the research field. Because some specific keywords are being included in the abstract as a general explanation.

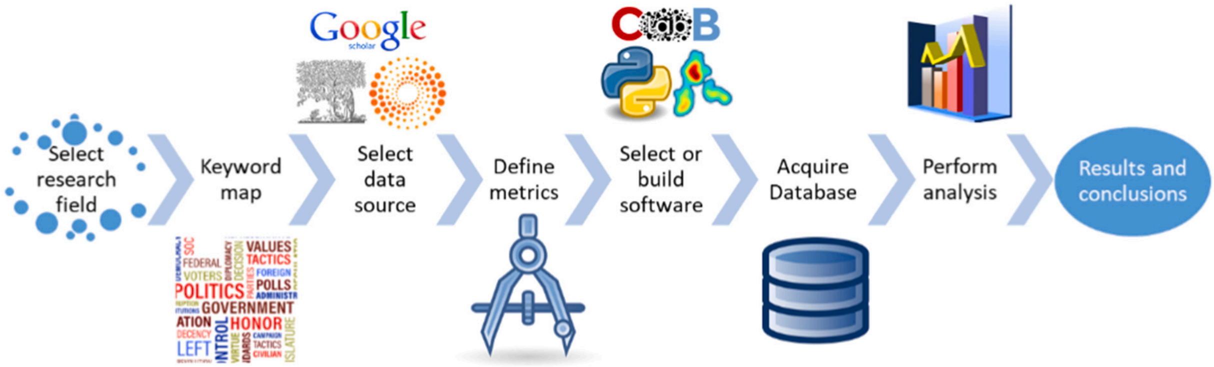

Fig. 1. Methodology for the development of bibliometric studies [36].

Table 1
Query strings used in the WoS search.

	Query
1st	TS = ((("thermal storage" OR "heat storage" OR "thermal energy" OR "energy storage") AND ("thermochemical" OR "thermo-chemical" OR "sorption")) NOT ("hydrogen" OR "bio-fuel*" OR "biofuel*" OR "biomass" OR "ion batter*" OR "*capacitor*" OR "semiconductor" OR "forces" OR "chromatography"))
2nd	TS = (("hydrogen" AND ("thermochemical" OR "thermo-chemical") AND ("thermal storage" OR "heat storage" OR "thermochemical storage" OR "thermo-chemical storage")) NOT ("bio-fuel*" OR "biofuel*" OR "biomass" OR "heat pump" OR "nano*" OR "lithium*"))

TS: topic; *: any character or group of characters.

Nevertheless, bibliometric analysis is a powerful tool to analyse the TCS field.

3. Results and discussion

3.1. Publication and keyword bibliometrics

Fig. 2 shows the total number of publications (bars) and citations (line) in the TCS field for the past 20 years. The number of publications over the years is also presented for the SHS (dashed line) and CRHS (dashed-dotted line) sub-areas. For the TCS field, the number of publications remained relatively stable between 2000 and 2011, with a maximum of 16 publications in 2007. The number of citations also presented a maximum in 2007 and in 2009, related to the publications of 'Solar air conditioning in Europe - an overview' by Balaras et al. [38] and 'A review on long-term sorption solar energy storage' by N'tsoukpoe et al. [39], both in the SHS sub-area, which are in the fifth and fourth most cited document in the TCS field. From 2012 to 2017, there was an exceptional increase in the number of publications. Over the past three years, the number of citations has decreased as the most recent documents have not been cited yet. These documents need more time to attain their full citable potential.

The general trend for publications in the TCS field indicates that there will be an increase in the coming years. This growth can be attributed to the increase and promotion of the use of renewable energies to reduce CO_2 emissions in order to meet the Paris Climate Accords target by 2050 [40]. The International Renewable Energy Agency (IRENA) [41] reports that the global market for TES in 2030 may triple due to investments in cooling and power for TES applications, which are expected to reach 28 billion USD. Furthermore, the global installed renewable energy capacity of 2019 was 7.4% (176 GW) higher than that of 2018 [41]. Since TES technologies have been identified as a key enabling technology (KET) for the massive development of renewable energy and given that TCS technologies are considered to be the most promising due to their high capacity to store thermal energy, the interest in implementing them has increased [6,42].

SHS has been the most studied technology over the years. However, both sub-areas reviewed almost the same fundings. Among the articles on SHS, 76% mention financing, while 71% of the articles on CRHS are financed. The CRHS sub-area presented a constant growth in the number of publications until 2016. Since then, publications in this sub-area have doubled, which could have been influenced by an increase in funding in the last four years.

The 15 most cited documents in the TCS field are presented in Table 3. As expected, most of them are reviews (14) and 12 are related to SHS.

The SHS sub-area is the most explored one due to the low temperature of the absorption or adsorption process and its potential applications. Documents on solar and building applications are present in the top 10 most cited articles. These studies mainly use SHS technologies. In addition, in the top 10 most cited articles, one article is on CRHS and four articles are on both sub-areas (SHS and CRHS). This indicates that the CRHS sub-area is at an earlier technological stage than the SHS sub-area.

Evolution of the most used keywords in the TCS field and the SHS and CRHS sub-areas between 2016 and 2018 are presented in Fig. 3. Evolutions of the keywords for TCS, SHS and CRHS are presented in Fig. 3(a), (b) and (c), respectively. Each circle represents a keyword, with the size of the circle correlating with the number of papers in which the keyword appears. The lines between the circles represent the co-occurrences of keywords, and their thicknesses are the times that they appear together. Moreover, the colour of the figure represents the year

Table 2
Sub-area classification search and exception phrases.

