ABSTRACT

Objective. This paper presents an overview of Green Chemistry research from 1990 to 2017, identifying its specialties, comparing their relative importance, and inferring emergent trends.

Design/Methodology/Approach. Co-citation analysis of 14,142 documents retrieved in Web of Science by CiteSpace software, using network analysis to describe research fronts by clustering, their relevance by clusters indicators, and emergence by citation burstiness.

Results/Discussion. Sixteen clusters were found and then grouped into six big specialties. Some specialties are more persistent and general (e.g. GC Characterization, Metal Catalysis, and Microwave Activation) and others are more recent and focused (e.g. Deep Eutectic Solvents). Mechanochemistry and Photochemistry are emergent trends in Green Chemistry.

Conclusions. This paper presents a more quantitative/objective panorama of GC research, comparing the relevance of research fronts inside the field, and helping future researchers and decision-makers in further developments of GC. CiteSpace showed some limitations in clustering. Data collection was hurdled by changes in the Keyword Plus algorithm in Web of Science and by the lack of authors keywords in main journals of the field. Although large, the dataset was restricted to the Web of Science database.

Originality/Value. To the best of our knowledge, this is the first quantitative analysis of research specialties of GC. It advances past peer evaluation of the field by using indicators and metrics to describe the emergence, extension, and decay of specialties.

Keywords: Green Chemistry; Research front; Knowledge mapping; Co-citation analysis; CiteSpace

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1. INTRODUCTION

Green Chemistry (GC) emerged around 1990 mainly in the United States, although practices towards reducing the pollution in the chemistry industries were being developed elsewhere and even earlier under different names, such as clean, sustainable, benign chemistry, and others. Its initial objective to contribute to the prevention of chemical-based pollution has been outlined and expressed through the Twelve Principles (Anastas & Warner, 1998), which have served the so-called green chemists as guides in their procedures, especially synthetic ones, aiming at reducing or eliminating the production and use of hazardous substances.

There is no consensus in the literature whether GC is a field, an area, an epistemic community, or a philosophy of Chemistry. This research adopts the concept of field in terms of Pierre Bourdieu, as a social space in which agents (green chemists) interact with each other’s knowledge under the convergence of interests and from hierarchical relationships (Gilding & Pickering, 2011; O’Neil & Ackland, 2020). Although we do not consider it to be a discipline, GC has its own, well-defined identity, being compared to a social movement (Woodhouse & Breyman, 2005) or an epistemic community (Epicoco et al., 2014). For this reason, this research focuses on the GC field and uses only the search term “green chemistry”, even though proposals for environmentally benign chemistry are carried out by other names, such as clean chemistry, sustainable chemistry, and other terms.

Despite being a new field within Chemistry, its output in the past few years is notoriously large and the scientific appraisal has been considerable. In 2017, GC papers were among the top 1% most cited articles in Chemistry forming a research front on Green Chemistry, sustainability, and metrics (Chinese Academy of Sciences and Clarivate Analytics 2018). Research fronts describe a recent workgroup that is highly cited and linked to a set of restricted, highly cited literature published a few years earlier (Li & Chu, 2017; Price, 1965). Due to their large numbers of citations, research fronts represent the subjects that most mobilize the scientific community at a given moment, and the literature directly cited by the research fronts configures its intellectual basis (Chen, 2017; Clarivate Analytics and Chinese Academy of Sciences, 2019). Several authors (Chen, 2017; Small, 1973; Small & Griffith, 1974) argue that the analysis of the patterns of co-occurrence of citations within a set of papers, i.e. co-citation analysis, can be an effective strategy to describe and analyze research fronts and specialties.

Some attempts have been made in understanding the nature and boundaries of GC, however, as Clark et al. (2014) point out, there are no established criteria on what GC is, and its boundaries are still somewhat unclear. Previous studies attempted to summarise the area presenting an overview of their practices and challenges (Anastas et al., 2016, 2018; Clark et al., 2014; Ivanković, 2017), generally departing from the Twelve Principles and pointing to exemplary practices as a basis for tacit knowledge about GC. Research demonstrates the richness of GC in association with the Twelve Principles, but it is limited by its subjectivity.

CiteSpace is a powerful and efficient tool for co-citation analyses (Zhang et al., 2020), a viable tool to avoid possible subjectivity in the qualitative judgment of a field (Clarivate Analytics and Chinese Academy of Sciences, 2019). This software is based on research specialties, a time-variant network (F (t)) created by the relation between a group of citing papers (the research front, Y (t)) and the co-cited papers (the intellectual base, W (t)), as in Equation 1.
The analysis of the temporal evolution of the specialties is done by the creation of co-citation networks in time slices, which are then fused into a single heterogeneous net that can be divided into clusters. The measure of separation between clusters, showing how much these groups differ, is made by modularity Q (Newman, 2006) and the silhouette is the measure of internal group cohesion (Rousseeuw, 1987). Separation into clusters allows us to study themes that are trends in the field under study, and to identify groups of researchers that are more active and engaged in the investigation of a given object.

CiteSpace has been used previously to investigate the structure and dynamics of scientific fields concerning environmental issues (Li et al., 2019; Luo et al., 2017; Zhang et al., 2020). Therefore, this paper uses CiteSpace to investigate the questions: 1) what are the scientific specialties of GC? 2) What is their relative importance? 3) What are the possible emerging trends of the field?

Section 2 presents the methodology. Section 3 presents the results and characteristics of the specialties in GC (sections 3.1 up to 3.8). Section 4 discusses the extension and immediacy of specialties by their CPT value (section 4.1), emerging trends in GC (section 4.2), and elements of results validation (section 4.3). Finally, the conclusions presented in section 0.

