

Bibliometric Evaluation of Research in Hydrochar and Bio-oil

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ABSTRACT

Using biomass to produce an alternative and sustainable source of energy is an attractive possibility. Hydrothermal carbonization is a relatively new technique that is growing in popularity due to the fact that its products have use not only as a source of energy but also in the fields of nanotechnology and material science. The purpose of this study is to examine current research trends and characteristics of hydrochar and bio-oil, the solid and liquid products of hydrothermal carbonization, during the periods of 2009-2018 and 2010-2018, respectively. A bibliometric analysis was performed in order to have a better understanding of the current research being done in the fields of hydrochar and bio-oil and their different applications. The implication of this study is to shed light on the potential uses of the by-products (hydrochar and bio-oil) produced by the thermochemical technique, hydrothermal carbonization. Using the Web of Science Core Database, 659 articles discussing hydrochar and 71 articles analyzing bio-oil were examined. Furthermore, scientific research produced by various institutions, journals, authors and countries have been recorded and scrutinized. Gephi was used for network analysis of relative co-authors, co-citations and co-keywords used within the two fields.

Keywords: Hydrochar, Bio-oil, Biomass, Hydrothermal carbonization, Web of Science, Bibliometric.

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INTRODUCTION

Two of the main current global challenges are a growing world population and an increasing demand for energy. The current global energy consumption is 524 exajoules per year and this is expected to increase by 65% by 2040,^[1] There is a need to shift from fossil fuels to a sustainable and alternative source of energy because fossil fuels are non-renewable resources that contribute towards climate change. Thus, the use of biomass from various wastes is being examined as a potential and sustainable alternative source of energy.

Biomass is an organic material that can be separated into two main categories: lignocellulosic biomass such as woody materials and straw and non-lignocellulosic biomass such as sewage sludge and food waste. When biomass waste decays or is composted, carbon dioxide and methane gas emissions are released into the atmosphere. Thus contributing to an increase in greenhouse gas emissions and climate change.^[2] Currently, the abundance of biomass waste that can be turned

into energy and chemical products is being regarded as an important sustainable source of clean and renewable energy. Also, energy generated can be used for heat or electricity and thereby help in decreasing the need for fossil fuels.^[3]

Biomass can be treated thermochemically through pyrolysis and hydrothermal carbonization (HTC). Thermochemical processes when applied to biomass results in solid (biochar in the case of pyrolysis and hydrochar in the case of HTC), liquid (liquor or bio-oil) and gas (little or none in the case of HTC) fractions. Similar to pyrolysis, HTC has been used primarily on lignocellulosic biomass and recently has been applied to non-lignocellulosic biomass and mixtures of different types of biomasses. One of the main differences between the two methods is the moisture content of the feedstock. Pyrolysis treats dry biomass with moisture contents less than thirty percent in an inert or oxygen-free environment at elevated temperatures.^[1] HTC converts wet biomass with moisture contents greater than thirty percent.^[1]

Water acts as both a solvent and a catalyst for HTC.^[4] Since drying of the biomass is not required, this would decrease the overall cost of the process. The raw material is treated at temperatures between 150 and 250°C in a closed container and an increase in pressure occurs autogenously. During this process, five main simultaneous reactions are occurring within the biomass. These are hydrolysis, dehydration,

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decarboxylation, aromatization and re-condensation.^[5] The conditions for HTC and the type of feedstock being thermally treated will result in hydrochar and bio-oils with different characteristics which could lead to various potential applications of these products.

However, it is important to note that HTC does have some challenges associated with it. HTC is susceptible to prolonged residence time and non-selective/superficial heating. HTC utilizes an external source of heat and is thus dependent on heat transfer by either convection or conduction. Consequently, the heating process is difficult for users to control.^[6] By using microwave energy as the source of heat, these challenges can be alleviated. With microwaves, heating is volumetric and occurs within the product, thereby minimizing limitations of heat transfer into the material and decreasing processing time and power consumption associated with the process.

Woody materials,^[7] seafood wastes,^[8] agriculture wastes;^[9,10] and sewage sludge^[11] are just a few examples of the type of biomasses that are currently being used to create hydrochar and bio-oil. Hydrochar and bio-oil can be used as a source of fuel. Moreover, depending on the operating conditions for HTC, the resulting hydrochar can be used as a soil amendment and a low-cost absorbent material for pollutants, toxic metals and biotic contaminants found in soil.^[12] Additionally, the bio-oil can be used as a fertilizer for crops.

A bibliometrics analysis can be described as a statistical analysis of publications.^[13] It provides evidence on the impact of the research, discovers new and emerging areas of research while identifying potential research collaborators and journals.^[14] The field of hydrothermal carbonization and the use of its by-products from various sources of biomass is rapidly growing. Thus, research activities in the aforementioned fields have increased. The main objective of this bibliometric review is to analyze the literature on hydrochar and bio-oil to provide light on the current state of the research. And also, to highlight hidden information such as publication trends, research areas of current interest and to identify scholars, countries and institutions with maximum productivity during the period of 2009-2018 for hydrochar and of 2010-2018 for bio-oil.