Sub-area	Search phrase	Exception phrase
SHS	"Sorption", "adsorption", "hydration", "dehydration", "salt hydrated"	"Absorption", "heat pump"
CRHS	"Chemical reaction", "reactance", "reversible", "conversion", "kinetic", "redox reaction", "carbonatation", "metal/metal hydrate", "oxide/hydroxide"	"Zeolite", "zeolites", "hydration", "salt hydrated"

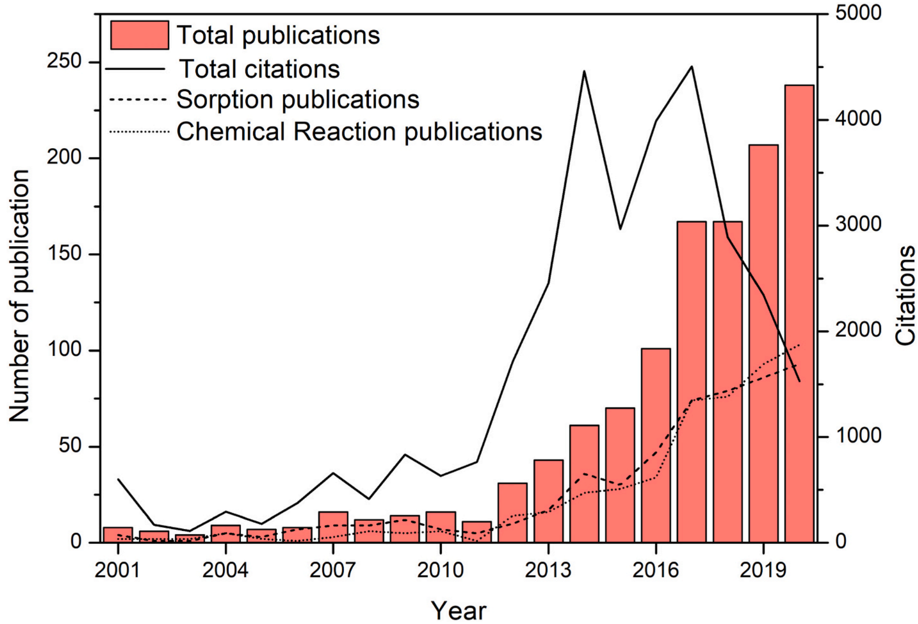

Fig. 2. Publications and citations in the TCS field during the last two decades.

Table 3
The most cited publications in the TCS field.

Authors	Title	Journal	Type	Cites	Year	Country	Sub-area
Furukawa et al. [43]	Water adsorption in porous metal-organic frameworks and related materials	*Journal of the American Chemical Society*	Original research article	1180	2014	USA	SHS
Liu et al. [44]	Review on concentrating solar power plants and new developments in high temperature thermal energy storage technologies	*Renewable & Sustainable Energy Reviews*	Review	446	2016	Australia	SHS/ CRHS
Pardo et al. [9]	A review on high temperature thermochemical heat energy storage	*Renewable & Sustainable Energy Reviews*	Review	426	2014	France	CRHS
N'tsoukpoe et al. [39]	A review on long-term sorption solar energy storage	*Renewable & Sustainable Energy Reviews*	Review	358	2009	France	SHS
Zhang et al. [45]	Thermal energy storage: Recent developments and practical aspects	*Progress in Energy and Combustion Science*	Review	348	2016	Belgium, China, Chile	SHS
De Gracia et al. [46]	Phase change materials and thermal energy storage for buildings	*Energy and Buildings*	Review	303	2015	Chile, Spain	SHS
Tatsidjodoung et al. [47]	A review of potential materials for thermal energy storage in building applications	*Renewable & Sustainable Energy Reviews*	Review	298	2013	France	SHS/ CRHS
Yu et al. [48]	Sorption thermal storage for solar energy	*Progress in Energy and Combustion Science*	Review	282	2013	China	SHS/ CRHS
Xu et al. [19]	A review of available technologies for seasonal thermal energy storage	*Solar Energy*	Review	279	2014	China	SHS/ CRHS
Balaras et al. [38]	Solar air conditioning in Europe — an overview	*Renewable & Sustainable Energy Reviews*	Review	278	2007	Netherlands, Israel, Austria, Germany, Greece	SHS

when the keywords appear: purple for older keywords and yellow for more recent keywords.

The evolution of the research on thermochemical materials (TCMs), applications and, more importantly, the maturity of the technology can be observed by studying the most used keywords relating to them and their evolution. The most used keywords in the TCS field (see Fig. 3(a)) are "Thermal Energy Storage", "Thermochemical Energy Storage", "Performance", "Energy Storage" and "System", some of which are general and descriptive terms for TES. However, the keywords "Performance", "System" and "Design", which appear more recently, illustrate how this technology is maturing because of the use of these keywords in manuscripts trying to upgrade a known technology for a certain application. In recent years, the keywords "Concentrated Solar Energy", "Salts", "CO_2 Capture", "CaO" and "Composite" have been used the most frequently, while "Adsorption", "Water" and "Silica gel" had been used the most often in previous years. This means that new applications are being studied for TCS. Moreover, the new terms reflect the interest in studying more complex materials to further develop TCS technology and increase its efficiency. The keyword "Sorption" appears in the purple colour, indicating that SHS is an older technology than CRHS. Therefore, SHS is probably the more advanced technology [41].

For SHS, "Adsorption", "Sorption", "Thermal Energy Storage", "Energy Storage" and "Performance" are the most used keywords (Fig. 3 (b)). Keywords associated with TCMs can also be detected, such as