2. METHODOLOGY

The figure 1 presents a summary of the criteria for selecting the input data in CiteSpace. All data were collected in the Web of Science (Core Collection, all Indexes) from 1990 to 2017, the beginning of the decade in which GC emerges (ACS 2015; Anastas et al., 2016) until the last full year at the time of analysis. We searched for records of documents that usually contain references, selecting the following database categories: articles, reviews, proceedings papers, and book chapters. From that point on, the search strategy divides itself into two: searching for the term "green chemistry" in titles, keywords, and abstracts to explicit affiliation to GC, and searching for all records published in the Green Chemistry Journal and Green Chemistry Letters and Reviews. The search in the specialized journals was necessary because their texts do not always use the descriptor "green chemistry" in their titles, abstracts, and keywords, as this is stated in the names of the journals. Those two journals were chosen for being specialized in the field (as indicated by their name) and for their big output, being among the top 20 journals publishing texts with the term "green chemistry" in the titles, abstracts or keywords.

A final set of 14,142 different records (duplicates excluded) was obtained, being 8,587 records with the term "green chemistry" and 5,987 in specialized journals, analyzed by CiteSpace software (version 5.2.R1.3.9.2018). I was used Look Back Year (LBY) of -1, meaning that no time limit is imposed on the formation of specialties and that all cited texts can be considered in the co-citation analysis. The time slice and the node selection criterion (Top N) were determined to generate the highest value of Modularity Q and Mean Silhouette (published as a supplementary material). The final parameters for analysis in CiteSpace are: Look Back Year (LBY): -1; Time Slice: 3 years (1990-2017); Node types: Cited reference; Top N.: 100. Other parameters followed the default program settings.

The algorithm for the generation of clusters was applied and their names attributed manually
by investigating similar topics (words, concepts, tools, and substances) in the titles and abstracts of articles in the research front. This proved to be more precise than the automatic naming-tool provided by CiteSpace. The final label for the clusters followed the type "# cluster number – cluster name", e.g. "#0 – Ionic Liquids". CiteSpace attributes the cluster numbers in decreasing order of intellectual base size. That means cluster #0 has the largest intellectual base and #18 the smallest.

To highlight the relative importance of a specialty, we used the CPT indicator created by Clarivate Analytics to measure how extensive and immediate a research front is (Clarivate Analytics and Chinese Academy of Sciences, 2019). It evaluates the citation impact of a research front by the number of its citing paper (C); it highlights the emerging character and the endurance of a research front by measuring its time span (T), and it considers the extension of a cluster by the number of core papers (P) in its intellectual base. CPT is obtained by dividing the average citation impact of a research front (C/P) by the age of the citing papers (T), then

$$CPT = C/(P \cdot T) \quad \text{(Equation 2)}$$

High CPT values may be achieved when a specialty has a big research front, co-citing a small intellectual base in a short time. That means that the specialty has a large community of researchers dedicated to analyzing a very defined and restricted theme in a short period.

CiteSpace’s citation burstiness considers the sudden increase in the number of citations to work as indicative of the community’s interest in its content and possibly as an element of the degree of innovation presented by the research (Chen, 2006, 2017). Recent papers with high values of citation burstiness may represent an emerging trend of a domain. We selected papers published up to five years before the research (i.e. up to 2012) and whose citation burstiness lasted until the year of analysis (2017). This provided information on recent papers that most attracted the interest of the scientific community.
3. RESULTS

The final network has 457 nodes and 1,353 links (edges) in its largest connected component. According to Table 1, it was only from 1996-1998 that it was possible to establish a co-citation network within the chosen parameters, close to the publication of important books for the area, such as *Green Chemistry: Designing Chemistry for the Environment* (Anastas & Williamson, 1996) and the important *Green chemistry: theory and practice* (Anastas & Warner, 1998), which launches the Twelve Principles of GC. In 1999-2001, almost ten times more references are found than in the previous years, indicating the contribution of the *Green Chemistry Journal* (created in 1999) to the formation of a cohesive GC network. In the following years, the number of co-cited papers grows, showing the expansion of the field. In Table 1 the total amount of references is bigger than the references in the input data because a reference may appear in multiple time slices. Also, some nodes may be either repeated in multiple time slices or not included in the final network.

| Time Slice | N. References | Nodes |
|------------|---------------|-------|
| 1990-1992  | 0             | 0     |
| 1993-1995  | 9             | 0     |
| 1996-1998  | 924           | 38    |
| 1999-2001  | 8754          | 127   |
| 2002-2004  | 19637         | 124   |
| 2005-2007  | 36710         | 101   |
| 2008-2010  | 63773         | 117   |
| 2011-2013  | 119145        | 105   |
| 2014-2016  | 167595        | 102   |
| 2017-2017  | 82628         | 102   |
| **Total**  | **499175**    | **816** |

*Table 1. Distribution of nodes and references by time slices.*

The network Modularity Q was 0.8718, above the recommended in the literature (Chen, 2006; Zhang et al., 2020), and the mean silhouette value was 0.4188, but the individual result for each one of the 16 clusters was higher than 0.7 (Table 2). Those values indicate the network is reliable.

Sixteen clusters were generated, labeled from #0 to #18. Clusters #13 to #15 are detached from the main network and, therefore, are not included in this analysis. The name of the clusters (column “cluster” in Table 2) was attributed considering the most frequent terms (words or groups of words) in the titles of texts in the research fronts (available at https://bit.ly/2Ls4Nsd), complemented and refined by reading the abstracts of the texts in the research front and looking for similarities in concepts, techniques, or methodology. This also leads
to grouping the clusters in big specialties (Column 1 in Table 2), according to the thematic proximity found in reading the abstracts. For example, all clusters in big specialty A address the issue of solvents, either by using water, no solvent or supercritical fluids. Although ionic liquids can be used as solvents, they stand out as a very cohesive and emblematic group, making up their big specialty (B). Cluster #1 is general and big enough and cluster #7 is distinct enough to stand out as individual big specialties.

