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Review

Phase Change Slurries for Cooling and Storage: An Overview of Research Trends and Gaps

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Abstract: Phase change slurries (PCSs) have great potential as both a heat transfer fluid and an energy storage medium for cooling processes, cold energy storage, and cold energy transportation due to desirable thermophysical properties. One of the major benefits of PCSs compared to pure phase change materials is their fluidity, thus making them cooled or heated by a heat exchanger, pumped through pipes, discharged, and stored directly in a thermal energy storage tank. The use of encapsulated phase change slurries and gas hydrate slurry has thus attracted considerable interest as reflected in the literature with a rising number of publications and institutions involved in the area. The use of bibliometric techniques has found a recent interest in the literature to define the progress of different scientific topics and inspire researchers to identify novelties. In this paper, bibliometric analysis and a detailed systematic review are carried out to show the state-of-the-art development of PCSs for cooling applications. Research gaps and hotspots are identified to help define future perspectives on this topic.

Keywords: phase change slurry; gas hydrate slurry; cooling; transport; thermal energy storage; bibliometric analysis

1. Introduction

The rising demand for space cooling is putting enormous strain on electricity systems in many countries, as well as driving up emissions. To address such a challenge, many related studies were carried out to develop highly efficient heat transfer fluid which can minimize energy loss, and novel cold storage technologies which can shave the electricity consumption peaks. Phase change slurries (PCSs) which can be used as both heat transfer fluid and cold storage media are therefore considered a promising solution [1]. PCSs are actually a binary system, which consists of a carrier fluid, mostly water as the continuous phase, and a phase change material (PCM) as the dispersed phase. One of the major benefits of PCSs compared to other latent heat storage solutions is that PCSs provide fluidity and high heat storage capacity [2]. Moreover, there are still several challenges that hinder the actual commercialization and/or large-scale use of organic and inorganic PCMs in their original form. Currently, specific problem solving was proposed depending on the particular problem. Supercooling can be solved by adding nucleating agents or by encapsulation, poor heat-transfer performance by the addition of highly conductive materials (encapsulating or as additive), and leakage mainly by macro, micro, or nanoencapsulation. Indeed, encapsulation of PCMs is one of the most effective methods which solve many shortcomings at once [3]. Hence, the use of encapsulated PCM slurries (EPCM) is gaining interest since such materials are capable to enhance the thermal capacity of secondary fluid systems. Thermal performance improvement of the EPCM in a slurry is accompanied by the boost in turbulence force and boiling nucleation spots created by the encapsulated additives [4]. Moreover, PCMs as fluids can be cooled or heated by a heat exchanger, pumped through pipes, discharged, and stored directly in a standard tank.

Four main categories of encapsulated PCMs were identified: shape-stabilized PCM, PCM emulsion, clathrate hydrate PCM slurry, and nano/microencapsulated PCMs [1]. However, the suspension stability of EPCMs slurries should be conserved in a long-term storage period and under mechanical–thermal loads, and it can be affected by several phenomena (Figure 1) [5]. Therefore, it is not enough to characterize the behavior of the material encapsulated within the fluid, but also to analyze its stability in cooling/heating cycles, as well as over a long period of time.

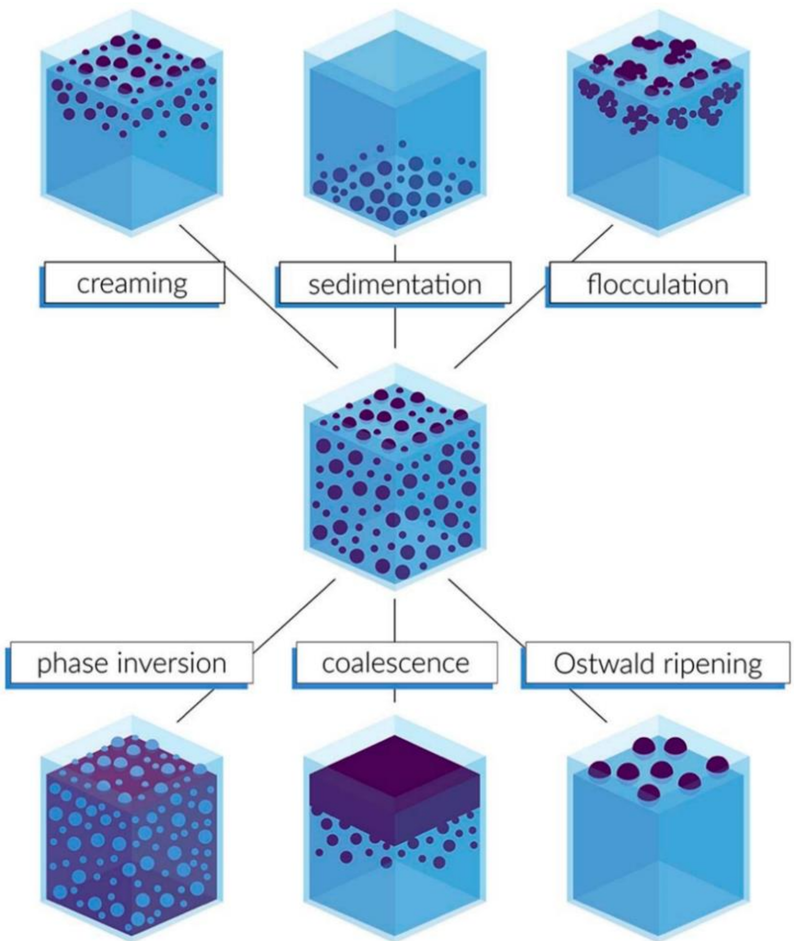

Figure 1. Instability processes in emulsions associated with microencapsulated slurries [5].

The research indicates that EPCMs-based PCSs are advantageous alternatives for cooling, cold energy storage, and cold energy transportation due to their elevated phase change temperature compared to ice and ice slurry [6]. Another superior option for cold storage and transportation is the use of PCS consisting of clathrate hydrates (also known as gas hydrates), which are crystalline structures in which small gas molecules are trapped inside hydrogen-bonded water molecule cages [7].