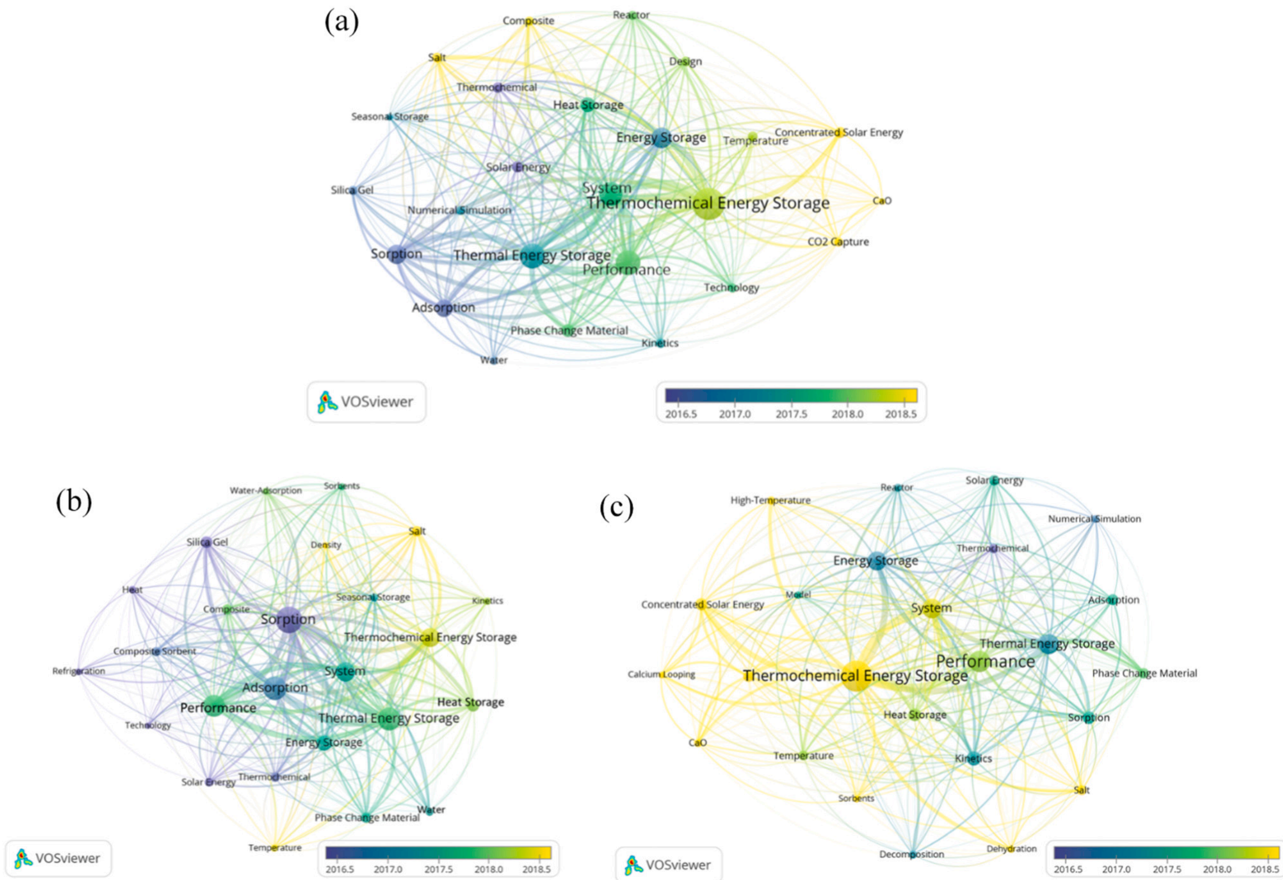

Fig. 3. Co-occurrence of keywords: (a) in the TCS field, (b) in the SHS sub-area, and (c) in the CRHS sub-area.

"Silica Gel" and "Salts". This implies that these are the most studied materials in the SHS sub-area. In addition, there are keywords relating to applications like "Seasonal Storage" and "Solar Energy". Seasonal storage, also called long-term storage, is a technology for storing energy for a few months or an entire season to offset seasonal energy demands. This technology can be applied in the building sector or the solar energy production industry. Halides are the most commonly salts used TCMs for seasonal storage [48]. Moreover, keywords like "System", "Design" and "Performance" are old words indicating that this is a mature technology.

In the CRHS sub-area, the most used keywords are "Thermochemical Energy Storage", "Performance" and "Energy Storage" (Fig. 3(c)). Generally, all the keywords shown in Fig. 3 are relatively recent, as reflected by the predominance of the yellow colour. Keywords associated with TCMs also appear in this sub-area, such as "Salt" and "CaO". Regarding CaO, it is a promising material for use in CSP plants, with "Concentrated Solar Energy" appearing as a keyword associated with applications. The use of CaO as a TCM consists of carbonating and decarbonating CaO, a process called "calcium looping" (CaL) [49–51]. It is interesting to note that there are pilot-scale studies, suggesting that this technology is increasingly maturing with a higher level of technology readiness (TRL) [52,53].

Keywords like "Kinetics", "Numerical Simulation", "Phase Change Material" (PCM) "Sorption" and "Absorption" are common in the two sub-areas. The "Kinetics" keyword appears in both sub-areas because TCS is based on reversible reactions, where the kinetics of a reaction are an important parameter for using the material in TES. "Numerical Simulation" is a useful tool that can be applied in both sub-areas. The bibliometric data extracted also indicated that "Numerical Simulation" is present in 23% of all the publications. Numerical simulation is highly used to characterise the sorption isotherm; however, there is a lack of kinetics studies that use numerical simulation [35]. Moreover, the keywords "Phase Change Materials", "Sorption" and "Absorption" appear in both sub-areas, which is due to new investigation trends about the hybrid systems TCM/PCM and SHS/CRHS. Both hybrid systems have been studied with the aim of developing more efficient materials, eliminating the need to add an external low-temperature source in the discharging stage of TCS [45,54,55].

Not only are the keywords that are present in the keyword maps important, but also those that are missing. This was the case for the lack of keywords like pilot plant, degradation, stability and components, which clearly indicate the low maturity of both technologies (SHS and CRHS). When these keyword co-occurrence maps are obtained for technologies with a higher TRL [22,25], the keywords are associated with the concepts mentioned above.

In addition, studies on the porous material used to store energy need to be explored. In the SHS keyword map, composite, composite sorbent, silica-gel and salt appear as the main materials used. The composite formulation of the materials used for SHS is required since they need a media that can support the material to store thermal energy, with most studies and developments following this trend even if the energy density decreases. In the CRHS keyword map, only salt, CaO and calcium looping appear as the main materials used to store thermal energy. These are the main materials studied, but there are many others that are not in the list.

