HOLOS
ISSN 1807 - 1600

APPLICATION OF MANGANESE-BASED OXIDES AS OXYGEN CARRIERS IN CHEMICAL LOOPING PROCESSES: A BIBLIOMETRIC ANALYSIS

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Submitted April 18, 2024 - Accepted July 2, 2024

DOI: 10pts.15628/holos.2024.17226

ABSTRACT

This article describes a general study of manganese-based oxygen carriers (OCs) in chemical looping (CL) processes between 2006 and 2023 through a careful bibliometric analysis. This was achieved through the selection of scientific articles and checking bibliometric parameters, highlighting the main challenges and the current state of this area of research. Using keywords, 426 documents were found on the Web of Science database and 65 of them were selected using the ProKnow-C method. Analysis of the main articles indicates that these materials have decreased friction rates and a low tendency to agglomerate in reactors with continuous fluidized beds. Furthermore, this study informs the possible optimization of the physicochemical properties of oxygen carriers, with emphasis on the oxygen transport capacity, reactivity, and friction rate. In addition, this research highlighted the great potential of synthetic manganese-based OCs for applications in CL processes.

KEYWORDS: Oxygen carrier; Manganese; Bibliometric analysis; Chemical Looping; Chemical Looping Combustion

APLICAÇÃO DE ÓXIDOS À BASE DE MANGANÊS COMO TRANSPORTADORES DE OXIGÊNIO EM PROCESSOS DE RECIRCULAÇÃO QUÍMICA: UMA ANÁLISE BIBLIOMÉTRICA

RESUMO

Este artigo descreve um estudo geral dos transportadores de oxigênio (TOs) à base de manganês em processos de recirculação química (RQ) entre 2006 e 2023 através de uma análise bibliométrica cuidadosa. Para tal, foram selecionados artigos científicos e verificados parâmetros bibliométricos, destacando os principais desafios e o estado atual desta área de investigação. Através de palavras-chave, foram encontrados 426 documentos na Web of Science e 65 foram selecionados através do método ProKnow-C. A análise dos principais artigos indica que esses materiais apresentam taxas de atrito reduzidas e baixa tendência à aglomeração em reatores de leito fluidizado contínuos. Além disso, o estudo informa sobre uma possível otimização das propriedades físico-químicas dos transportadores de oxigênio, com destaque para a capacidade de transporte de oxigênio, a reatividade e a taxa de atrito. Além disso, esta pesquisa destacou o grande potencial dos TOs sintéticos à base de manganês para aplicações em processos de RQ.

Palavras chave: Transportador de oxigênio; Manganês; Análise bibliométrica; Recirculação Química; Combustão por Recirculação Química

1 INTRODUCTION

In recent years, concerns about climate change have intensified because of the rapid growth in the excessive use of fossil fuels for industrial, energy, and transportation purposes. This is caused by the anthropogenic emission of greenhouse gases, mainly carbon dioxide, increasing the temperature of planet Earth and causing catastrophic impacts, resulting in more intense droughts, very heavy rainfall, tsunamis, and hurricanes (Nandy *et al.*, 2016; Tutuncu, 2021).

Because it has the highest anthropogenic emissions among greenhouse gases (up to 76%) and remains in the atmosphere of our planet for long periods, carbon dioxide is the greatest cause of climate change (Adánez *et al.*, 2012; Archer, 2005; IPCC, 2014; Nunes, 2023). To reduce these emissions, more strict measures are needed to ensure that the cap on emissions (450 ppm) is not exceeded (Adánez *et al.*, 2012; Nandy *et al.*, 2016). Countries that are part of the United Nations Framework Convention on Climate Change (UNFCCC) signed the Paris Agreement in 2015, to establish various measures to reduce anthropogenic CO_2 emissions (MSTI, 2015).

One of the answers is investing in and adopting renewable energies (solar, wind, hydro, nuclear, biofuels, among others), however, their large-scale application presents a very high cost, making them difficult to implement with energy security. Thus, fossil fuels remain the most widely used ince they are less expensive, requiring the application of new technologies to capture and store carbon (CCS technology) in energy and H2 production processes.

Conventional CCS technologies fall into three categories: precombustion, postcombustion, and oxy-fuel combustion. However, they have high economic costs and suffer energy penalties because of the processes used to separate carbon dioxide from other combustion gases (IPCC, 2005; Li *et al.*, 2017). To solve these problems, chemical looping (CL) technologies have emerged. They use a metal oxide, called an oxygen carrier (OC), to react with the fuel and perform combustion, without the need for contact between the fuel and atmospheric air, minimizing economic costs and energy penalties (Li *et al.*, 2017; Mendiara *et al.*, 2014; Nascimento, 2019).

Chemical Looping technologies have two objectives: combustion and hydrogen production (Li *et al.*, 2017). Chemical looping combustion (CLC), in-situ gasification chemical looping combustion (iG-CLC), and chemical looping with oxygen uncoupling (CLOU) are generally used for combustion (Ksepko & Lysowski, 2021; Li *et al.*, 2017). To produce hydrogen, CLR technology is used, which conducts catalytic reforming to produce a synthesis gas through a partial combustion process; the H2 is separated from the other gases in a WGS+PSA unit (Adánez *et al.*, 2012). Hydrogen can be used for energy generation and as an intermediate aggregate to produce methanol, ammonia, and petrochemical processes (Adánez *et al.*, 2012; Li *et al.*, 2017).

Therefore, for CL systems to work most effectively, it is very important to choose a good oxygen carrier. It can be synthetic, which is a metal oxide usually based on nickel, cobalt, copper, manganese, or iron as the active phase, supported on an inert material such as Al_2O_3, $MgAl_2O_4$, SiO_2, TiO_2, or ZrO_2; or a mineral. Thus, the oxygen carrier must have good reactivity with the fuel, oxygen transport capacity, resistance to friction, mechanical strength, low carbon deposition, a high melting point, low cost, and be environmentally friendly (Adánez *et al.*, 2012; Li *et al.*, 2017; Nandy *et al.*, 2016; Rydén *et al.*, 2010). However, OCs based on nickel, cobalt, and copper have a high economic cost, and the first two can generate toxic compounds, which is the main problem for their large-scale application (Adánez *et al.*, 2012; Costa, 2019; Mineral commodity summaries, 2022; Nascimento, 2019). However, OCs based on manganese and iron are very promising since they are low-cost and nontoxic and present a high melting point, high reactivity with different fuels, and good oxygen transport capacity (Johansson *et al.*, 2006; Li *et al.*, 2017; Matzen *et al.*, 2017; Mei *et al*., 2022).