Table 2. Size, silhouette, and median year of publication in the intellectual base and research front of Green Chemistry.

| Big Speciality | Cluster | Silhouette | Size (C) | Median Year | Period | Size (P) | Median Year | Period (T) | CPT |
|----------------|---------|------------|----------|-------------|--------|----------|-------------|------------|-----|
| A-Solvents     | #4 – Organic Reaction in Aqueous Media | 0.888 | 31 | 2005 | 1980-2014 | 30 | 2010 | 1999-2017 | 0.0509 |
|                | #5 – Supercritical Solvents | 0.915 | 30 | 1994 | 1989-2000* | 2 | 1996 | 1996 | 0.0667 |
|                | #17 – Deep Eutectic Solvents | 0.994 | 6 | 2013 | 2003-2016 | 10 | 2015 | 2014-2017 | 0.4167 |
|                | #18 – Solid State Organic Reaction | 0.97 | 5 | 1997 | 1990-2000 | 1 | 2000 | 2000 | 0.2000 |
| B-Ionic Liquids| #0 – Ionic Liquids | 0.768 | 55 | 2001 | 1982-2011* | 17 | 2002 | 2002-2010 | 0.0343 |
|                | #6 – Recycling and Recovery of Solvents | 0.843 | 29 | 1997 | 1973-2000 | 3 | 2000 | 1999-2000 | 0.0517 |
|                | #8 – IL Toxicity | 0.972 | 19 | 2005 | 2002-2007 | 5 | 2010 | 2005-2010 | 0.0439 |
|                | #12 – IL Preparation | 0.947 | 9 | 2000 | 2000-2001 | 2 | 2002 | 2002 | 0.2222 |
| C-Biomass      | #3 – Biomass Transformation | 0.908 | 33 | 2008 | 2002-2014 | 34 | 2010 | 2010-2014 | 0.2061 |
|                | #11 – Lignin Valorisation | 0.987 | 10 | 2014 | 2010-2016 | 7 | 2017 | 2017 | 0.7000 |
|                | #16 – Glycochemistry | 0.974 | 6 | 1995 | 1993-1997 | 1 | 1999 | 1999 | 0.1667 |
| D-Catalysis    | #2 – Metal Catalysis and Microwave Activation | 0.865 | 38 | 2001 | 1986-2013 | 30 | 2010 | 1999-2014 | 0.0493 |
|                | #9 – Solid Acid Catalysis | 0.953 | 12 | 2003 | 2002-2017* | 10 | 2010 | 2010 | 0.8333 |
|                | #10 – Catalytic Oxidation of Alcohols | 0.994 | 11 | 2000 | 1981-2006 | 6 | 2010 | 2002-2010 | 0.0606 |
|                | #1 – Characterization of Green Chemistry | 0.816 | 45 | 2006 | 1991-2016 | 56 | 2010 | 1999-2017 | 0.0655 |
|                | #7 – CO2 as Substrate | 0.943 | 28 | 2002 | 1981-2015 | 18 | 2013 | 1999-2017 | 0.0338 |

* Papers placed between two research fronts, reflecting their difference of age.

In the period column of the intellectual base (Table 2), there are nodes whose publication year is more recent than the period of the research front (marked with an asterisk). These nodes are set between clusters with research fronts with different ages and, somehow, they were attributed to the wrong side. For instance, Meehan et al. (2000) are in the intellectual base of cluster #5 – Supercritical Solvents, but it is cited by a paper in the neighbor research front (Webb, Kunene, and Cole-Hamilton 2005), #7 – CO2 as Substrate. This seems to be a
problem to be addressed in the CiteSpace software.

The intellectual base of several specialties has papers published before 1990, which could not be explicitly affiliated with GC. In cluster #4, for example, the oldest text is Rideout and Breslow (1980) on the acceleration of Diels-Alder reactions in water, which is relevant to the theme of the specialty, but not explicitly affiliated with GC.

We present below the six big specialties and their main clusters with a big intellectual base or high CPT value.

3.1. A – Solvents

The high volume of solvents used in the chemical industry is a determining factor in environmental costs and impacts (Anastas et al., 2018) and justifies the existence of a big specialty dedicated to the study of organic reactions in aqueous media (#4), supercritical solvents (#5), solid-state (#18) or deep eutectic solvents (#17), the clusters constituting big specialty A.

3.1.1. Cluster #4 — Organic Reactions in Aqueous Media

Some of the articles that stand out the most for their coverage of the intellectual base are Soleimani et al. (2011) (with their paper on beta-cyanocarbonyl synthesis in aqueous media and no catalytic agents), Bhar & Panja (1999) (demonstrating the reduction of carbonyls in diols using metallic catalysis in aqueous media) and Cadierno et al. (2010) (coupling reactions promoted by metallic catalysis in aqueous media). As for the number of citations, the contributions of Anastas & Eghbali (2010) (a general GC review) and Polshetwar & Varma (2010) (a review on nano catalysis in GC).

The main documents of the intellectual base according to their frequency deal with organic reactions in water in general (Li & Chen, 2006; Narayan et al. 2005), with a focus on the formation of carbon-carbon bonds (Li, 2005), or on with the stereoselectivity of syntheses (Lindström, 2002).