In order to investigate the trends of a certain topic and to make a clear picture of the state-of-the-art, bibliometric techniques showed the potential to be a powerful tool to identify gaps and hotspots. In literature, bibliometric techniques were also successfully applied to investigate the trend in the thermal energy storage field. In this paper, the research trends on the use of phase change slurry in cooling applications were assessed by combining a bibliometric analysis and a detailed systematic review, to offer researchers interested in this topic a wide overview of the state-of-the-art with a highlight on the research trends and future perspective.

2. Materials and Methods

The literature search was carried on 6 September 2022 out using the database Scopus as a reference. This database was used since it contains more documents on technologies compared to other available ones including Web of Science and Google Scholar [8]. The query was formulated in order to include all studies performed on phase change slurries for energy storage, cooling, and transportation. The query used was TITLE-ABS-KEY ((“hydrate slurr *” OR “phase change slurr *”) AND (“cooling” OR “cold” OR “storage” OR “refrigeration”) AND NOT (“offshore” OR “oil and gas” OR “natural gas”)) and allowed to obtain a total of 221 documents. The bibliometric data were used to evaluate the trend of publications in literature, the main journals where documents were published, and the top institutions and authors publishing on the topic. Moreover, in order to spot the research trends and gaps, the keywords contained in each document and their correlation were analyzed through the open-source software VOSviewer. This program allows for generating and analyzing bibliometric networks based on the co-occurrence of keywords that are represented in a visual map with colored circles of different colors and sizes. In particular, the size is related to the number of occurrences or the link strength with other keywords, while the colors help to identify the different clusters on which the different keywords are grouped.

3. Results

3.1. Literature Trends: Number of Publications, Top Journals, Authors, and Institutions

This section reports the literature trends on the study of PCSs in cooling applications obtained and elaborated with the query described above. The number of publications per year is shown in Figure 2. The first publications on phase slurry used for cooling appear in 1976 with a study from Roebelen, Jr. [9] where a heat sink system with a phase change slurry material was designed to be used for aerospace applications. The next studies appear between the years 1984 and 1985 published by Kasza and Chen on the use of PCSs for storage applications to improve the performance of solar energy systems or waste heat applications [10]. The number of documents published on the topic started to rise in 2005. The most cited document was published that year by Darbouret et al. [11] on the study of the rheological behavior of aqueous solutions of tetrabutylammonium bromide (TBAB) used as hydrate slurry for cooling applications. The number of publications raised until the year 2019 with a drop in 2020 and 2021. This drop could be attributed to the pandemic situation of COVID-19 that limited the experimental activities with the lab closure in most countries. From Figure 3 it is possible to notice that most of the document published are articles, but there is a consistent number of conference papers that indicates that this topic is highly promoted in dedicated congresses. The top journals where studies were published is shown in Figure 4. International Journal of Refrigeration (Q2) is the top choice for researchers to publish studies on the topic followed by Energy and Applied Energy ranked in Q1. It is worth noticing that most of the journals where those studies are published are not open access or hybrid.

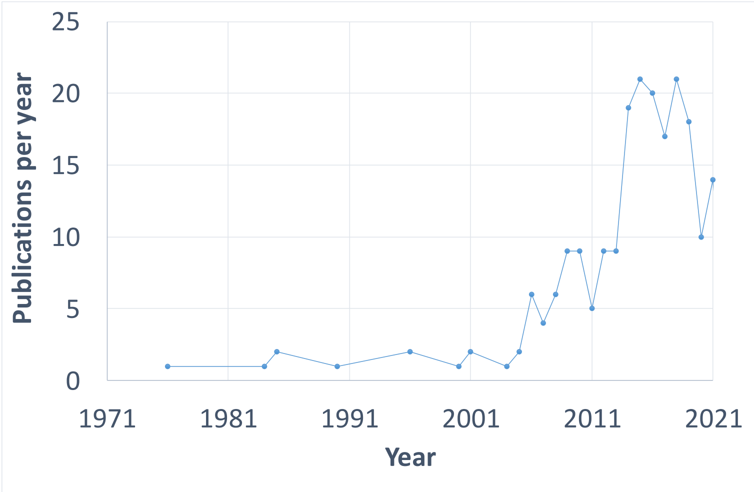

Figure 2. Number of documents published per year.

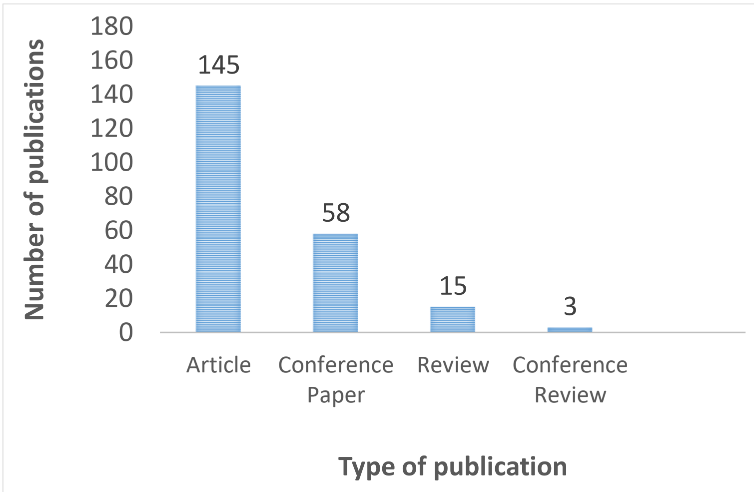

Figure 3. Type of documents published.