However, since relatively low operating temperatures (below 800 °C) are required to obtain relevant equilibrium concentrations in the CLOU system, the use of pure manganese oxides as OCs is not promising (Azimi *et al*., 2013; Li *et al.*, 2017). However, this temperature can be increased by combining pure manganese oxide with other materials (e.g., Fe, Ni, Si, Mg, and Ca) to improve its intrinsic characteristics, such as low mechanical strength. Thus, the use of synthetic and mineral OCs is an excellent alternative for replacing pure manganese oxide in chemical recirculation processes, since these compounds have other metals, in addition to manganese, which improves the mechanical resistance, reactivity, and oxygen transport capacity of the material (Adánez-Rubio *et al.*, 2023; Johansson *et al.*, 2006; Ksepko & Lysowski, 2021; Liu *et al.*, 2020; Nascimento *et al.*, 2020; Sarshar *et al.*, 2011; Sun *et al.*, 2017).

In this scenario, bibliometric analysis has emerged as an essential quantitative and statistical tool aimed at analyzing observable parameters of a portfolio of scientific documents in relevant databases. This approach involves a systematic study of the literature and other media related to the research topic (Araújo, 2006; Ksepko & Lysowski, 2021; Nascimento *et al.*, 2022; Pimenta, 2017; Rotili *et al.*, 2022; Silva *et al.*, 2018). According to Pimenta *et al.* (2017), the main objective of these databases is to map and analyze the productivity of authors, institutions, areas of knowledge, and the impact factor (IF) of journals. Thus, based on bibliometric metrics, this study aims to contribute to research on CL processes by identifying trends through the analysis of recent publications, exploring optimized conditions for manufacturing OCs with satisfactory physicochemical properties for application in the CL process, promoting new knowledge and contributing to the technological advancement of this process.

A bibliometric analysis of a bibliographic portfolio of scientific articles from 2006 to 2023 related to the application of manganese-based OCs in CL processes will be conducted, through the careful selection of scientific articles and the evaluation of several parameters, including authorship, areas of study, temporal distribution of publications, sources of publication, institutional affiliations, countries of origin, types of publication, number of citations, and co-occurrences of keywords, highlighting the main challenges that will be faced in this area of study. It is worth noting that this article is part of A. B. SILVA master's thesis (Silva, 2024).

2 METHODOLOGICAL PROCEDURES

To select the portfolio, the ProKnow-C (knowledge development process – constructivist) method described by Lacerda, Ensslin, and Ensslin was chosen (Lacerda *et al.*, 2012). Initially, the keywords oxygen carrier, manganese, Mn, chemical looping combustion, and CLC were chosen for the research in the Web of Science and Scopus databases. The searches were performed using the following algorithms: ((Oxygen Carrier$) AND (Manganese OR Mn)) AND (Chemical Looping Combustion OR CLC). The search in the Web of Science database resulted in 426 documents, while in Scopus there were 266 documents. Therefore, the first one was chosen for the bibliometric analysis since it presented more results.

The documents generated by the Web of Science database were imported into an Excel spreadsheet and the titles were read to determine whether they were aligned with the research topic "manganese-based oxygen carriers for application in chemical looping processes". The chosen documents were sorted in descending order by the number of citations (NC), and then the percentage of citations (%CR) and the percentage of accumulated citations (%CRA) were calculated. Next, the most recognized documents were selected using the Pareto rule (%CRA ≤ 80%). Unrecognized documents published after 2021 were selected and classified as recent. The unrecognized and nonrecent ones went through a recap called the Bank of Recognized Authors; if any of the authors who recognized documents were present as coauthors, the document was also selected.

Subsequently, the abstracts of the selected documents were checked to see if they were aligned with the research theme. If so, their integral reading was performed to verify whether they contained data regarding the elemental composition of the oxygen transporters, active phases, mechanical strength, friction rate, porosity, temperature of the thermobalance or reactor, reactivity, oxygen transport capacity, and rate index. The documents that contained most of this data were selected to be part of the portfolio, and the remaining ones were excluded.

Soon after, bibliometric analyses were performed using the Web of Science database, the VOSviewer application, and the Excel spreadsheet. Thus, tables, graphs, and bibliometric maps (with keywords) were constructed. In the records obtained, the variable quantities were collected by author, field of study, year of publication, journal by year of publication, affiliation (institutions), country, and type. Figure 1 briefly describes the methodological procedures.

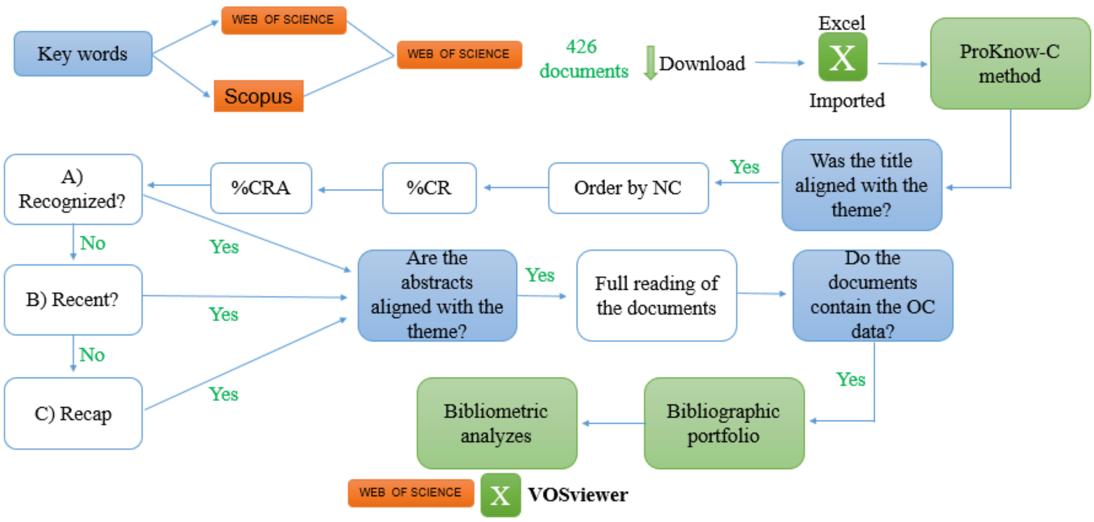

Fig. 1 Methodological procedures

3 RESULTS AND DISCUSSION

In the Web of Science database, 426 documents were identified, and the selection of documents by the ProKnow-C method is shown in Table 1. Thus, 65 documents were selected and the 12 coauthors with the largest number of documents are described in Figure 2. Alberto Abad has the largest number of documents (27 documents), with Abad *et al.* (2006) being the most relevant one (244 citations). This article tested a manganese-based OC supported on magnesium-stabilized zirconia in a laboratory-sized CLC unit with continuous flow, using methane and synthesis gas as fuels, obtaining 88 - 99% combustion efficiency with methane and 100% with synthesis gas. They also found no agglomeration or deactivation of the OC during the experiment.