3.2. Country and author bibliometrics

Table 3 and Fig. 4 show the top 10 publishing countries in the TCS field. Table 3 presents the total number of documents, the total number of citations, the performance ratio (P), the average performance ratio of the last 5 years (from 2015 to 2019) (P_5) and the number of citations of the most cited document from the top 10 publishing countries. The

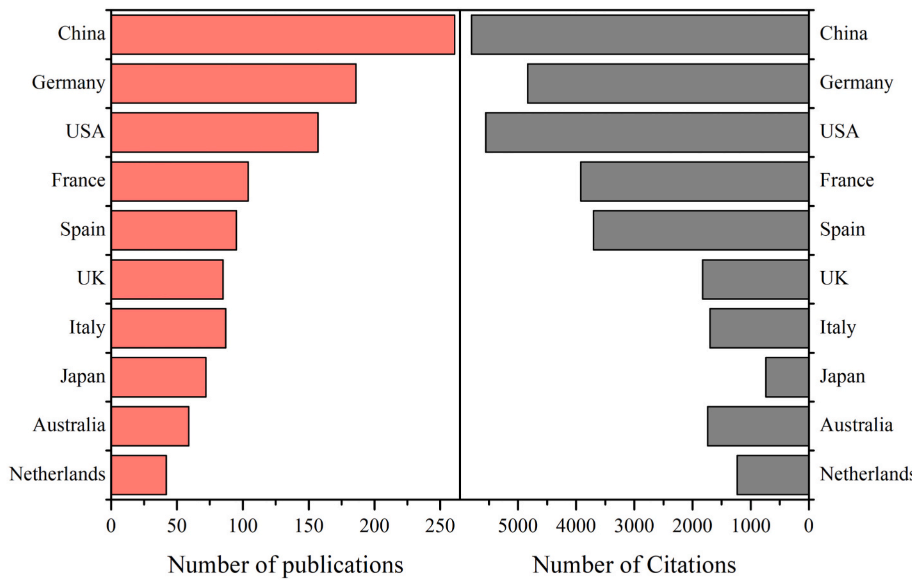

Fig. 4. Top 10 publishing countries in the TCS field by the number of publications and citations.

performance ratio is defined as the total number of citations divided by the number of publications. Fig. 4 presents a comparative view of publications over citations for the top 10 publishing countries.

China is the top publishing country with 261 publications, followed by Germany with 186, the United States of America (USA) with 157, and France with 104. When considering the populations of these countries, Germany and France present more publications per capita than China and the USA.

The amount of installed renewable energy capacity per country must be considered. The higher the installed capacity, the higher the investment and interest in incorporating TES systems into solar energy applications. According to IRENA [56], China had the highest installed renewable energy capacity (925 GW) in 2020, followed by the USA (311 GW) and Brazil (150 GW). Despite being the second highest publishing country in the TCS field, Germany was in fifth place for installed capacity (137 GW). Spain (62 GW), Italy (59 GW) and France (57 GW) were in eighth, ninth and tenth positions, respectively, for the amount of installed capacity in 2020.

China also has a target of reducing 65% of CO_2 emissions in their gross domestic production by 2030 [57,58]. China, the USA, Spain, Italy, Australia and India belong to the Sunbelt countries. Hence, the exploitation of solar energy is rising and the implementation of TCS technologies is under study in these regions [59]. Meanwhile, in Germany, France, the United Kingdom (UK) and Japan, where the solar energy source is smaller, their investigations are more in line with the building sector and residential heating, but they have also produced articles on solar energy applications.

In terms of citations, which reflect the impact of a study, China is the most cited country, followed by the USA, even though the USA has fewer publications than Germany (see Table 3 and Fig. 4). A similar phenomenon is observed with Japan and Australia. While Japan has more publications, Australia presents more citations. The most interesting data are the P (cites divide by publications) and P_5, where P_5 reflects the investigation trends over the last five years. The country with the highest P value is Spain (39), followed by France (38) and the USA (36). However, the country with the highest P_5 value is Australia (46), followed by Spain (31) and the Netherlands (30). Their investigations in the TSC field are growing, making them the predominant countries in the field in the last five years.

For the SHS and CRHS sub-areas, the number of publications per 10 million inhabitants was calculated for each country and technology and are presented on a world map in Fig. 5. This calculation was performed to normalise the number of publications per country. Countries with fewer than 5 publications in the topic were not included because these data could induce confusion. The countries that have published more papers per 10 million inhabitants are shown in darker colours in Fig. 5, whereas those in light green have fewer publications per 10 million inhabitants, and those in grey have published no papers in this field. SHS and CRHS are recurrent topics in the studies published in Europe, with a large proportion of the European countries presenting publications. Furthermore, China and the USA, which are both in the top three countries with the highest number of publications, present a low rate of publications per 10 million inhabitants due to their large populations. For SHS, Slovenia, the Netherlands and Belgium present the highest rates, whereas for CRHS, Switzerland, Austria and the Netherlands exhibit the highest rates. It should be mentioned that all these countries have fewer than 20 million inhabitants. This illustrates the effort made by small countries to develop and drive TCS technologies. Moreover, there are countries with larger populations that present remarkable rates of publications, such as France, Germany and the UK in the SHS research sub-area, and Australia, Spain and Germany in the CRHS sub-area.

The total number of publications and citations as well as the performance ratio in the SHS and CRHS sub-areas by country are presented in Table 5. China by far has published the most on SHS (114), followed by Germany (62). However, the distance between them is shorter regarding the number of publications on CRHS (120 and 85 publications, respectively). Regarding research on SHS technology, UK has the third highest number of publications (52), followed by the France (45), the USA (45) and Italy (42). However, the USA presents the highest P value with 59, followed by the Netherlands with 37, which is in seventh position in the number of publications produced. Regarding research on CRHS, the USA has the third highest number of publications (66), followed by Spain (41), France (39) and Japan (34). However, the country that presents the highest P value is Spain (45), followed by France (40) and the Netherlands (32). None of these three countries are in the top three most publishing countries.