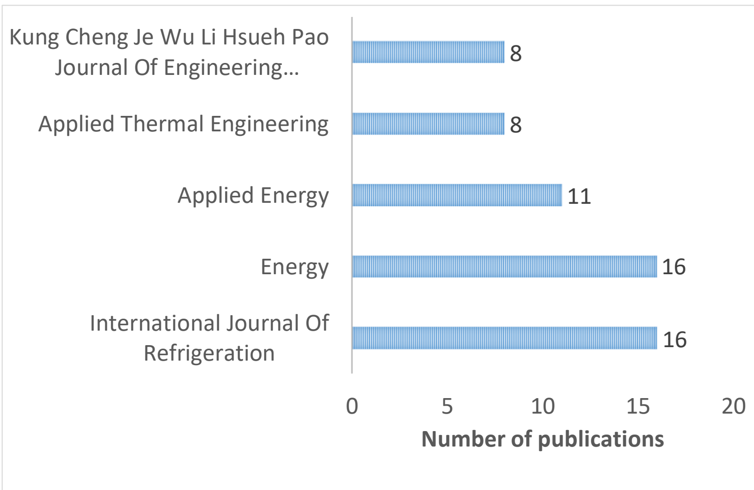

Figure 4. Top journals selected by researchers.

The top countries/territories that are publishing on the topic is published is shown in Figure 5. China and Europe (EU27) are leading the research with the almost same trend in the number of publications that started to rise from 2005. Amongst all European countries, France is leading the research with an increasing trend in the last 10 years. South Korea is also listed as one of the top countries that only started recently publishing on the topic in 2014.

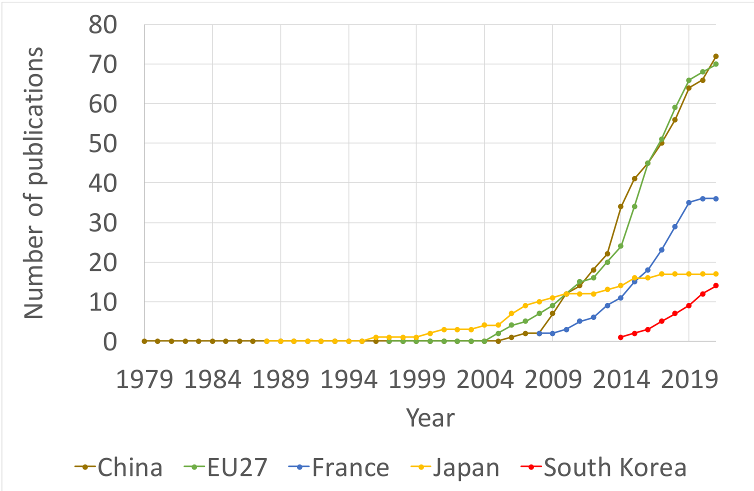

Figure 5. Trends of publications per top countries.

The top authors are listed in Table 1. In this case, it is interesting to notice that most of them are enrolled in French institutions. L. Fournaison and A. Delahaye from Universite Paris-Saclay are the top authors publishing on the topic with most of all documents being co-authored. The most cited paper is a study on the formation conditions and the latent heat of dissociation of tetrahydrofuran (THF)-CO2-water mixture hydrates used as a second refrigerant published in 2006 [12]. Another relevant study was published in 2008 regarding the rheological behavior of CO2 slurries in a dynamic loop for secondary refrigeration applications [13]. The studies of all other authors present in the list linked to French institutions are co-authored with L. Fournaison and A. Delahaye [14–17]. P. Zhang from Shanghai Jiao Tong University is another top author working on the topic.

Table 1. List of top authors publishing on the topic.

Author	Institution	Country	Number of Publications in this Query	Total Number of Publications	H-Index
L. Fournaison	Universite Paris-Saclay	France	35	80	27
A. Delahaye	Universite Paris-Saclay	France	34	80	26
P. Zhang	Shanghai Jiao Tong University	China	26	300	40
H.M. Hoang	Universite Paris-Saclay	France	14	60	18
P. Clain,	Pôle Universitaire Léonard De Vinci	France	13	19	8
D. Dalmazzone	ENSTA Paris	France	11	53	25
V. Osswald	Universite Paris-Saclay	France	11	15	6
Z.W. Ma	Durham University	UK	10	49	20
Z.P. Feng	University of Chinese Academy of Sciences	China	9	100	18
J. Oignet.	Génie des Procédés Frigorifiques pour la Sécurité alimentaire et l'Environnement,	France	9	9	5
X.J. Shi	Shanghai Jiao Tong University	China	9	16	10

Excluding reviews, one of the most cited studies was published by X.J. Shi on the comparison of different methods for the generation of TBAB hydrate slurry in a cold storage air-conditioning system [18]. This author has other studies co-authored with Z.W. Ma [19,20].

3.2. Keywords Analysis

Figure 6 shows the network map of the keywords contained in the documents related to studies on phase change slurries obtained with the query above. From the figure is possible to notice that there are four main clusters.