3.1.2. Cluster #17 — Deep Eutectic Solvents

The articles promote deep eutectic solvents as viable solvents for reactions under ambient conditions. Other important papers on this research front do not directly address eutectic solvents, but study reactions under room temperature and pressure (Jérôme et al., 2014; Vidal & García-Álvarez, 2014). The paper by Pena-Pereira & Namieśnik (2014) is the most cited, with 87 citations.

Among the most frequent works, two are reviews on properties and applications of eutectic solvents (Smith et al., 2014; Zhang et al., 2012), and the third is communication on new uses of a classical eutectic system as a solvent (Abbott et al., 2003).

3.2. B – Ionic Liquids

This big specialty reflects green chemists’ concern to address the large generation of waste by solvent usage. The first GC specialties identified in this research deal with supercritical solvents (#5), and solvent recycling and recovery (#6); it is within the latter that the big specialty B is generated. As Sheldon (2017) points out, the major problems of solvents are their storage, and potential for recovery and reuse in future processes, one of the promises of ionic liquids and supercritical fluids (Anastas et al., 2018; Ivanković, 2017).
### 3.2.1. Cluster #0 — Ionic Liquids

Early papers in this specialty have the greatest coverage, and present researches that describe IL synthesis (Branco et al., 2002), analyze characteristics of ionic liquids in synthetic processes (Baker et al., 2002; Holbrey & Rogers, 2002; Swatloski et al. 2002), and the combination of those solvents and (bio)catalysts (Farmer & Welton, 2002; Gordon & Ritchie, 2002; van Rantwijk & Sheldon, 2007). An interesting article by Holbrey & Rogers (2002) questions the green status of ionic liquids, stressing the need to assess its entire process of production, use, and disposal. The most recent papers present an assessment of IL’s antimicrobial potential (Busetti et al. 2010), its use in synthetic processes (Aupoix et al., 2010; Ho et al., 2010), or present an overview of GC (Anastas & Eghbali, 2010) and multiphase catalyzes (Muldoon, 2009), focusing on the role of ionic liquids.

The top-cited papers in this research front are written by Branco et al. (2002), Holbrey et al. (2002), Sheldon et al. (2007), and Anastas & Eghbali (2010). The papers with the highest frequency in the intellectual base are reviews by Welton (1999) (on the role of IL in synthesis and catalysis), and Dupont & Suarez (2002), and an article (Wasserscheid & Keim, 2000) addressing the possibilities of IL in metal-catalyzed processes.

### 3.3. C – Biomass

The use of biomass in the synthesis of useful chemicals is a major GC specialty based on principle 7 – Use of Renewable Feedstocks, as a response to the imminent depletion of fossil fuels and the environmental impacts generated by the high emission of carbon dioxide in the atmosphere (Anastas et al., 2018; Ivanković, 2017). Concerns about possible competition between crops for food sources and industry (Anastas et al. 2018; Marion et al. 2017) are approached by second-generation biomass research, such as specialty #11 – Lignin Valorisation.

#### 3.3.1. Cluster #3 — Biomass Transformation

There is a special interest within this specialty in transforming biomass into biofuels (Alonso et al., 2010; Bozell & Petersen, 2010; Climent et al., 2014), in the use of catalysts to convert biomass into products of interest (Chidambaram & Bell, 2010; Liu & Chen 2014; Wang et al., 2014), and also in the use of glycerol in synthetic processes such as solvent or reagent (Li et al., 2010; Takagaki et al., 2010).

The main papers cited in the foregoing research front are two reviews by Bozell & Petersen (2010) (on available and necessary technology to expand the work of biorefineries besides the production of biofuels), and Alonso et al. (2010) (on the catalytic processes to convert biomass into biofuels). The paper by Anastas & Eghbali (2010) stands out by the high citation score. Chidambaram & Bell (2010) and Climent et al. (2014) wrote papers that stand out by the coverage of the research front.

The intellectual base of specialty #3 has four papers with the highest frequency, three of them deal with the conversion of biomass into chemicals of interest (Corma et al., 2007) or specifically into fuels (Huber et al., 2006; Ragauskas et al., 2006); the fourth deals with the dissolution and direct recovery of cellulose using ionic liquids, dispensing with previous treatments (Swatloski et al., 2002).

#### 3.3.2. Cluster #11 — Lignin Valorisation

This specialty is directed to investigating lignin recovery processes, transforming them into
carbon compounds with a high added-value (Bosch et al., 2017; Gillet et al., 2017; Huang et al., 2017; Kumaniaev et al., 2017; Lancefield et al., 2017; Pelckmans et al., 2017; Si et al., 2017). Papers in this research front have a low citation score, probably because the papers were recently published.

Among its main (high frequency) publications in the intellectual base is a review on the catalytic valorization of lignin for the production of renewable compounds (Zakzeski et al., 2010) and another review on the improvement of lignin refining processes in biorefineries (Ragauskas et al., 2014).

3.4. D – Catalysis

Catalysis is one of the most versatile tools of GC (Sheldon, 2007), allowing to reduce the energy required for transformations, to reduce the generation of residues, and to increase the selectivity of syntheses, as summarized by Anastas et al. (2018) e Ivankovic (2017). Heterogeneous catalysis, as promoted by solid acid catalysts (#9), has been proposed as more advantageous by using abundant and less hazardous metals (Anastas et al., 2018). The use of microwave irradiation is also cited in previous reviews as a possibility for increasing the energy efficiency of an entire process (Anastas et al., 2018; Ivankovic, 2017).