Different key indicators of the authors of the publications, such as the number of publications, the h-index, the number of citations and P, are shown in Table 6. All the parameters were calculated only for the articles published in the SHS and CRHS sub-areas. In the SHS sub-area, R. Z. Wang, Y. I. Aristov and T. Li are, respectively, the top three most published authors. Y. I. Aristov and T. Li present a high h-index concerning the number of publications. However, C. C. M. Rindt presents the highest performance ratio (38) despite being in eighth position for the h-index

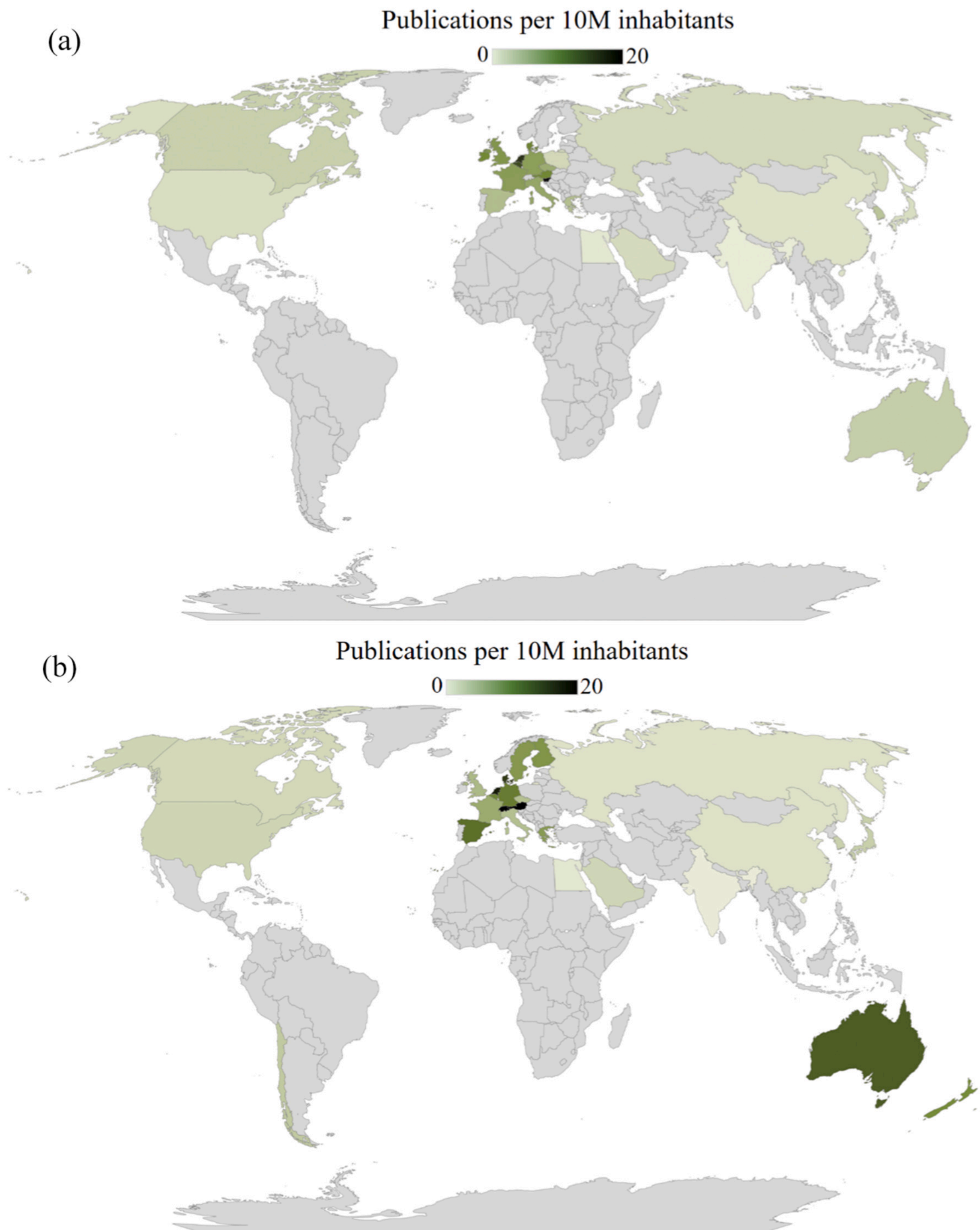

Fig. 5. Map of countries producing publications in the TCS research sub-areas: (a) SHS; and (b) CRHS.

and in tenth position for the number of publications, indicating that their publications have a high impact in the field. In the CRHS sub-area, J. M. Valverde and M. Linder are the most published authors and present the highest h-index. A. Wöerner, who stopped publishing in the field in 2014, presents the highest performance ratio (64). Remarkably, J. M. Valverde, who started publishing in this field in 2015, is now the top author in the CRHS sub-area. Something similar is observed with A. Perejon and L. A. Perez-Maqueda, who started publishing in 2015 and are now in the top 10 most published authors.

Other relevant data that must be highlighted are the affiliations of the authors. In the SHS sub-area, among the top 10 published authors, four are from Europe, four from China and two from Russia. In the CRHS sub-area, seven authors are from Europe, two from China and one from Russia among the top 10 published authors. Remarkably, there are no top 10 published authors from the USA and France, which are the third and fourth countries, respectively, with the highest number of publications in the SHS and CRHS sub-areas. This is not necessarily a sign of weakness for these countries, it suggests that there is a wider distribution of high-performance authors.