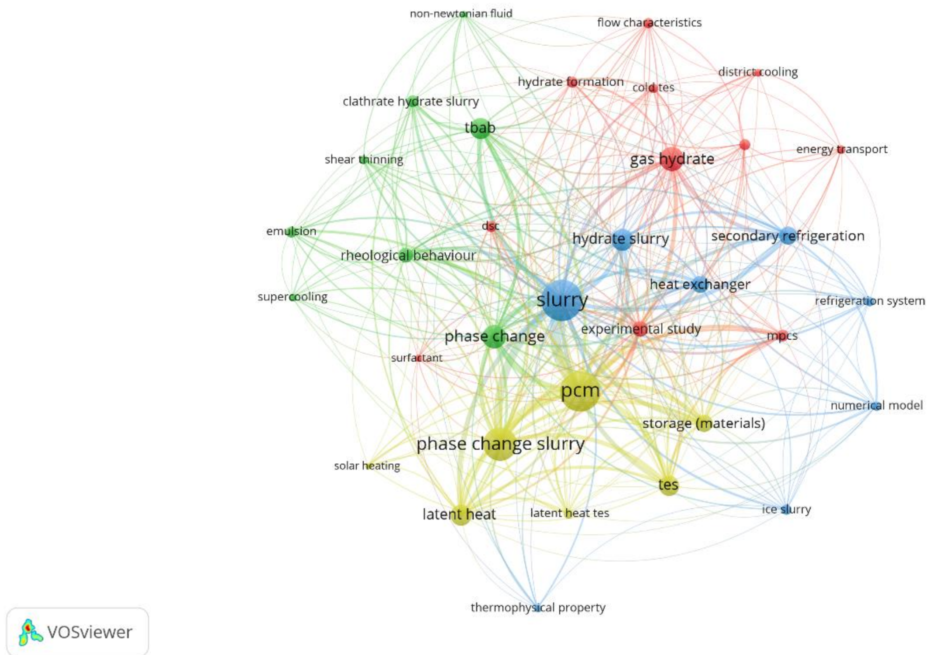

Figure 6. Co-occurrence of keywords made with the software VOSviewer.

3.2.1. Keywords Related to Gas Hydrates

The cluster at the top of Figure 6 (red cluster) is mainly related to "gas hydrate". Gas hydrates (called also Clathrate hydrates) were discovered by Joseph Priestley in 1778 [21] and first documented by Sir Humphrey Davy in 1811 [22,23]. They are crystalline water-based solids, similar to ice from the physical point of view, in which small guest gas molecules are confined inside cages of hydrogen-bonded, frozen water molecules. The working media of a cold-storage system directly influences the capacity and efficiency of the system. Moreover, hydrates used for cold storage should be environmentally friendly, safe, and abundant, and present a high reaction heat, good thermodynamic properties, low supercooling degree, and high growth rate. The cluster shown in Figure 6 includes all different applications of gas hydrates including "cold TES" [24,25], "energy transport", and "district cooling" [26]. Gas hydrate slurry, including carbon dioxide (CO_2) and hydrate slurry, can be used as phase change material as it has an extremely high latent heat of fusion (500 kJ/kg, at $p > 1$ MPa) at an elevated temperature (5–10 °C) [27]. Recent research shows that gas hydrate slurries have the properties of good compatibility with conventional air conditioning, cold storage and heat exchange, and transport [28]. Karanjkar et al. [29] studied the effect of the fluidity of cyclopentane (CP) slurry on the operating conditions of cold storage devices. The results showed that the viscosity of the hydrate slurry increases with the volume fraction of water of the emulsion leading to poor fluidity and a cooling effect [30]. In addition, Ogawa et al. [31] proposed the conceptual design and developed numerical modeling of an innovative hydrate-based refrigeration cycle using the hydrate of difluoromethane (HFC-32)/CP guest pair. The COP of the system was found to be up to 8.0. Moreover, a laboratory-scale prototype was developed and tested.

In recent years, because of non-toxic, non-flammable, and low Global Warming Potential (GWP), more attention was paid in develop CO_2 hydrate-based VCR systems, which combine the advantages of CO_2 as refrigerant and hydrate slurry as cold storage and transportation media. Xie et al. [32] proposed a novel CO_2 hydrate-based refrigeration system and the simulation using Aspen Plus showed that a COP of 6.8 is achievable. Choi et al. [33] constructed a lab-scale experimental system to investigate the CO_2 hydrate formation process using high-grade cold recovered from liquified natural gas (LNG) regasification. Recent studies also indicate that in typical district cooling scenarios, the life cycle cost of a CO_2 hydrate cooling and cold storage system is half of that of HFC systems, due to the capability of peak demand reduction, as well as the reduction of the storage tank, pipe diameters, and pump powers for cold storage and transportation [34].

3.2.2. Keywords Related to Microencapsulated Phase Change Slurries

From Figure 7, it is possible to notice that the red cluster includes the keywords "mpcs" (microencapsulated phase change slurries), "experimental studies", "surfactant", and "dsc". In particular, those keywords are far from the main cluster bridge with other clusters. The keywords "dsc" and "surfactant" are connected to the green one related to studies on the evaluation of the behavior of hydrate slurries and gas hydrates. The keywords "experimental study" is connected to all clusters (green, yellow, and blue). Highlighting the keyword "mpcs", as shown in Figure 7, it is possible to notice a connection with "refrigeration system" (blue cluster), "phase change material" (yellow cluster), and "rheological behavior" (green cluster).

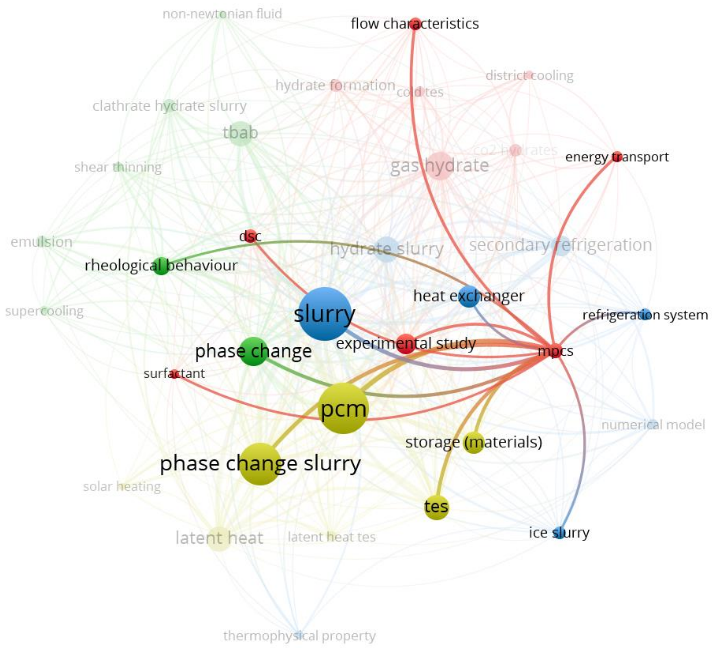

Figure 7. Co-occurrence of the keyword "mpcs".