Table 1 ProKnow-C Method

Procedure	Number of selected documents
Title aligned with the subject	176
(A) Recognized	74
(B) Recent	17
(C) Recap	50
A + B + C	141
Abstract aligned with the subject	123
Document aligned with the data referring to the characteristics of oxygen transporters	65
Bibliographic Portfolio	65

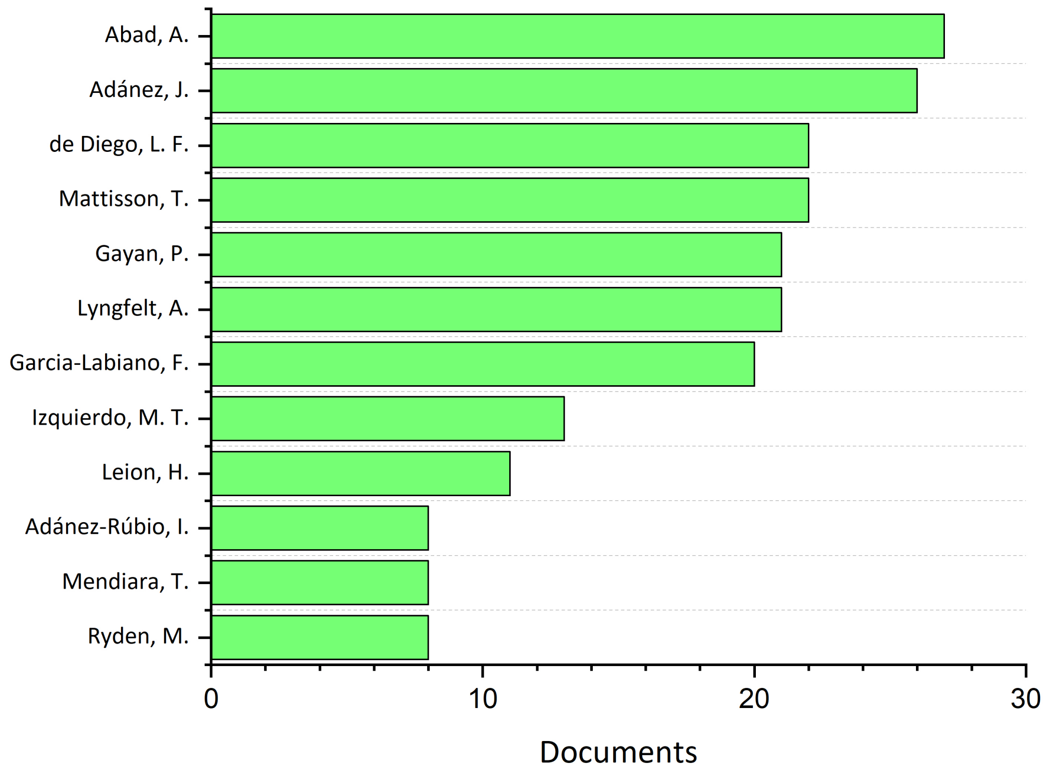

Fig. 2 Coauthored documents
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

Juan Adánez, with 26 documents, and Luis Francisco de Diego, with 22 documents, are coauthors of Abad *et al.* (2015), which is the most relevant document of both authors (56 citations). This paper established the kinetics of the chemical reactions during the redox cycles in the CLC and CLOU processes of a perovskite-type oxygen carrier with the formula $CaMg_{0.1}Ti_{0.125}Mn_{0.775}O_{2.9-\delta}$, and determined the reactivity and oxygen transport capacity of the material during reduction with

CH_4, CO, H_2, and N_2. Juan Adánez, Luis Francisco de Diego, and colleagues observed that the reactivity of the material increased with each redox cycle, while the total oxygen transport capacity decreased from 8.5 to 8.0% by weight.

Figure 3 describes the percentage of documents by field of study. Sixty documents were from the Engineering field (43.8%), 52 from Energy Fuels (38%), 13 from Chemistry (9.5%), 7 from Science & Technology – Other Topics (5.1%), 2 from Thermodynamics (1.5%), and 3 from Other Fields (2.2%). Engineering comprised the development of OCs and reactors for CL processes; in Energy Fuels, the articles were more focused on the application of fuels (methane, hydrogen, synthesis gas, coal, biomass, among others) in CL processes; in Chemistry, articles focused more on the chemical reactions between OCs and fuel and between OCs and air; in Science & Technology – Other Topics, there are more articles related to creating new OCs, testing prototype reactors for CL processes, and reactor operation. In addition, the influence of heat treatment on the reactivity and structural composition of OCs has been evaluated.

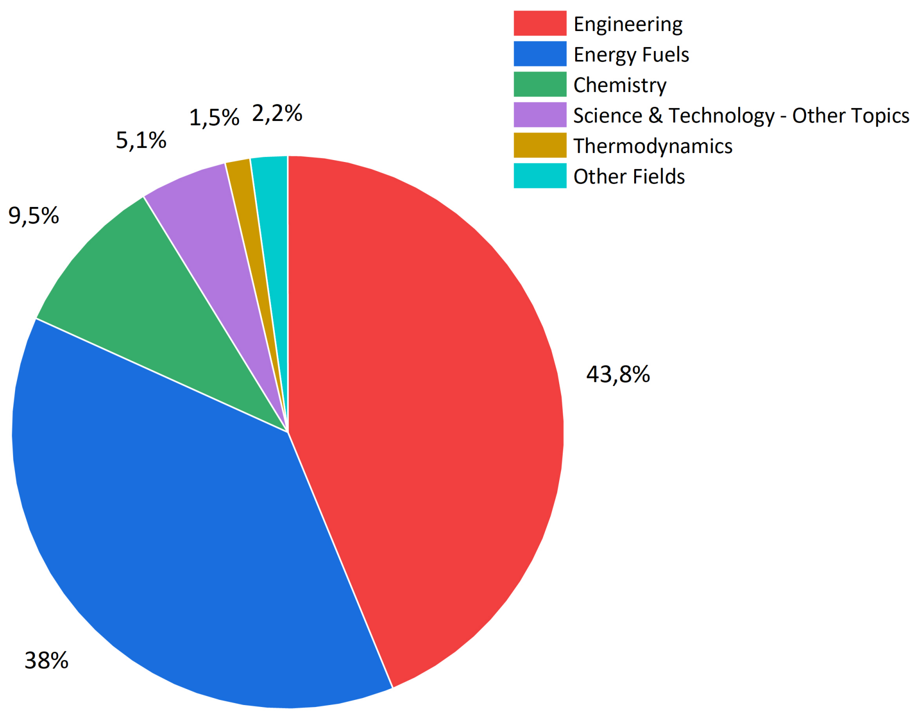

Fig. 3 Documents by field of study
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