3.5. Cluster #2 — Metal Catalysis and Microwave Activation

This specialty seems to deal mainly with the use of metallic catalysts, and the energetic activation of organic reactions using microwaves generally developed without the use of solvents. Among the most cited papers in the research front of #2, there is one broad presentation of GC (Anastas & Eghbali 2010), two papers related to nano catalysis (Polshettiwar & Varma, 2010; Varma, 1999). Procopio et al. (2010) have a high degree of coverage, addressing the issues of the microwave, organocatalysis, and solvent-free reactions.

The intellectual base of specialty #2 addresses three main themes: solvent-free organic reactions (Tanaka & Toda, 2000; Varma, 1999), use of catalysts (Miyaura & Suzuki, 1995; Sheldon et al., 2007), and use of microwaves in organic syntheses (Kappe, 2004; Varma, 1999). It is worth noting that Varma (1999) was part of a first research front in 1999, and later became an intellectual basis for later fronts.

3.6. Cluster #9 — Solid Acid Catalysis

Papers in #9 deal with synthesis, characterization, and evaluation of solid-state acid catalysts produced from carbon to hydrolyze organic macromolecules such as cellulose (Hara, 2010; Hu et al., 2010; Suganuma et al., 2010; Xiao et al., 2010). The subject of this specialty seems close to the great specialty C – Biomass (same substrate), showing the complexity of activities involved in GC. Papers by Suganuma et al. (2010) and Xiao et al. (2010) stand out from this research front for their coverage (higher than 0.5). Papers by Hara (2010) e Peng et al. (2010) receive many citations.

The intellectual base of #9 has four articles prominent because of their frequency (Anastas & Eghbali, 2010; Anastas & Kirchhoff, 2002; Clark, 2002; Poliakoff et al., 2002), three of them are known references of GC, presenting general themes (Anastas & Eghbali, 2010; Anastas & Kirchhoff, 2002; Poliakoff et al., 2002). The fourth text is a defence of acid soils as catalysts to improve the “greenness” of chemical processes (Clark, 2002).
3.7. Cluster #1 – Green Chemistry Characterization

In the research front, papers by Clark (1999), and Anastas & Eghbali (2010) have the highest coverage. Highly cited papers are written by Poliakoff et al. (2002), and Varma (1999). Excepting Varma (1999), who deals with solvent-free reactions, all other highly cited texts deal with general aspects of GC.

The intellectual base of the specialty #1 is strongly influenced by the seminal book by Anastas & Warner (1998), about the relation between Chemistry and environment, which tackles issues such as regulation policies for chemical activity, and culminates in the creation of GC. Other important papers that make up the intellectual base are an article by Trost (1991) (on atom economy as the search for efficiency in chemical synthesis, suggesting the use of transition metals as catalysts), a state of the art by Sheldon (2005) (on green and sustainable solvent alternatives for organic synthesis), and a review on the impact of the E-factor, a mass efficiency metric, on waste minimization and sustainability reach in the chemical and pharmaceutical industry (Sheldon, 2007).

3.8. Cluster #7 – CO2 as Substrate

In GC reviews, carbon dioxide is described among the renewable approaches, as it is fixed from the atmosphere by the growth of biomass (Anastas et al., 2018; Ivanković, 2017). It is also presented as a safer alternative during some reactions involving organic carbonates (Anastas et al., 2018; Ivanković, 2017); that is the case of this specialty.

The research front of cluster #7 has papers dealing with reactions in continuous flow processes (King et al., 1999; Webb et al., 2005), syntheses in the biphasic system (Hou et al. 2002; King et al. 1999), and synthesis of dimethyl carbonate using CO2 (Dhakshinamoorthy et al., 2010; Juárez et al., 2010; North et al., 2010; Yan et al., 2010). North, Pasquale & Young (2010) have the top number of citations.

The main articles in the intellectual base address the issue of the reactivity of CO2 and its derivatives, such as three reviews on the reactivity of carbonates (Sakakura et al., 2007; Shaikh & Sivaram, 1996; Tundo & Selva, 2002), and a book on supercritical fluids as a reactive medium (Jessop & Leitner, 2007).

4. DISCUSSION

Figure 2 shows the entire co-citation network in a partitioned way, in which the nodes belonging to the same cluster were collapsed into a single vertex. The radius of the nodes indicates the size of the research front and, consequently, the size of the specialty. The width of the lines is proportional to the number of papers co-cited between two nodes.
Specialty #1 – Green Chemistry Characterization is the largest cluster, followed by big specialties C (46 papers), A (43), and D (42). Big specialty #7 – CO2 as Substrate is the smallest, with only 18 members in the research front.

Figure 2 shows that specialty #1 occupies a central place in the network, establishing links with almost all other big specialties. This demonstrates its role in supporting the other specialties, and especially in defining what GC is. Woodhouse & Breyman (2005) compare GC to a social movement and the search for identity is a crucial moment for the collective, which seems to be the main topic in #1. The themes present in this specialty reflect the main ideas of the other specialties found in this analysis, such as the use of supercritical CO2 as solvent (Barwinski et al., 2017), solvent-free processes (Varma, 1999), use of eutectic solvents (Subramaniam 2010), ionic liquids (Stark et al., 2010), biomass (Collinson & Thielemans, 2010; Hernáiz et al., 2010), and the need to address metrics (Marion et al., 2017; Sheldon, 2017; Tobiszewski et al., 2017) in chemical processes. The fact that this specialty presents the same themes in other clusters corroborates the network analysis as a whole and reinforces the coherence of the GC overview presented here.
Big specialty B is a very cohesive aggregate, as its clusters are very close. The links that they establish with specialty #1 indicate some degree of approximation between their practices. The specialties composing big specialty A are scattered through the network and are not directly linked to one another, showing that they do not share the same intellectual foundations, and possibly the same methodologies, although their themes seem very similar. They surround #1, establishing links between the core of GC and other specialties, especially B and D.