Griffiths and Eames [30] investigated microencapsulated phase change slurries (MPCSs) as both the energy storage and transportation media in a cooling ceiling system. In general, MPCS is the suspension of encapsulated PCM microparticles (>1 µm) in water. The shell of PCM microcapsules protects the core material from interacting with a carrier fluid, which enhances the stability of the material and also avoids particle aggregation. The efforts over the last three decades clearly revealed improved thermal transport and storage properties (with thermal capacity 2–4 times higher than that of the carrier liquid). These potential applications of MPCSs are mainly in HVAC (Heating, Ventilation, and Air Conditioning systems), and mini/micro-channel heat sinks for electronic device cooling, which can make full use of their superior thermal storage capacity and decent heat transfer ability. In a study carried out for California Energy Commission [35], MPCS was used as a cold storage material for peak shifting, resulting in 40% of peak load shaving. In Narita Airport (Tokyo, Japan) project, the ice storage was replaced with MPCSs, resulting in decreases of 40% in storage volume and 32% in operating cost [36]. The MPCSs are also expected as a promising heat transfer fluid in mini/microchannels for electronic device cooling, although the enhancement of heat transfer is partly offset by the high pumping power due to the increase in pressure drop and viscosity compared to the base fluid [37].

Nano-encapsulated phase change slurries (NPCS) were recently developed as a potential thermal energy storage medium in terms of small size, large specific surface, and high heat transfer rate [6]. Both slurries are subject to large specific heat and heat transfer coefficients but considerable supercooling and low heat transfer efficiency as well as low working temperature (≤30 °C) [38]. The combination of nanoparticles and MPCS/NPCS can improve the thermal conductivity and specific heat of the fluid [39]. Experiments showed that the addition of multi-walled carbon nanotubes (MWCNT) into MPCS can effectively improve the thermal conductivity of water-MPC suspensions [40]. Except for the preparation, heat transfer, and flow property characterization of MPCS, the thermal and hydraulic performance of heat exchangers with MPCS or NPCS as a working medium has been studied experimentally and numerically. For example, heat transfer of poly-α-olefin with nano-encapsulated phase indium particles in a microchannel heat exchanger was tested for high applications (150–180 °C), and an improved heat transfer coefficient as high as 47,000 $W/m^2 \cdot K$ was achieved [41]. The thermal and hydraulic performance of water-MPCS suspension in a helically coiled tube heat exchanger was measured, and it was shown that MPCS can enhance the thermal performance compared with water, but the performance was restricted by increased viscosity and low latent heat of MPCS [42]. The heat transfer of water-MPCS turbulent flow in a coiled heat exchanger was simulated by using a homogeneous and single-phase flow model in ANSYS Fluent and by employing an analytical method [43]. The heat transfer of water-MPCS suspension turbulent flow was predicted by using a homogeneous and liquid-solid two-phase flow model in ANSYS Fluent 19.3, and the trajectories of MPCS particles were calculated based on the discrete phase model after the prediction was finished [44]. The heat transfer of water-MPCS suspension turbulent flow in a microchannel heat exchanger was simulated based on a homogeneous and single-phase flow model in ANSYS Fluent 6.3 [45]. Obviously, the heat transfer of water-MPCS suspensions in various heat exchangers needs to be investigated more intensively by experiment and simulation in the future. Different reviews were also published regarding the flow and heat transfer characterizations of microencapsulated phase change slurry [46], their hydrodynamic mechanisms in circular tubes [47], or in mini/microchannel heat sinks [37], even related to the impediments confronting this PCMs slurries in photovoltaic thermal applications [48].

For cooling applications, materials with lower temperature ranges are needed, depending on the system being analyzed. A 43.0% of microencapsulated PCM (paraffin) and polymethyl methacrylate (as the shell) slurry was employed to develop six PCS with different concentrations of the encapsulated paraffin in a water solution, with the following mass fraction: 8.6, 12.9, 17.2, 21.5, 25.8, and 30.1 wt%. The six PCS were characterized by a delay method (Figure 8), performing cooling from 50 to 10 °C. The obtained results showed an improvement in a range of 9.2 to 33.7 kJ/kg when increasing the amount of encapsulated PCM from 8.6 wt.% to 30.1 wt%, respectively; while the specific heat decreased from 4.0 to 3.8 kJ/(kg·K) for 8.6 wt.%, and 30.1 wt.% of microencapsulated PCM, respectively [49].

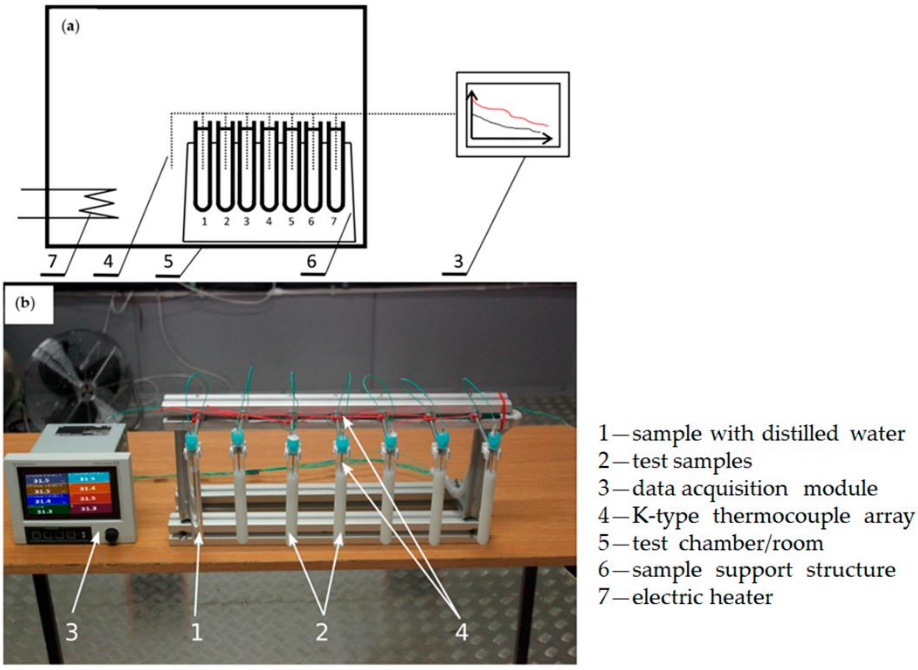

Figure 8. Representation of the assay system (**a**) and an impression of the measuring sector inside the temperature-controlled chamber (**b**) [49].