The 65 documents in the portfolio were published between 2006 and 2023. An analysis reveals that the largest number of publications occurred between 2014 and 2022 (Figure 4), with 2017 and 2018 being the most prolific years, with 8 and 10 documents, respectively. The most relevant document in 2017 (43 citations) was Sun *et al.* (2017). In it, thermogravimetric analysis was conducted to determine the reactivity and redox performance of OCs from ilmenite ore with the addition of cerium, zirconium, nickel, and manganese oxides against methane gas. The addition

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of manganese oxide to the ilmenite ore had a positive effect on the OC, increasing the oxygen transport capacity, resistance to agglomeration, and reactivity during methane combustion, due to the formation of ferrimanganese oxides.

The most relevant document in 2018 (52 citations) was Adánez-Rúbio *et al.* (2018). This article evaluated the combustion of different biomasses in a 1.5 kW_{th} continuous CLC unit using Cu-Mn oxide and found that this oxygen carrier has CLOU properties, high CO_2 capture, and 100% combustion efficiency. In 2019, there was a very significant decline in the number of publications, which included, within the limitations of the research, four documents. However, in the last two years, the number of publications has increased to eight (five in 2022 and three in 2023). Of these, six articles (Abad et al., 2022; Adánez-Rubio et al., 2023; Adánez-Rubio et al., 2022; Barua et al., 2022; Liang et al., 2023; Ma et al., 2022) focused on synthetic OCs (75%) and two of them (Liu et al., 2023; Zornoza et al., 2022) on minerals (25%). Thus, there has been a tendency to focus the research on synthetic OCs optimized for CL since manganese-based synthetic OCs have a lower friction rate and low particle agglomeration. Three of these synthetic OCs tested pure manganese oxide and the other three evaluated OCs supported on Al_2O_3, SiO_2 and MgO, and Fe-Mn.

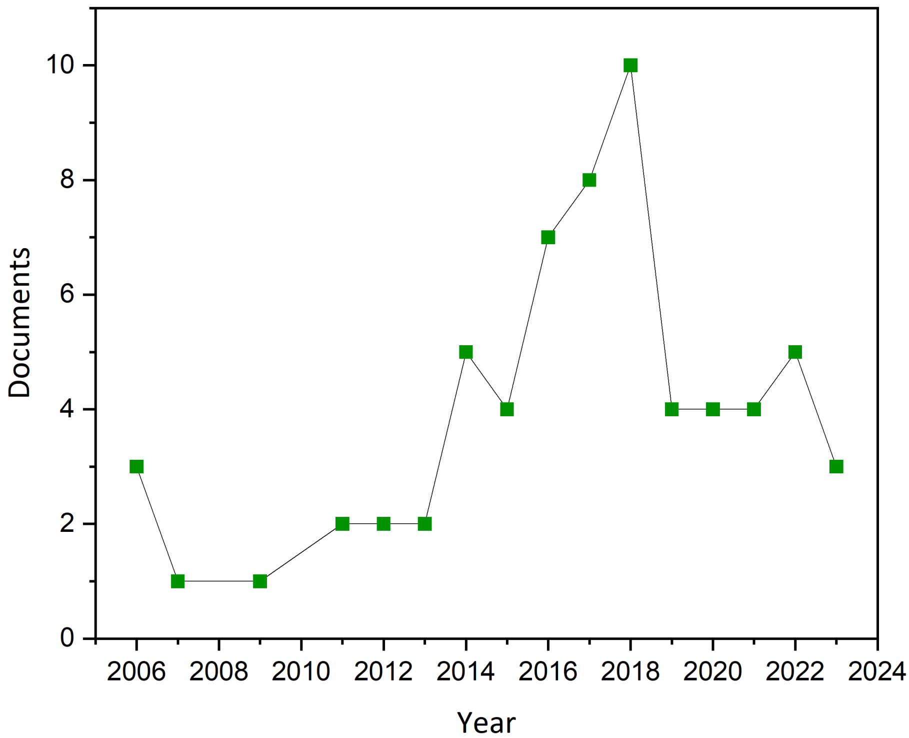

Fig. 4 Documents by Year of Publication
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

Regarding research sources and year, according to Figure 5, seven articles were from Fuel, between 2019 and 2023, which published most of the studies in this portfolio, followed by the Fuel Processing Technology and Industrial & Engineering Chemistry Research, which published five and two articles, respectively. The other research sources published only one (01) article each.

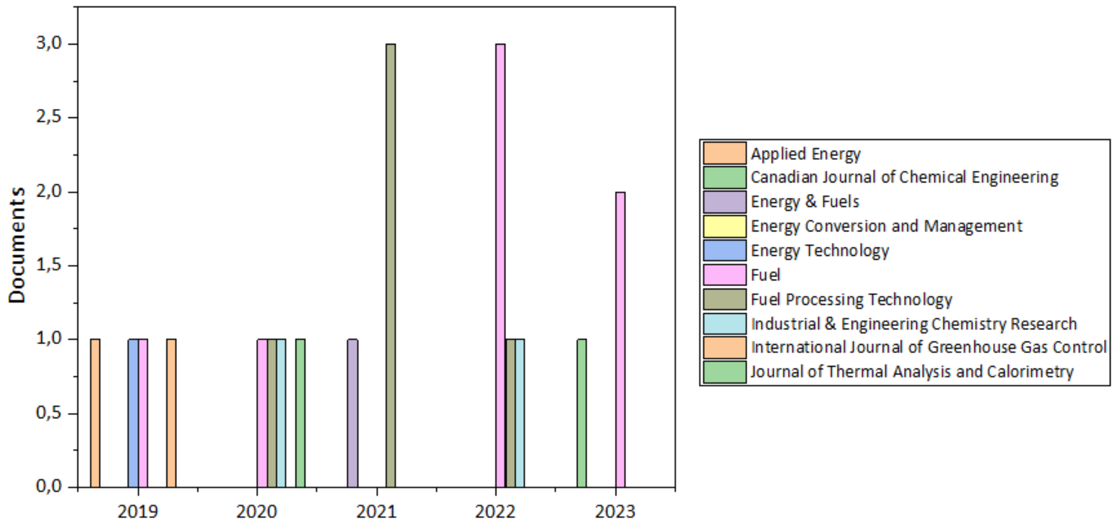

Fig. 5 Documents by Research Journal and Year
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