Specialty #7– CO2 as Substrate is more distant from the other clusters, showing links to #5 – Supercritical Solvents (of which CO2 is a possibility), #1 – GC Characterization and #2 – Metal Catalysis and Microwave Activation. Although it seems that the use of carbon dioxide as a substrate is related to the subject of biomass, this specialty does not present links with great specialty C, suggesting a more focused perspective on the mechanisms and control of the transformations involving organic epoxides and carbonates.

Big specialty C also has defined behavior, showing the highest degree of separation from the other components of the network, and a close link between #11 – Lignin Valorisation, and #3 – Biomass Transformation. Its approximation with the other big specialties is given by interactions with #0 – Ionic Liquids, #9 – Solid Acid Catalysis, and #4 – Organic Reactions in Aqueous Medium. This demonstrates the specificity of this specialty (by its distance) and its complexity, in its connection to very different specialties.

Overall, the structure of the network corroborated some of our classifications into big specialties. Nevertheless, two big specialties just have a thematic closeness (A and D), since their clusters are scattered across the whole network. However, this shows how solvents and catalysis are complex and broad themes, with very different approaches.

4.1. Extension and immediacy of specialties

The CPT value varies from 0.0338 to 0.833, with 9 clusters below 0.1 and 7 above it (Table 2). The factors that contributed to the lower CPT values (<0.1) were either a large time span of the research front or many core papers in the intellectual base. In the first case, we can mention the clusters #7– CO2 as Substrate, #2 – Metal Catalysis and Microwave Activation, #4 – Organic Reactions in Aqueous Media and #1 – GC Characterization in which the low CPT value reflects the large time span of their research fronts (>16 years) (Table 2). This may indicate that these are more consolidated specialties or more persistent research trends within the field. Another factor that affects this group is the proportion between the size of the research front (C) and the size of the intellectual base (P), indicating a low concentration of citation in a specific theme and a more general character to the specialties.

The second group of specialties with low CPT has a research front concentrated in a shorter time, but with a very large intellectual base, as in the case of #0 – Ionic Liquids, #8 – Ionic Liquids Toxicity, #6 – Recycling and Recovery of Solvents, #10 – Catalytic Oxidation of Alcohols, and #5 – Supercritical Solvents. This suggests that they had a concentrated interest either in a period or in a more restricted community of researchers with many shared references. It is interesting to note that 3 of these specialties are related to ionic liquids, which may indicate the restriction of those themes to certain research groups or specific periods.

Among the highest CPT values (> 0.1), most clusters have a research front concentrated in 1 year (#16 - Glycochemistry, #18 – Solid-State Organic Reactions, #12 – Ionic Liquids Preparation, #11 – Lignin Valorization and # 9 – Solid Acid Catalysis), representing a more momentary or recent interest. The main factor for the increase in CPT in this low T group
is the ratio between research front and intellectual base, indicating that there are many researchers interested in specific literature, specific to a theme; this is the case for clusters #11 and #9. Cluster #17 – Deep Eutectic Solvents draws attention because it has a large research front and a small intellectual base. Cluster #3 has the largest intellectual base among the highest CPT values and 5 years, indicating that it is a strong and growing trend within GC.

4.2. Emerging trends in Green Chemistry

Twenty-one works were selected by being published between 2012-2017 and with citation burstiness that lasted until 2017 (Table 3). Cluster #3 – Biomass Transformation has the highest accumulated value of citation burstiness, showing the continued interest of the scientific community in this research topic. Cluster #3 also presents the largest number of papers with high citation burstiness, 9 in total, followed by clusters #1 – GC Characterization and #17 – Deep Eutectic Solvents with 3 papers each. This corroborates the idea that these specialties have continued to arouse the strong interest of the scientific community in recent years. Clusters #3, #11, and #17 – also have high CPT values, as discussed in 4.1, corroborating the importance and the emergence of these specialties. In 2018, the Chinese Academy of Sciences and Clarivate Analytics (2018) reported “Deep eutectic solvents and their applications”, same topic of cluster #17, as one of the key hot research fronts in Chemistry.

| Reference | Cluster | Citation Burstiness |
|-----------|---------|---------------------|
|           |         | Strength | Begin  | End    |
| (Prier, Rankic, and MacMillan 2013) | *       | 243,008   | 2014   | 2017   |
| (James et al. 2011)          | *       | 200,721   | 2014   | 2017   |
| (Sheldon 2012)               | 1       | 395,044   | 2013   | 2017   |
| (Dunn 2012)                  | 1       | 220,229   | 2014   | 2017   |
| (Gu and Jérôme 2013)         | 1       | 194,221   | 2014   | 2017   |
| (Ragauskas et al. 2014)      | 11      | 298,271   | 2015   | 2017   |
| (Zhang et al. 2012)          | 17      | 282,104   | 2014   | 2017   |
| (Smith et al. 2014)          | 17      | 233,865   | 2015   | 2017   |
| (Francisco, van den Bruinhorst, and Kroon 2013)| 17 | 166,201 | 2014 | 2017 |
| (Gawande et al. 2013)        | 2       | 174,746   | 2014   | 2017   |
| (Gallezot 2012)              | 3       | 376,834   | 2014   | 2017   |
| (van Putten et al. 2013)     | 3       | 334,326   | 2014   | 2017   |
| (Besson, Gallezot, and Pinel 2014) | 3 | 244,662 | 2015 | 2017 |
| (Clark et al. 2014)          | 3       | 225,345   | 2015   | 2017   |
| (Alonso, Wettstein, and Dumesic 2013) | 3 | 208,951 | 2014 | 2017 |
| Reference              | Cluster | Citation Burtness | Cluster | Citation Burtness |
|------------------------|---------|-------------------|---------|-------------------|
| (Climent et al. 2014)  | 3       | 181,227           | 2014    | 2017              |
| (Lange et al. 2012)    | 3       | 181,227           | 2014    | 2017              |
| (Brandt et al. 2013)   | 3       | 161,928           | 2014    | 2017              |
| (Tuck et al. 2012)     | 3       | 17,798            | 2014    | 2017              |
| (Simon and Li 2012)    | 4       | 266,078           | 2015    | 2017              |
| (Gawande et al. 2013)  | 4       | 213,725           | 2014    | 2017              |