Different applications were proposed for these encapsulated PCS, among them the use of an enhanced slurry for passive systems as cement slurries to be applied in deep-water regions or permafrost, consisting of paraffin wax with low phase change temperature and urea formaldehyde resin as a shell. These materials were attained by an in-situ polymerization process based on different steps (Figure 9). The melting point, melting enthalpy, and core content of MPCM were 35.85 °C, 85.69 J/g, and 66.54%, respectively, with the aid of avoiding destabilization of hydrates in deep-water environments [50].

MPCM.

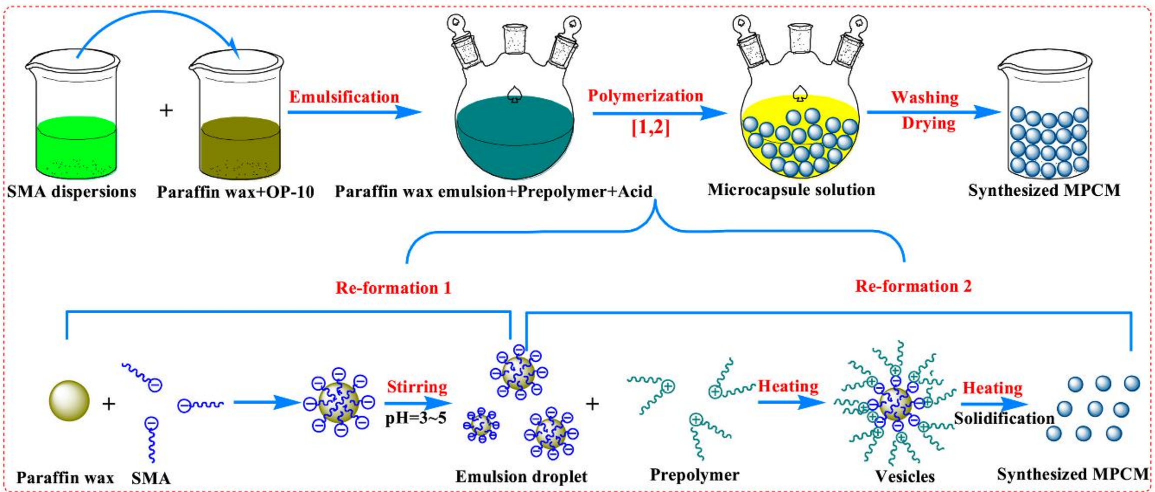

Figure 9. Representation of the synthesize of MPCM [50].

3.2.3. Keywords Related to Hydrate Slurries for Refrigeration

The blue cluster shown in Figure 2 is related to the application of hydrate slurry in refrigeration. Hydrate crystal and water are the main constituents of the hydrate slurry, and they are pumpable when the concentration of crystal is lower than a certain threshold value. In this last case, the hydrate slurry could be used as a cold storage medium in a secondary refrigerant in air-conditioning systems. The major parts of the known structures were synthesized in the nineteenth century and their crystallographic structures are classified in sI, sII, and sH, based on their shape and cavity size. Regarding the keywords, the strongest relation of hydrate slurry in the blue cluster includes "secondary refrigeration", "refrigeration system" and "heat exchanger". From Figure 2 it is possible to notice that the keywords hydrate slurry and second refrigeration are strongly related to PCM. Phase change materials were proposed as an emerging candidate for cold storage, for their higher cold energy storage density than traditional cold storage medium-chilled water and ice [28]. However, regarding the most commonly employed classes of PCMs, inorganic salts may suffer from corrosion issues in metal containers, while organic PCMs present safety concerns related to their toxicity and flammability. In such a context, the CO_2 hydrate slurries were proposed as new PCMs for cooling applications, owing to their large latent heat and suitable phase transition temperatures (0–12 °C) [51]. The utilized hydrate slurries include TBAB semi-clathrate hydrate [25,51] and tetra-n-butylphosphonium bromide (TBPB) [17,52,53]. Generally, thermo-physical properties of TBAB aqueous solution are necessary for the calculation of the thermodynamic performance, pressure drop, and heat transfer coefficient. Ma et al. [54] gave their results measured under conditions with different mass concentrations, such as densities, specific heats, and thermal conductivity. Then thermo-physical properties of TBAB-CHS can be determined from the corresponding properties of the liquid phase (TBAB aqueous solution) and the solid phase (TBAB hydrate crystal). All these properties can be found in Table 2.

Table 2. Thermo-physical properties of TBAB solution and TBAB-CHS [54].