Regarding affiliation (Figure 6) and country (Figure 7), it was verified that most of the five institutions with the highest number of publications between 2006 and 2023 were from Spain since 25 documents were produced by the Institute of Carbochemistry ICB CSIC. Followed by Sweden, with 24 papers from the Chalmers University of Technology; and China, with nine papers from the Tsinghua University (three documents), the Huazhong University of Science and Technology (two documents) and other universities (four documents). Figure 6 shows three documents from South America, produced by the Federal University of Rio Grande do Norte, in Brazil, and one from the University of Valle, in Colombia, demonstrating a very small number of studies related to manganese-based oxygen carriers for use in chemical looping processes on this continent.

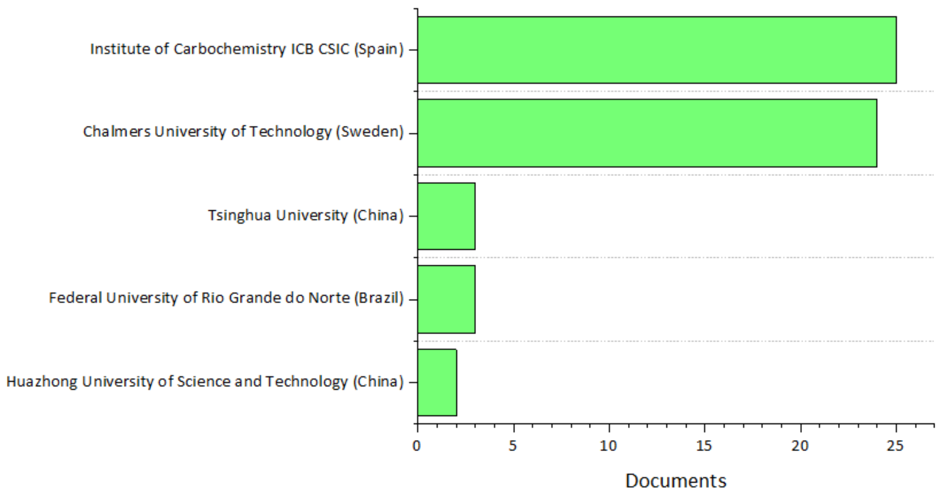

Fig. 6 Documents by Affiliation
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

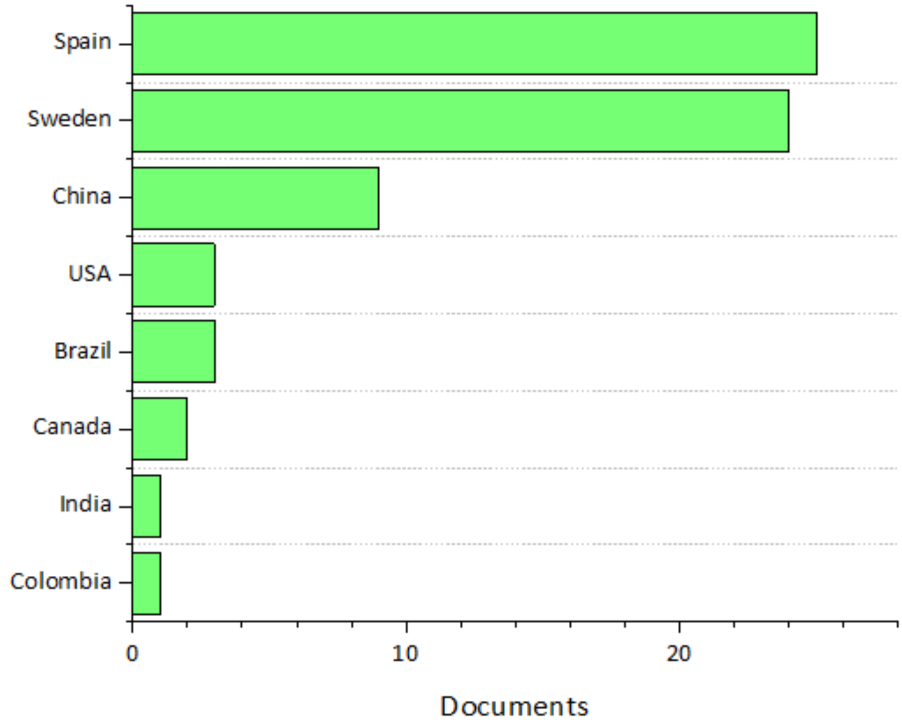

Fig. 7 Documents by Country
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

When analyzing the documents by country, it is possible to conclude that the most relevant one produced in Spain (55 citations), by the ICB CSIC, was that of Abad *et al.* (2015), already discussed here. In Sweden, the most relevant article (244 citations) was that by Abad *et al.* (2006), produced by Chalmers University of Technology, which was also already discussed. In China, with 50 citations, the most relevant article was that by Mei *et al.* (2015), produced by the Huazhong University of Science and Technology, who conducted a study in a fluidized bed reactor of four manganese ores as OCs and found that the MnSA and MnGBHNE materials are promising for combustion with coal since they showed excellent reactivity with H_2 and CO, excellent mechanical strength, and a high friction rate. The most relevant document produced in Brazil (35 citations), by the Federal University of Rio Grande do Norte, is Costa *et al.* (2018), who prepared five oxygen carriers by impregnating Mn_3O_4 or Mg_6MnO_8 on three commercial supports based on zirconia and synthetic calcium aluminate and found that the OC with the ZrO_2 support (Mn-ZrSG) had high reactivity, low friction rate and no agglomeration, making it a possible candidate as oxygen carrier for the iG-CLC process using coal or biomass.