**Table 3.** Papers published in 2012-2017 with high citation burstiness up to 2017.

Besides, two papers emerged with a high citation burstiness value without belonging to a specific cluster. Although these researches have attracted attention, there still seems to be no large research community that shares the same literature on the topic, i.e. there is still no research front. These papers may indicate very recent and innovative research topics in GC with the possibility of developing into specialties in the coming years. One of the papers presents a critical review of the mechanochemical synthesis, pointing out its advantages for the reduction or elimination of solvent and its more sustainable character (James et al., 2011). The second paper deals with the use of visible light to catalyze organic syntheses (Prier et al., 2013).

Papers with the biggest citation burstiness in #3 – Biomass Transformation highlight the more industrial side of biomass chemistry (Besson et al., 2014; Gallezot, 2012; van Putten et al., 2013), especially in the work of Huber et al. (2006). Papers in cluster #1 – GC Characterization focus on the efficiency of the synthesis processes (Sheldon 2012) and environmental metrics and criteria for solvent choice (Dunn, 2012). Regarding cluster #17 – Deep Eutectic Solvents, papers deal with syntheses, properties and applications of deep eutectic solvents (Francisco et al., 2013; Smith et al., 2014; Zhang et al., 2012), particularly as an alternative to ionic liquids (Francisco et al., 2013).

### 4.3. Validation of Results

The network generated presented good internal coherence, indicated by the Modularity Q value of 0.8718 and cluster silhouette above 0.7. Editorials or reviews on the field, functioning as specialists’ testimonials, were used as the basis for expert validation. Thirteen editorials were chosen from the themed collection celebrating the 25th anniversary of GC (HSA) (Anastas et al., 2016; Delidovich & Palkovits, 2016; Jackson et al., 2016; Jessop, 2016; Li, 2016; Llevot & Meier, 2016; MacFarlane et al., 2016; Peters & von der Assen, 2016; Quadrelli, 2016; Scott & Lee, 2016; Sheldon, 2016; Sneddon, 2016; Wakaki et al., 2016), and one editorial celebrating the 20th anniversary of the publication of the GC principles (GCP) (Anastas et al., 2018). About 10% of the texts in the intellectual base of the network are referenced in the HSA editorials and 11% in the GCP editorial (Table 4).

Several editorials highlight substitution for greener solvents in chemical processes (Anastas et al., 2018; Jessop, 2016; Li, 2016; Sneddon, 2016), such as water, ionic liquids, supercritical fluids, or no solvents at all. Solventless syntheses (Jessop, 2016; Li, 2016; Sneddon, 2016) address the challenge of activating substances by microwave irradiation, photochemistry, or mechanochemistry, for example. Those strategies are in their infancy and much has to be
developed (Anastas et al., 2018). Those are the same topics addressed in A – Solvents, B – Ionic Liquids, and #2 – Metal Catalysis and Microwave Activation. Eutectic or neoteric solvents (as in cluster #17 – Deep Eutectic Solvents) in general are not explicitly discussed in any editorial. This corroborates the idea of an emerging field in GC.

Regarding big specialty D – Catalysis, metal catalysts are an important tool in GC (Delidovich & Palkovits, 2016; Li, 2016; Sheldon, 2016; Sneddon, 2016; Wakaki et al., 2016) and their recovery and reuse is a pursued aim (Anastas et al., 2018). Solid acids and bases are described by their abundance (Anastas et al., 2018), the possibility of recovery, and the low generation of residues as it prevents the formation of salts (Delidovich & Palkovits, 2016). Wakaki et al. (2016) use oxidation of alcohols as a practical example to discuss less hazardous chemical synthesis.

| Big specialty | Specialty                               | REF in HSA | REF in GCP | Size IB |
|---------------|-----------------------------------------|------------|------------|---------|
| A – Solvents  | #4 – Organic Reaction in Aqueous Media  | 4          | 2          | 31      |
|               | #5 – Supercritical Solvents             | 2          | 0          | 30      |
|               | #17 – Deep Eutectic Solvents            | 0          | 0          | 6       |
|               | #18 – Solid-State Organic Reaction      | 0          | 0          | 5       |
| B – Ionic Liquids | #0 – Ionic Liquids                  | 0          | 3          | 55      |
|               | #6 – Recycling and Recovery of Solvents | 0          | 0          | 29      |
|               | #8 – IL Toxicity                        | 0          | 0          | 19      |
|               | #12 – IL Preparation                    | 0          | 0          | 9       |
| C – Biomass   | #3 – Biomass Transformation             | 4          | 4          | 33      |
|               | #11 – Lignin Valorisation               | 0          | 0          | 10      |
|               | #16 - Glycochemistry                    | 0          | 0          | 9       |
| D – Catalysis | #2 – Metal Catalysis and Microwave Activation | 2          | 4          | 38      |
|               | #9 – Solid Acid Catalysis               | 2          | 4          | 12      |
|               | #10 – Catalytic Oxidation of Alcohols   | 2          | 0          | 11      |
|               | #1 – GC Characterization                | 15         | 22         | 45      |
|               | #7 – CO₂ as Substrate                   | 4          | 4          | 28      |
| **Total**     |                                         | **35**     | **42**     | **368** |

Table 4. The number of texts in the intellectual base (IB) referenced in the editorial from the collections “Happy Silver Anniversary” of GC (HSA) and 20th anniversary of GC principles (GCP).