	Density (kg/m^3)	Specific Heat (kJ/kg·K)	Thermal Conductivity (W/m·K)
		TBAB solution	
ω = 0.10	1010.22	4.03	0.521
ω = 0.20	1019.86	-	0.472
ω = 0.30	1030.82	-	0.418
ω = 0.40	1040.98	-	0.351
		TBAB-CHS	
ω = 0.10	1009.83	3.97	0.502
ω = 0.20	1009.67	3.98	0.507
ω = 0.30	1009.51	3.99	0.523
ω = 0.40	1009.34	3.99	0.577

For the properties of TBAB-CHS. Density and specific heat can be determined based on the mass and energy balance, and thermal conductivity can be determined by Maxwell's equation. In the study by Ma et al., they measured the thermal conductivities of TBAB-CHS with a simple transient hot-wire unit [54]. The research focus on hydrates slurry is still in an early stage and includes: the determination of thermodynamic properties [17], the effect of the particle size distribution [16], crystallization kinetics [24], and other basic features needed to evaluate the applicability of this class of materials as a cold storage medium. The studies related to the evaluation of the rheological behavior and the evaluation of flow characteristics of gas hydrates are a fundamental part of its applications and they are related to the green cluster. Relevant studies related to the rheological behavior were published studying the following aspects: investigations on the measurement methods and instruments [55], models to predict the viscosity of hydrate slurries [56], and water-oil emulsion in the presence of hydrate particles in high water cut systems [57], experimental studies on the rheological behavior of clathrate hydrate slurry [58] and modified CO_2 Hydrate Slurry with additives [59,60], the influence of some important parameters such as pre-treatment temperatures, cooling/heating rates, and final temperature of cyclopentane hydrate formation [61].

3.2.4. Keywords Related to Phase Change Slurries for Latent Thermal Energy Storage

The last relevant cluster is related to "PCM" and "phase change slurries" for "latent heat thermal energy storage". Youssef et al. [62] published a literature review on different types of PCSs for secondary refrigeration and air conditioning in a melting temperature range from 0 to 20 °C. In literature, different 1-component slurry for cooling such as ice slurry, slush nitrogen, and slush hydrogen was defined as non-encapsulated phase change slurries (PCSs) [63], and different preparation methods of these PCSs were summarized and divided into two groups: for slush hydrogen and slush nitrogen (freeze-thaw, Auger, Nozzle expansion, and Helium gas/liquid injection methods) and for ice slurry and clathrate hydrate slurry (supercooling release, scraping, direct contact, fluidized bed, and vacuum methods) [63]. In addition, these non-encapsulated PCSs were systematically reviewed aiming at their thermo-fluidic properties (rheological behaviors, flow pattern, pressure drop, and heat transfer performance, among others). However, some contradictive results about these reported characteristics revealed that more rigorous investigations are still required to attain a thorough interpretation of this type of PCMs [64]. As mentioned above, this cluster is related to the keyword "mpcs" (microencapsulated phase change slurries).

3.2.5. Overlay Visualization of Keywords

Figure 10 shows the overlay visualization of keywords obtained with the software VOSviewer that highlights the research trends. In particular, it is possible to notice that the most recent studies foused on the application of gas hydrate for district cooling and the shear thinning on the rheological behavior of emulsions.

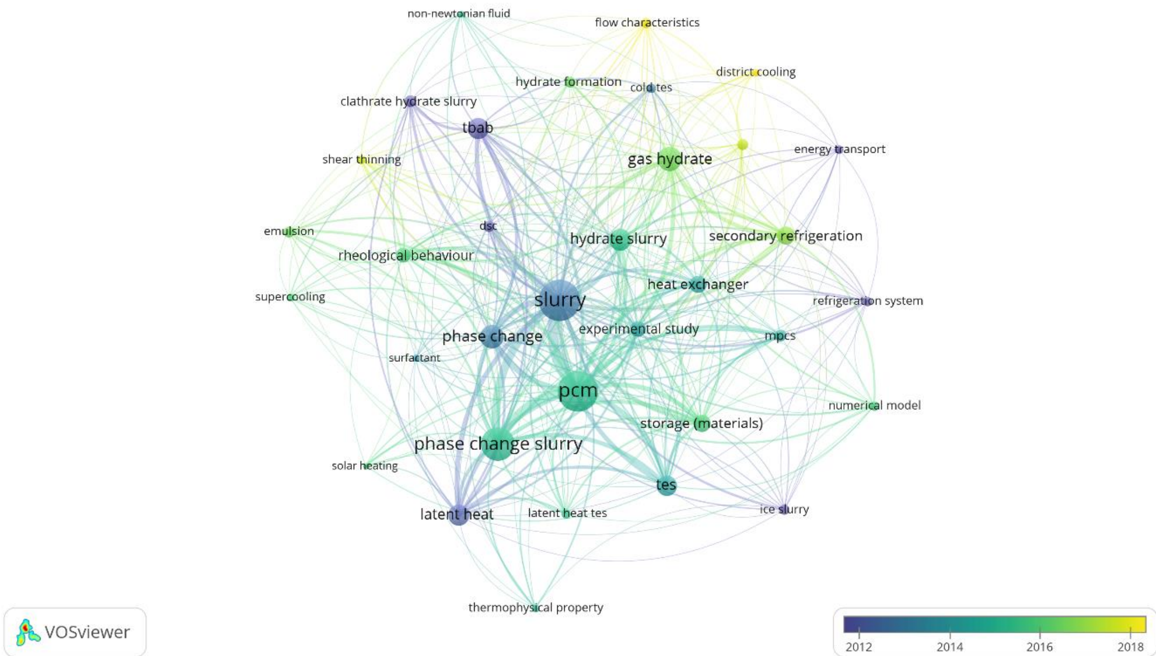

Figure 10. Overlay visualization of keywords obtained with the software VOSviewer.

4. Discussion

The bibliometric techniques and a detailed systematic review here applied proved to be a powerful tool to identify gaps and hotspots in the use of phase change slurry for cooling applications. Moreover, the analysis of the countries that lead these inquiries will be very valuable for the establishment of research, internships, and international projects among the different researchers and students throughout the world, allowing a global vision of the type of institutions, the authors, institutions, and the most outstanding scientific journals in this area. The keyword analysis allowed us to examine the different systems and selected materials used for cooling and storage applications: gas hydrates slurries, phase change slurries, and different encapsulated slurries. The previous sections showed the main trends in the research on phase change slurries for cooling and storage applications.