According to Figure 8, the authors with the greatest number of citations are Lyngfelt, A. (1342 citations), Mattisson, T. (1307 citations), and Abad, A. (1015 citations). Table 2 describes the ten (10) most relevant documents in the bibliographic portfolio, and the three (3) most relevant ones with the highest number of citations. According to Table 2 and Figure 9, they are Abad *et al.* (2006), with 244 citations, already discussed above; Linderholm *et al.* (2012), with 156 citations, evaluated ilmenite and manganese ore as possible OCs for application in a continuous flow CLC unit and the manganese ore considerably increased the coal gasification rate and gas conversion;

and Leion *et al.* (2009), with 133 citations, who conducted analyses with a perovskite-type material with the formula $CaMn_{0.875}Ti_{0.125}O_3$ in a thermobalance and fluidized bed using methane and petroleum coke as fuels. They concluded that the material showed promising results in both tests, making it a possible OC candidate for CLOU. Finally, the types of documents in the portfolio were investigated. According to Figure 10, there are 62 articles (93.9%) and 4 conference papers (6.1%).

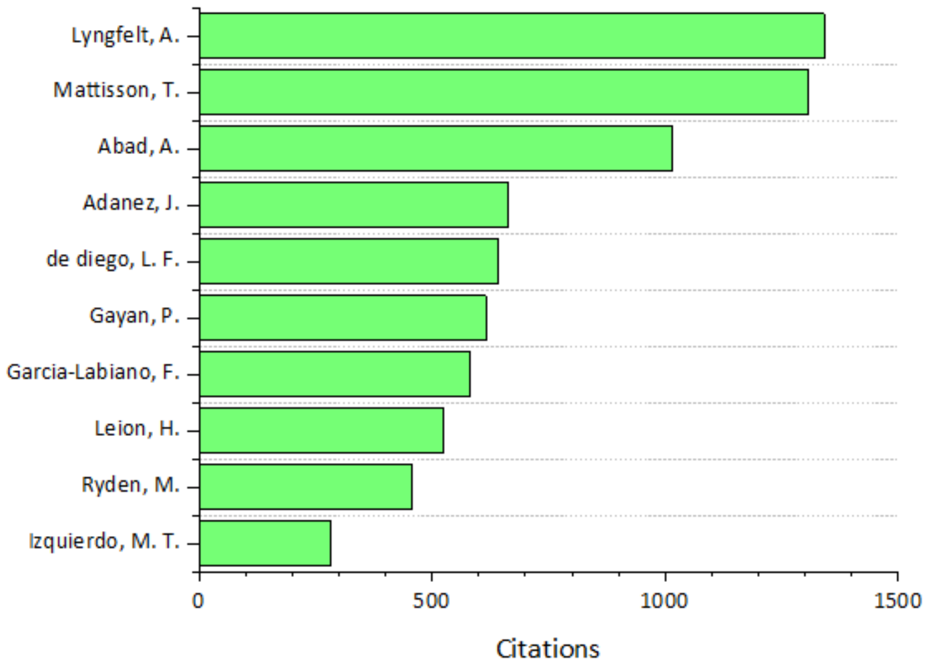

Fig. 8 Number of citations per author
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

Table 2 List of the 10 most relevant documents in the bibliographic portfolio

Rank	Title	Authors	Year	NC	Journal	IF
1	Chemical-looping combustion in a 300 W continuously operating reactor system using a manganese-based oxygen carrier (Abad *et al.*, 2006)	A. Abad; T. Mattisson; A. Lyngfelt; M. Ryden	2006	244	Fuel	7.4
2	Chemical-looping combustion of solid fuels - Operation in a 10 kW unit with two fuels, above-bed and in-bed fuel feed and two oxygen carriers, manganese ore and ilmenite (Linderholm *et al.,* 2012)	C. Linderholm; A. Lyngfelt; A. Cuadrat; E. Jerndal	2012	156	Fuel	7.4
3	Use of CaMn0.875Ti0.125O3 as Oxygen Carrier in Chemical-Looping with Oxygen Uncoupling (Leion *et al.,* 2009)	H. Leion; Y. Larring; E. Bakken; R. Bredesen; T. Mattisson; A. Lyngfelt,	2009	133	Energy & Fuels	5.3
4	Reduction and oxidation kinetics of Mn3O4/Mg-ZrO2 oxygen carrier particles for chemical-looping combustion (Zafar *et al.,* 2007)	Q. Zafar; A. Abad; T. Mattisson; B. Gevert; M. Strand	2007	119	Chem. Eng. Sci.	4.7

5	Investigation of different manganese ores as oxygen carriers in chemical-looping combustion (CLC) for solid fuels (Arjmand *et al.,* 2014)	M. Arjmand; H. Leion; T. Mattisson; A. Lyngfelt	2014	116	Appl. Energy	11.2
6	Investigation of Mn3O4 with stabilized ZrO2 for chemical-looping combustion (Johansson *et al.,* 2006)	M. Johansson; T. Mattisson; A. Lyngfelt	2006	114	Chem. Eng. Res. Des.	3.9
7	Defluidization conditions for a fluidized bed of iron oxide-, nickel oxide-, and manganese oxide-containing oxygen carriers for chemical-looping combustion (Cho *et al.,* 2006)	P. Cho; T. Mattisson; A. Lyngfelt	2006	112	Ind. Eng. Chem. Res.	4.2
8	Chemical - Looping with oxygen uncoupling using Mn/Mg-based oxygen carriers - Oxygen release and reactivity with methane (Shulman *et al.,* 2011)	A. Shulman; E. Cleverstam; T. Mattisson; A. Lyngfel,	2011	98	Fuel	7.4
9	Novel oxygen carriers for chemical looping combustion: La1-xCexBO3 (B = Co, Mn) perovskites synthesized by reactive grinding and nanocasting (Sarshar *et al.,* 2011)	Z. Sarshar; F. Kleitz; S. Kaliaguine	2011	91	Energy Environ. Sci.	32.5
10	Ca(1-x)A(x)MnO(3) (A = Sr and Ba) perovskite based oxygen carriers for chemical looping with oxygen uncoupling (CLOU) (Galinsky *et al.,* 2015)	N. Galinsky; A. Mishra; J. Zhang; F. X . Li	2015	82	Appl. Energy	11.2