Several editorials address the possibilities of biomass-derived products (as in big specialty C – Biomass) as renewable alternatives as substrate and solvents (Delidovich & Palkovits, 2016; Li, 2016; Llevot & Meier, 2016; Quadrelli, 2016; Sheldon, 2016; Wakaki et al., 2016), especially processes using second-generation biomass, such as lignin (Anastas et al., 2018; Li, 2016). The use of carbon dioxide as a building block for the generation of organic compounds is approached in four editorial (Anastas et al., 2018; Delidovich & Palkovits, 2016;
Llevot & Meier, 2016; Wakaki et al., 2016), the same topic as cluster #7 – CO2 as Substrate.

One of the hot topics in #1 – GC Characterization, metrics are discussed in many editorials (Delidovich & Palkovits, 2016; Jackson et al., 2016; Quadrelli, 2016), especially if waste is still a suitable metric (Peters & von der Assen, 2016) and strategies to assess the greenness of practices employing GC principles (Anastas et al., 2018). This analysis corroborates that peer review is complementary to bibliometric investigations (Abramo et al., 2019).

5 CONCLUSIONS

In the 27 years considered in this research, 6 different and interrelated big research fronts were identified in GC: A – Solvents; B – Ionic Liquids; C – Biomass; D – Catalysis; #1 – GC Characterization; and #7 – CO2 as Substrate. Specialty #1 – GC Characterization has the largest research front and gathers papers to delimit GC, tracing its history, and pointing its challenges, functioning as a nucleus for the field. The clusters that made up those big specialties are presented in Table 2.

The CPT values show that some specialties have a more general approach and persistence inside a research theme, as in #7 – CO2 as Substrate, #2 – Metal Catalysis and Microwave Activation, #4 – Organic Reactions in Aqueous Media and #1 – GC Characterization. Specialties #0 – Ionic Liquids, #8 – Ionic Liquids Toxicity, #6 – Recycling and Recovery of Solvents, #10 – Catalytic Oxidation of Alcohols, and #5 – Supercritical Solvents have activity restricted in time and by a smaller group of researchers in the research front. Finally, #16 - Glycochemistry, #18 – Solid-State Organic Reactions, #12 – Ionic Liquids Preparation, #11 – Lignin Valorization, #9 – Solid Acid Catalysis and #3 – Biomass Transformation have a big research front sharing a small set of references in a relatively small time. This means those may be cutting edge trends in GC.

Citation burstiness corroborates cluster #3 – Biomass Transformation as an emerging trend, a specialty that is continuously rising interest, especially on industrial applications of biomass to produce valuable substances. Cluster #1 – GC Characterization has burst citation on environmental and sustainability metrics. Cluster #17 – Deep Eutectic Solvents has shown recent interest in using eutectic solvents as an alternative to ionic liquids. Two other research themes were found outside the clusters, mechanochemistry, and photochemistry, indicating the new potential for GC innovation.

Here it is presented an overview of GC specialties in its 27 years. Although it is not an exhaustive description of the topics studied in GC, the co-citation analysis presented here gives an idea of the foci of interest of the community of green chemists. CiteSpace showed to be a relevant tool to analyze the GC field. However, the lack of author keywords in some journals, such as Green Chemistry, hurdled the retrieval of information. Also, the changing of an algorithm for Keywords Plus in Web of Science makes it difficult to retrieve the same registers nowadays. A thoughtful standardization of databases and indexation is required and worth considering in future research. Comparisons with qualitative descriptions made in the field corroborate the coherence of the results of this research, and eventual discrepancies seem to reflect differences in the approach to information in the field: the analyses made by experts start from the Twelve Principles as prior categories for the organization of the GC, while this research draws specialties from the field’s citation patterns. This overview here also calls for reflection on who the researchers are that furnish the basic knowledge for the rise of a specialty (their intellectual authorities), and who the individuals are that contribute the most to disseminate research on a particular topic, forming research groups around the same goal.
We hope to address these topics in future research.

Notes
This article is an extended version of the paper presented at the EAI DIONE 2020 conference held on 17 April in Florianopolis, Brazil.

Conflicts of interest
The authors declare that there is no conflict of interest.

Contribution statement
Resources, data curation, and formal analysis, writing – review & editing: Leonardo Victor Marcelino, Adilson L. Pinto, and Carlos A. Marques.
Writing – Original draft: Leonardo Victor Marcelino

Statement of data consent
The Input Data.zip and Cluster Analysis.xls generated during the development of this study has been deposited in Open Science Framework (OSF) and it is accessible at https://osf.io/2x93a/?view_only=77b24359252745a8bdd0a702df238e9e.

Funding
This research was supported by Capes/PDSE/Process n. 88881.189651/2018-0 and CNPq 141131/2018-7.

Acknowledgments
We thank Prof. Dr. Chaomei Chen (Drexel University, USA), Prof. Dr. Jesper Sjöström (Malmö University, Sweden), and Prof. Dr. Adélio A. S. C. Machado (University of Porto, Portugal) for their insights and attention to the research.

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