Fig. 6 presents the author communities in groups of circles for the SHS (Fig. 6(a)) and CRHS (Fig. 6(b)) sub-areas. The figure was plotted using the software CLab, which analyses a list of publications to describe

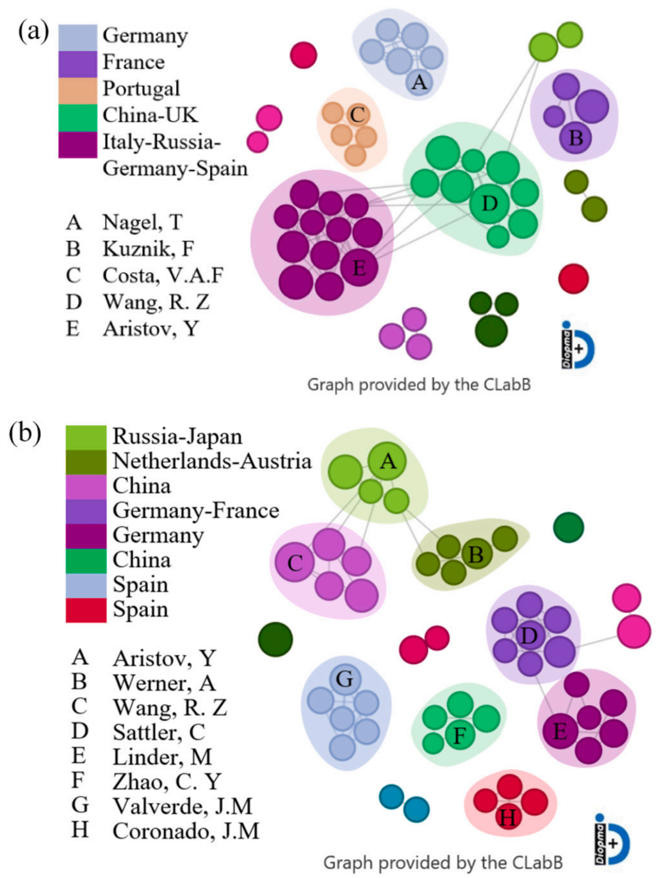

Fig. 6. Author communities based on the interaction of their published papers in the SHS sub-area (a) and the CRHS sub-area (b).

Table 4
Top 10 publishing countries in the TCS field.

Country	N°$_{Publ.}$	Citations	P	P_5	C_{MP}
China	264	5809	22	20	348
Germany	186	4952	27	16	176
USA	158	5741	36	22	1180
France	104	3919	38	23	429
Spain	95	3700	39	31	303
United Kingdom	87	1893	22	18	270
Italy	87	1732	20	23	128
Japan	72	797	11	9	51
Australia	59	1940	33	46	460
Netherlands	42	1331	32	30	139

N°$_{Publ.}$: number of publications; P: performance ratio; P_5: performance ratio average from 2016 to 2020; C_{MP}: citations of the most cited article.

Table 5
Top 10 publishing countries in the SHS and CRHS research sub-areas.

Country	SHS			CRHS		
	N°$_{Publ.}$	Citations	P	N°$_{Publ.}$	Citations	P
China	114	2457	22	120	2535	21
Germany	62	1610	26	85	2407	28
United Kingdom	52	969	19	24	533	22
France	45	980	22	39	1545	40
USA	42	2461	59	66	1472	22
Italy	38	792	21	21	425	20
Netherlands	25	916	37	26	825	32
Spain	21	725	35	41	1856	45
Japan	16	240	15	34	321	9
Australia	7	139	20	31	925	30

N°$_{Publ.}$: number of publications; P: performance ratio.

the attrition force between the authors (circles) and groups them into communities by employing an algorithm. Moreover, the lines between the different authors indicate cooperation that is not strong enough to make a community. Fig. 6 includes the most representative authors and the countries of each community. It should be mentioned that most of the countries in Fig. 6 are also in Table 4.

There are five relevant communities in the SHS sub-area (Fig. 6(a)), where the most significant authors mostly match with the most published authors (see Table 5). R. Z. Wang is the top author for the number of publications and citations as well as the h-index and is the most relevant author in the community represented in light aquamarine in Fig. 6, working between China and the UK. The community shown in purple is the largest one, comprising collaborations between different organisations from Italy, Russia, Spain and Germany, as well as presenting many connections with the community shown in aquamarine. The community shown in purple is led by the second most published author in the SHS sub-area, Y. I. Aristov. Furthermore, there are isolated communities that do not interact with the other communities, such as that depicted in green from Germany, the community shown in dark green from Portugal and the community depicted in light purple from France.

Table 6
Top 10 authors in the SHS and CRHS research sub-areas.

Author	Affiliation	h-index	N°$_{Publ}$	Citations	P
SHS					
Wang, R.Z.	Shanghai Jiao Tong University, China	20	39	970	25
Aristov, Y.I.	Boreskov Institute of Catalysis RAS, Russia	14	21	521	25
Li, T.	Shanghai Jiao Tong University, China	13	19	680	36
Wang, L.W.	Shanghai Jiao Tong University, China	12	26	601	23
Gordeeva, L. G.	Boreskov Institute of Catalysis RAS, Russia	11	14	385	28
Roskilly, A.P.	Sir Joseph Swan Centre for Energy Research, Newcastle University, UK	10	19	268	14
Palomba, V.	Istituto di Tecnologie Avanzate per l'Energia, Italy	9	14	175	13
Rindt, C.C.M.	Eindhoven University of Technology, Netherlands	9	12	458	38
Yan, T.	Shanghai Jiao Tong University, China	9	13	397	31
Frazzica, A.	Istituto di Tecnologie Avanzate per l'Energia, Italy	9	20	249	12
CRHS					
Valverde, J. M.	University of Seville, Spain	14	21	799	38
Linder, M.	German Aerospace Center – DLR e.V., Germany	13	26	561	22
Perez-Maqueda, L.A.	CSIC-USE - Instituto de Ciencia de Materiales de Sevilla ICMS, Spain	11	15	454	30
Wang, R.Z.	Shanghai Jiao Tong University, China	10	15	546	36
Aristov, Y.I.	Boreskov Institute of Catalysis RAS, Russia	10	14	312	22
Worner, A.	German Aerospace Center – DLR e.V., Germany	10	10	654	65
Sattler, C.	German Aerospace Center – DLR e.V., Germany	9	13	573	44
Perejon, A.	CSIC-USE – Instituto de Ciencia de Materiales de Sevilla ICMS, Spain	9	12	349	29
Rindt, C.C.M.	Eindhoven University of Technology, Netherlands	8	9	161	18
Li, T.	Shanghai Jiao Tong University, China	8	9	323	36

Table 7
Top 10 journals in the TCS field.