*NC: number of citations
IF: impact factor

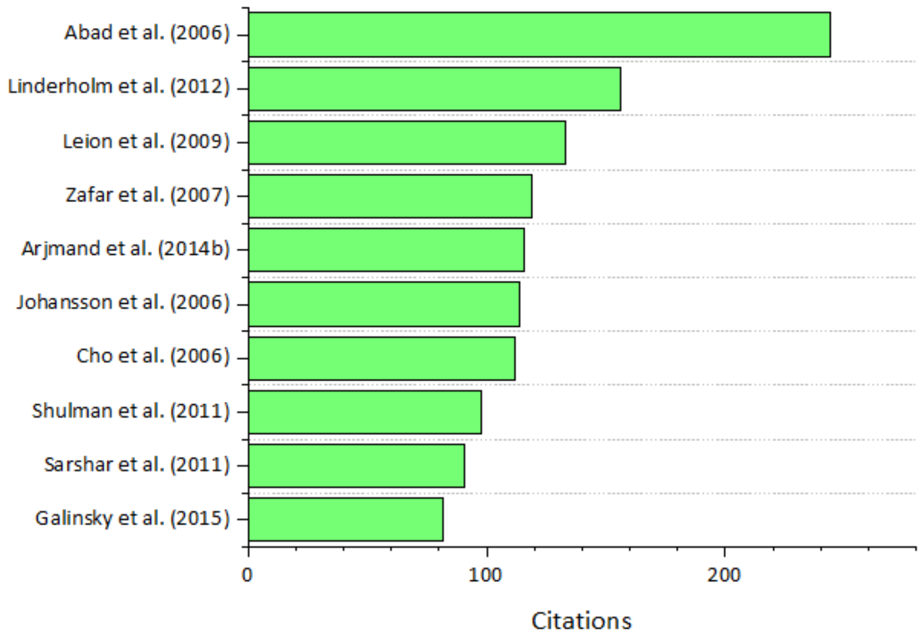

Fig. 9 Number of citations per document
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

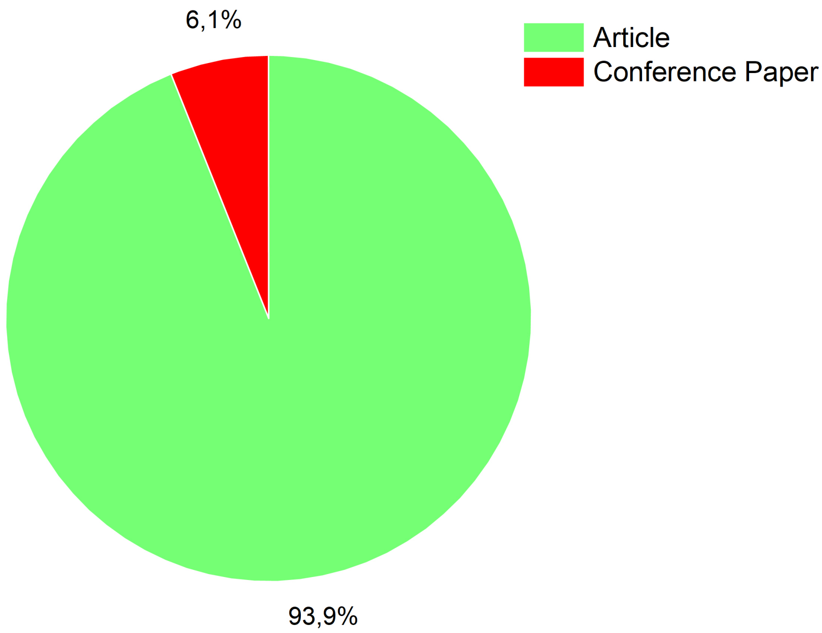

Fig. 10 Documents by Type
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

According to Figure 11, the most frequent keywords in the abstracts and titles of the articles were chemical-looping combustion (45 occurrences), CO_2 capture (28 occurrences), oxygen carrier (26 occurrences), chemical-looping with oxygen uncoupling (25 occurrences), and solid fuels (23 occurrences). The keyword chemical-looping combustion has a strong relationship with the keywords oxygen carrier, manganese ore, solid fuels and biomass, showing that research has focused on testing manganese ores and synthetic oxides as potential OCs using biomass as fuel in recent years, as seen in Condori *et al.* (2021), Adánez-Rubio *et al.* (2023), Adánez-Rubio *et al.* (2022), and Sundqvist *et al.* (2018). Figure 12 illustrates the CLC and CLOU processes using manganese-based OCs, highlighting the types of carriers, carbon dioxide capture, OC reduction, and the use of solid and gaseous fuels.

Despite the increase in research into manganese-based OCs for their use in CL technologies over the last 18 years, finding an OC that can withstand the stress of fluidized beds and has a long service life remains the greatest challenge for this type of material in CLC and CLOU processes, as most manganese-based carriers have a high friction, agglomeration rate, and low mechanical strength. However, several OCs have recently been developed with improvements in these three deficient properties. Adánez-Rubio *et al.* (2021) studied two Cu-Mn mixed oxides with and without the addition of kaolin, and the OC containing it had a higher resistance to friction and the particles did not agglomerate, but the reactivity decreased; Adánez-Rubio *et al.* (2023) obtained two very promising OCs for CLOU, M24Mg76 and M48Mg51, which showed good oxygen transport capacity, excellent reactivity, low friction rate, and good mechanical resistance; Liang *et al.* (2023), who examined the oxygen decoupling capacity for CLOU and the stability in redox cycles of two perovskites based on red mud ($CaMn_{0.5}Fe_{0.5}O_{3-\delta}$ - red mud and $CaMn_{0.75}Fe_{0.25}O_{3-\delta}$ - red mud), concluded that these perovskites showed excellent results in both aspects investigated.

In addition to the search for manganese-based OCs that are optimized for CLC/CLOU, current research seeks to develop synthetic materials with inert supports for the active phases that improve their reactivity and have good mechanical strength and magnetic properties (Abad *et al.,* 2022). Abad *et al.* (2022) synthesized a copper-based OC supported on Mn50fe-1200 (49% Mn and 51% Fe at 1200 °C), which showed high reactivity and good mechanical and magnetic characteristics. Adánez-Rubio *et al.* (2022) obtained a Cu30MnFe-Mag carrier using a Mn-Fe support and found that it was highly reactive to different biomasses and had excellent mechanical and magnetic characteristics. Pérez-Vega *et al.* (2019) determined that a mixed Mn-Fe oxide doped with TiO_2 (Mn66FeTi7) showed excellent reactivity with solid fuel, magnetic properties, mechanical strength, and oxygen decoupling capacity.