Regarding gas hydrate slurries, cold storage characteristics and transportability in pipelines are always hot research topics to which the relative new cooling and storage technologies and applications are a concern [65]. Studies [7,14] have reported that single hydrate slurries are not able to meet the requirements of cold storage in terms of temperature, pressure, reaction speed, and supercooling degree. Thus the possibility of forming mixture-gas hydrates at low pressure (p < 1 MPa) in the phase transition temperature range of practical refrigeration applications (7–12 °C) while maintaining a high dissociation enthalpy (330–450 kJ/kg) is still challenging and a hotspot in near future [66], as well as the controllable and rapid hydrates formation and dissociation technologies for the better compatibility with different cooling and cold storage scenarios in order to achieve high energy efficiency values [33]. Experimental and numerical research on the kinetic parameters, which link to the gas hydrate slurry flow and rheology as well as mass and heat transfer in various media (aqueous, organic) and different channels are ongoing and crucial [67,68]. In addition, the research found that the COP of the cold storage integrated refrigeration system using gas hydrate slurries as the secondary two-phase refrigerant was low, and it was not applicable for cooling at a high ambient temperature above 303 K [69]. Hence, hydrate-based refrigeration, which uses gas hydrate slurries as the primary refrigerant, has great potential to improve the coefficient of system performance by being pressured and condensed separately to decrease the energy consumption of the compressor. The number of publications on relative technologies, e.g., the design and integration of key components [70] and multi-stage processes and the optimization of operation strategies [71] is still limited.

Regarding encapsulated phase change slurries, several applications were proposed: surface casing cementing, in deep-water regions or permafrost [50,72], photovoltaic thermal systems [48], microchannel heat sinks [73], double-pipe heat exchanger [74], jet impingement heat [75] and for cold energy storage [76]. Many other areas will benefit from the use of EPCMS, among them the most outstanding is the automobile industry, with the important and necessary improvement in lithium battery cooling systems [77,78]. EPCMS are more suitable for cooling applications such as air conditioning, PV/T panels, heat storage tanks, heat sinks, and engines. The complete phase change of EPCMS is favorable to heat absorption, and it should be satisfied when an EPCMS flow system is designed. The concentration of EPCMS is a key factor to control the specific heat, heat transfer coefficient, and viscosity of EPCMS. The encapsulation of organic PCMs is more efficient and easier than the encapsulation of inorganic PCMs, thus, the organic EPCMS should be selected first.

Recently, several experimental and modeling studies were proposed for comprehending the behavior of these EPCMS. Henceforth, research on the energy efficiency of these materials will be expanded, as well as on their rheological properties, which have a direct impact on maintenance costs. In this regard, the use of nano-additive to create nano-enhanced EPCMS should be exploited at maximums level in the near future to improve thermal conductivity and stability. Moreover, adding nanoparticles to EPCMS could improve not only the specific heat of the fluid but also other properties such as thermal conductivity [39]; still, some induced problems such as disaggregation of the employed additives and/or an increase in viscosity should be resolved [79]. Hence, the use of metallic nanoparticles, metallic core encapsulation, or even nano-encapsulated PCS will be a possible solution for enhancing these problematics and even those related to stability (Figure 4).

According to our criteria and to the bibliographic search carried out here, the work with gas hydrate slurries is broader and more diverse.

Nevertheless, both gas hydrate slurries and phase change slurries present control and stability problems over time. Moreover, EPCMS suffer from a few disadvantages such as high cost, short durability, and destructive effect on both the human body and the environment due to hazardous chemical and toxic properties under leaking conditions. Supercooling is one major obstacle for EPCMS to be applied in industrial sectors. Hence, an increase in the number of investigations and investments in the development of new encapsulated materials is expected. Indeed, despite some studies being published related to EPCMS for cooling applications, there are limited works performed in the literature. An increase in projects, PhD and Post-doctoral research, manuscript, patents, pilot plant designs, and more are soon expected in this theme, which will drive these products to the market, expecting that over time their costs can decrease thanks to improvement through optimization of their large-scale synthesis methods.

5. Conclusions

Phase change slurries have found great potential in cooling applications both as a storage medium and heat transfer fluid due to their chemical and physical properties compared to conventional materials. In recent years this attracted several researchers to investigate these materials and overcome the actual challenges. In this study, bibliometric techniques were used to draw a picture of the state-of-the-art research made in PCS to identify where the research is going and to spot the gaps. The main conclusions of this study are summarized as follows:

1. The first paper on PCS was published in 1976. However, research on the topic started to gain interest in 2005 and the number of publications per year raised until 2019. The COVID-19 pandemic situation could affect the number of studies published in 2020 and 2021 due to lab closures in most countries.
2. Most of the documents on PCS were articles published in Q1 journals, with Europe and China leading in the number of papers published. Most of the studies from Europe were performed at Universite Paris-Saclay in France.
3. Most of the gas hydrates-based PCS research was carried out from the application angle and at a system level, while the fundamental understanding of the fast formation and long-term stability of the PCS, as well as the related compatibility and flow behaviors, are less investigated, although its importance is fully recognized.
4. Encapsulated PCS were proposed as heat transfer fluids for heat exchangers at different temperatures employing different designs: helically coiled tube heat exchangers, circular tubes, or mini/microchannel heat sinks.
5. An interesting application and potential future use for encapsulated PCS is as a cooling medium to reduce the warming from the back of the photovoltaic modules.
6. The main base fluid for cooling applications with EPCMS was water, however, these materials can be applied in passive systems, i.e., cement slurries.
7. Special attention should be paid to the viscosity increasing and the final low latent heat of encapsulated PCS since they could be the main challenges in their applications. Consequently, the determination and characterization of their rheological properties are crucial.
8. Since the specific heat of PCS tends to decrease after the encapsulation, an improvement in thermal conductivity will be required to achieve a final material meeting all requirements of the desired application.
9. As well, numerical simulations of the thermal and hydraulic performance of heat exchangers with encapsulated PCS represent a significant step for optimal experimental applications.

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