Journal	TCS		SHS		CRHS		2020 IF	Quartile scoresE&F
	N°$_{Publ.}$	P	N°$_{Publ.}$	P	N°$_{Publ.}$	P		
Applied Energy	109	29	40	33	59	31	9.746	1
Applied Thermal Engineering	73	23	30	24	24	27	5.295	2
Solar Energy	77	36	9	32	38	35	5.742	2
Energy	68	29	27	26	29	33	7.147	1
Energy Conversion and Management	61	23	20	18	24	23	9.709	1
Journal of Energy Storage	31	12	13	9	11	17	6.583	1
Energies	35	6	8	4	17	6	3.004	3
Renewable & Sustainable Energy Reviews	33	121	10	73	11	119	14.982	1
Solar Energy Materials and Solar Cells	26	37	15	27	12	23	7.267	1
Renewable Energy	32	22	13	24	11	15	8.001	1

N°$_{Publ.}$: number of publications; P: performance ratio; IF: impact factor; E&F: energy and fuels.

Fig. 6(b) presents the communities in the CRHS sub-area, with eight relevant communities. All the communities contain 4 to 7 authors. The two communities in green and the community shown in light purple in Fig. 6 present different interactions among them, indicating that they work together. These three communities are led by the third, fourth and fifth most published authors in the CRHS sub-area. Moreover, the two communities shown in purple seem to work together, containing authors from Germany and France and being led by the first and sixth most published authors in the CRHS sub-area. There are three communities that do not present any connection with the others, which include the one in aquamarine from China, the one shown in red from Spain and the community depicted in blue also from Spain and led by the second most published author in the CRHS sub-area.

3.3. Journal bibliometrics

The publication journals in the TCS, SHS and CRHS fields were also studied. The most relevant data on the top 10 publishing journals are presented in Table 7. In the TCS field, *Applied Energy* had the highest number of publications (109 publications), which included one from the top 15 most cited articles. *Applied Thermal Engineering* and *Solar Energy* had 73 and 77 publications, respectively. *Renewable & Sustainable Energy Reviews* presented the highest performance ratio and had 5 documents from the top 10 most cited articles, as reviews usually have a higher impact than original research articles. *Solar Energy Materials and Solar Cells* (37) and *Solar Energy* (36) had the second and third highest performance ratios, respectively. *Energies* and *Journal of Energy Storage* are also promising journals. Although they are relatively new journals (their first-year publication ware 2016 and 2015, respectively), they are in the top 10 most publishing journals. This trend is in concordance with other topics in the thermal energy storage field based on previous publications [23,60].

In the SHS sub-area, *Applied Energy* had the highest number of publications (40), followed by *Applied Thermal Engineering* (30) and *Energy* (27). By contrast, the journals with the highest *P* values were *Renewable & Sustainable Energy Reviews* (73) and *Solar Energy* (32). In the CRHS sub-area, *Applied Energy* (59) and *Solar Energy* (38) were the top 2 publishing journals, while those with the highest *P* values were *Renewable & Sustainable Energy Reviews* (119) and *Solar Energy* (35). Therefore, these are the selected journals to publish about the TCS advances in order to influence within the audience that are working in this topic.

The quartile and impact factor (IF) of the top publishing journals in the TCS field were also evaluated. The quartile of a journal is the quotient resulting from the division of the rank of the journal in a category by the total number of journals in that category. Therefore, this factor is highly influenced by the number of journals in a category. In this case, TCS is included in the Energy & Fuels category, which contains numerous journals. Hence, achieving a highly qualified quartile is more difficult for a journal in this category [61]. For this reason, newer journals like *Energies* are in the top 10 most publishing journals, despite only presenting a quartile of three. The IF is a measure of the significance of a journal. The IF is calculated by dividing all the citations of a journal in the current year by the number of documents it has published in the last two years [62]. The journal with the highest IF was *Renewable & Sustainable Energy Reviews*, which is unsurprising as reviews achieve numerous citations compared to original research articles. For this reason, journals with high *P* values like *Solar Energy Materials and Solar Cells* and *Solar Energy* have the fifth (IF 7.267) and eighth (IF 5.742) highest IF, respectively.

4. Trends in TCS research

An overview of the 100 keyword co-occurrences can indicate trends in TCS research from an overall perspective (see Fig. 7).

In SHS systems, the most widely used sorbents are the two-component sorbents, active matrix, composites and inactive matrix [63]. Regarding the single-component sorbents, MOFs and aluminophosphates are good options, offering lower load temperatures, a higher water capacity and a higher sorption enthalpy than zeolites. However, these TCMs are costly compared to zeolites [64]. Composite sorbents, consisting of an active porous matrix filled with salt hydrates, are a promising cost-effective alternative (Fig. 7), with many terms associated with this alternative emerging in publications from recent years [65]. The aim of this matrix is high gas uptake with an active role of the matrix.

In CRHS systems, calcium looping is a hot spot of investigations due to its high reactivity and energy storage [50]. However, $CaCO_3$ is deactivated and agglomerated during cycles, which is a common issue in CRHS carbonates [64]. Therefore, strong research efforts have been undertaken to optimise TCMs and improve multi-cycle activity. Furthermore, the search for alternative TCMs for CRHS, like natural minerals and by-products, is also a focus of interest [66].