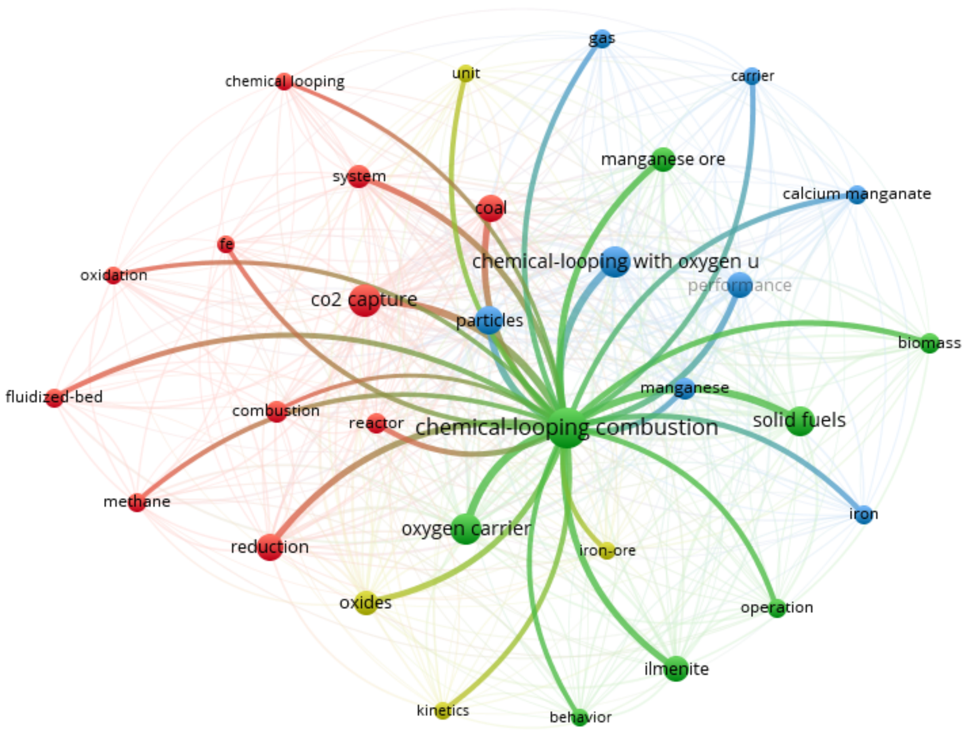

Fig. 11 Bibliometric map (chemical-looping combustion)
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

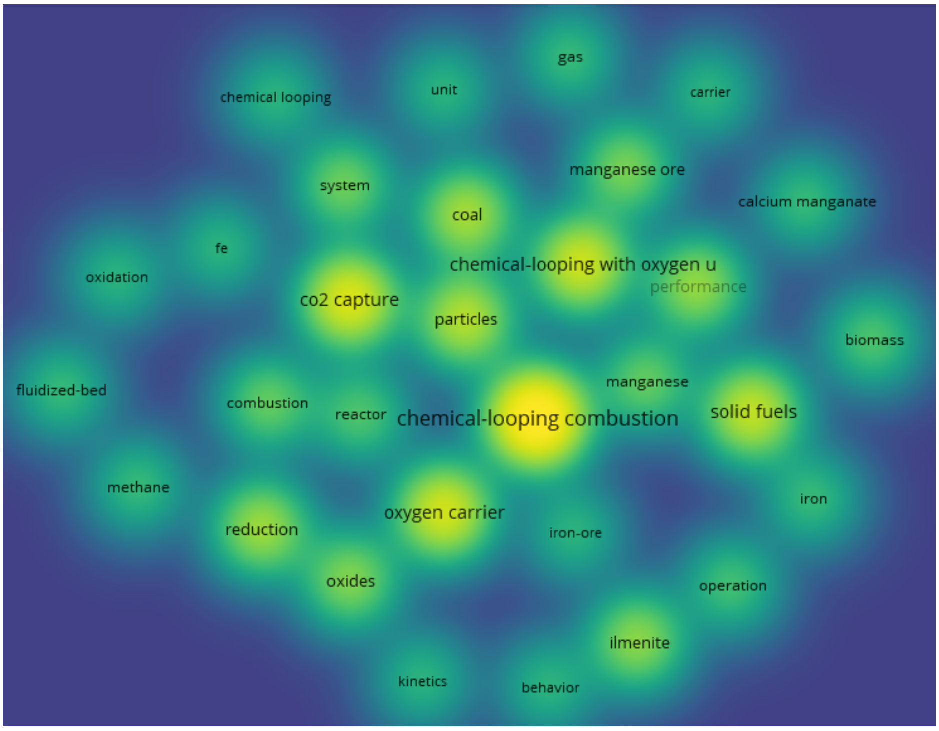

Fig. 12 Bibliometric map (CLC and CLOU processes)
(Source: https://www-webofscience.ez18.periodicos.capes.gov.br)

4 CONCLUSIONS

In summary, the bibliometric analysis revealed a growing trend in interest and research into synthetic manganese-based oxygen carriers. These OCs have shown very promising characteristics, such as a reduced friction rate and a low propensity to agglomerate in continuous fluidized beds. Therefore, this bibliometric study plays a crucial role in the optimization of these carriers, highlighting the main articles published in the last 18 years. This work will also provide a solid basis in the scientific literature to determine the most relevant articles in the field, facilitating the process of optimizing new manganese-based OCs to meet all the physicochemical requirements needed for applications in continuous fluidized beds.

ACKNOWLEDGEMENTS

The authors would like to thank the Prorector of Research at UFRN (PROPESQ) and the Postgraduate Program in Chemistry at UFRN (PPGQ) for their financial support.

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HOW TO CITE THIS ARTICLE:

Silva, A. B., Maria de Araújo Melo, D., Luiz Bezerra de Araújo Medeiros, R., Araújo Barros do Nascimento Santiago, R., & Maciel dos Santos, L. (2024). APPLICATION OF MANGANESE-BASED OXIDES AS OXYGEN CARRIERS IN CHEMICAL LOOPING PROCESSES: A BIBLIOMETRIC ANALYSIS. HOLOS, 2(40). https://doi.org/10.15628/holos.2024.17226.

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Editor: Francinaide de Lima Silva Nascimento
***Ad Hoc* Reviewer:** Helayne Sousa e José Fábio França Orlanda

Submitted April 16, 2024
Accepted July 2, 2024
Published July 17, 2024