In terms of applications, the use of CRHS in CSP is relatively recent, but seasonal and building applications have not been explored much [35]. Additionally, it has been generally observed that water-based TCM systems remain the most popular.

5. Conclusions

The TCS research field has shown almost exponential growth over the last decade. This field has over 1196 publications in relevant journals and books from the last decades. To date, there has been no other study using bibliometrics to assess the TCS research field, which has been analysed only from the whole TES perspective. This study presents the evolution of research in the TCS field over the last two decades. The strengths and weaknesses of the thermochemical materials and systems applied to energy storage are highlighted as follows:

The number of publications has grown exponentially in the TCS field and in both sub-areas (SHS and CRHS) and this demonstrate the importance of this field is stronger rather than two decades ago. Based

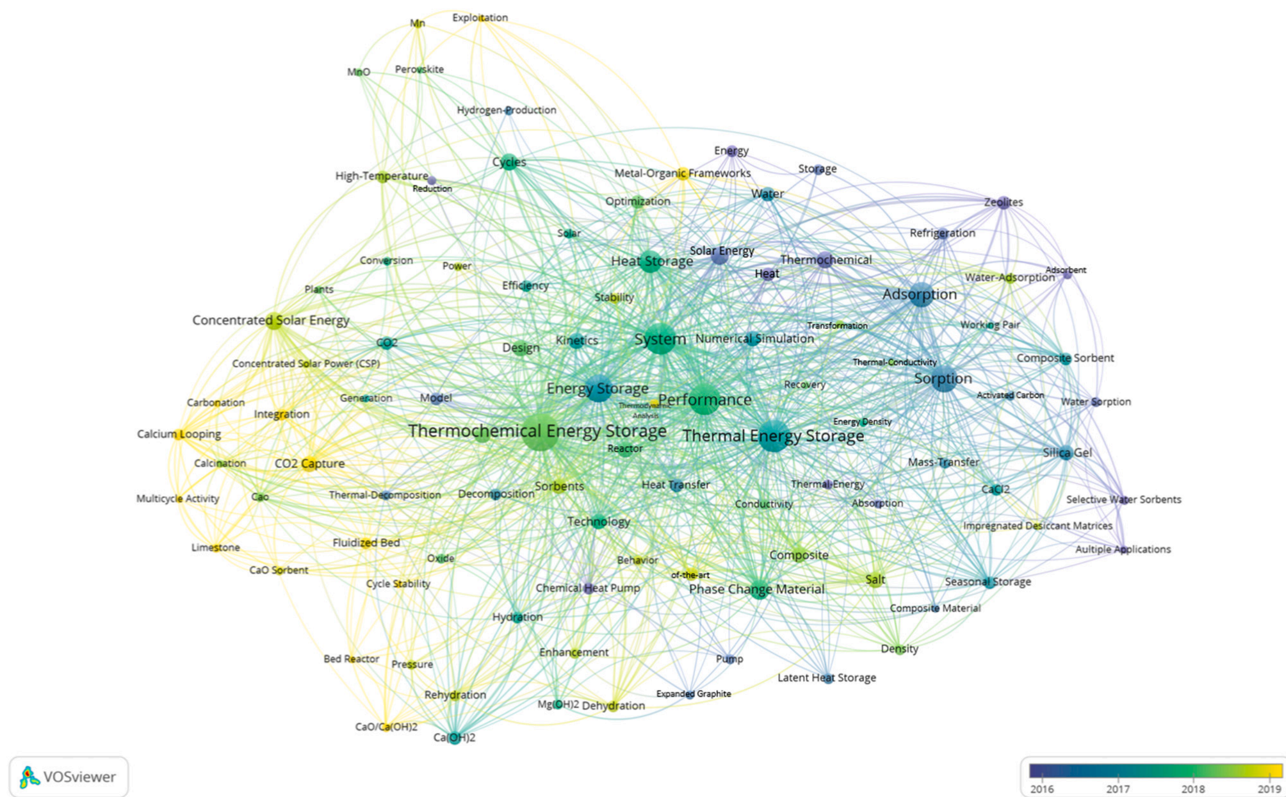

Fig. 7. General view of keyword co-occurrences in publications from recent years.

on the keyword co-occurrences, recent evolution in the TCS field reflects a technology maturity growth during the last time since most of the recent terms are associated to final use and/or final applications. In addition, it is remarkable that there has been a change from a total dependence on funding for scientific output into a scenario in which a significant number of publications mention no specific funding. From this information, authors understand that the interest regarding the TCS technology is growing up in public and private sectors because both fund the research in TCS topic and TCS research is not only performed at low TRL. To confirm a relationship between this trend and technology maturity based on the funding used to perform the research is required deeper analysis but it was not possible to achieve it with the keyword map used for this study.

The research regarding TCS technology in basically concentrated in Europe since the information of Fig. 5 shows. In addition, China and Germany are the leading countries in terms of the number of publications they have produced in the TCS field and in both sub-categories. The countries with the highest performance ratios over the last years in the TCS field and both sub-categories are Spain and UK. Strong bonds have been found between UK-China and China-USA, based on the analysis of the author communities (Fig. 6). Furthermore, bonds between European Union countries have been identified as an opportunity to develop common technology. China and the European Union are the main technology drivers in the TCS research field, based on this study.

Applied Energy, *Applied Thermal Engineering*, *Solar Energy* and *Solar Energy Materials and Solar Cells* are the top journals in the TCS field based on their output, citations, performance ratio and the quality of the publications. This trend is in concordance with other topics in the field of thermal energy storage based on previous publications. Moreover, current trends indicate that *Applied Energy* is becoming the most relevant journal.

A total of 11 research communities in the SHS and CRHS sub-areas have been identified, as well as the most relevant authors leading most of these research communities. The results concludes that there is lack of interaction between researcher communities, and this fact needs to be addressed in order to jump the technology to a new paradigm. In addition, it is remarkable that the interactions within each community is strong, but weak among other, even among some communities from the same country, particularly Germany.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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