DATA SOURCE AND METHODOLOGY

Data Collection

The data for hydrochar and bio-oil were collected from the Web of Science Core Collection database in January 2019 and May 2019 respectively. The Web of Science Core Collection is one of the most dynamic databases that indexes over 20,000 high quality peer reviewed journals in more than 250 categories such as science, social science and humanities. The functionality and sophistication of the Web of Science Core Collection database is superior to other databases such

as Scopus and Google Scholar (Norris and Oppenheim 2007). Hence, making it an easy choice for use in this study. No articles were found in this database on hydrochar and bio-oil before 2009 and 2010, respectively. Therefore, this study examined research publications published solely during the time periods of 2009 to 2018 for hydrochar and 2010-2018 for bio-oil. Information related to publications downloaded from the Web of Science consists of the names of all authors and their affiliations, keywords supplied by the authors, abstracts, cited references and funding information. Among all types of publications such as articles, reviews, proceeding papers, book chapters, editorial materials and discussions, only journal articles were analyzed for this review. The configuration of the assembly for this research and its analysis is shown in Figure 1.

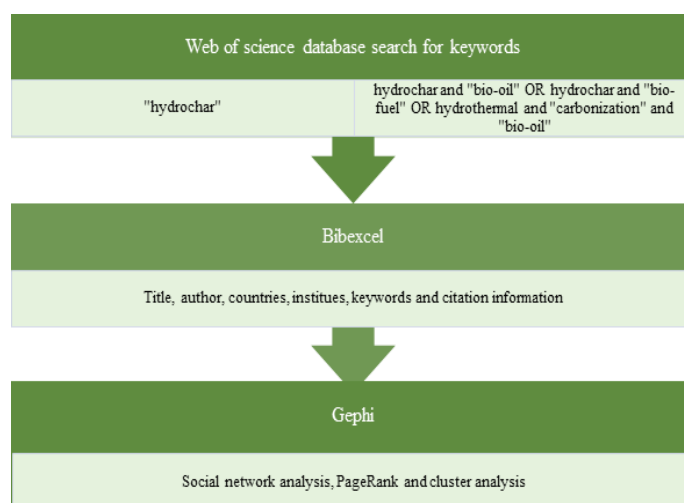


Figure 1: Bibliometric study and analysis flow chart.

In order to complete a thorough qualitative and quantitative review of the publications in the fields of hydrochar and bio-oil produced by HTC, performance and science mapping analyses were employed in the study.

Performance Analysis

A performance analysis consists of production as well as citation indicators. A production indicator informs the reader about the productivity in any research field, providing information such as the number of articles per year or number of articles per author. Moreover, citation indicators inform the readers about the impact of the specific research field, in terms of number of citations and their given h-indexes.^[15]

BibExcel software created by Olle Persson was used for the performance analysis of data downloaded as text files from the Web of Science.^[16] Apart from calculating various production indicators, BibExcel processes files that could be transported into other software like Pajek, EXCEL or Gephi for further mapping analysis.^[16]

BibExcel can process the imported text data to select and examine information related to institutions, author's name, keywords and journals. On-line tutorials by^[16] and by other for processing the data are available can be found on software websites¹.

Science Mapping Analysis

Science mapping helps in the visualization of the structure of the research by demonstrating how they relate to each other through the spatial representation of different fields, discipline or authors.^[17] Collaboration networks display the relationships among various authors, institutions and countries working together. Conceptual networks such as co-word networks reveal hot topics in the field that are currently being scrutinized by various scholars. Publication networks, such as co-citation networks reveal a more in-depth understanding about the hot topics being studied through cluster analysis.

A typical network consists of nodes which visually demonstrates an entity and edges that reveals the relationship between the various nodes. In this study, the network analysis was carried out using Gephi, an open source software. Gephi was developed by students at the University of Compiègne in France^[18] and can handle larger datasets than other software. Thus, Gephi is the preferred software when compared to others, such as Pajek^[19,20] and VosViewer.^[21]

Network files (.net) generated by BibExcel were imported into Gephi for analysis and graphical visualization of the results. Various statistical algorithms can be initiated to calculate different properties of the network such as its degree, PageRank and modularity class. For proper visualization of the network, formatting of the graphs is necessary. Formatting includes changing the degree range to show which nodes are the most important, editing the layout of the network or altering the color of the nodes, adjusting the size of the nodes depending on their degree or PageRank and editing the weight of each edge.

Cluster Analysis

A cluster analysis collects the nodes into groups in which the nodes have denser connections with each other than with nodes in other clusters. To detect a variety of associated groups or communities in the network, the modularity class value was used. The modularity class value is a scalar value and the network with high modularity values shows that the connections between the nodes of same cluster are denser than the connection of nodes between two different clusters.

In this study, the network analysis of various cited references or publications were combined into clusters depending on their modularity class via Gephi. In order to divide the network

analysis into clusters, the modularity class algorithm found in Gephi was used. If two publications are often cited together it is understood that they have a common research interest.^[22] The top five papers according to their PageRank were analyzed in order to find the common research area of that particular cluster. Moreover, partitioning the network analysis into clusters allowed for a clearer visual representation of the network analysis and size of the nodes.

PageRank Analysis

The number of citations often determines the importance of a paper. However, this can sometimes be misleading, as the web page is not always properly ranked. PageRank was developed by Google to ensure proper ranking of a web page.^[23] In a bibliometric analysis, the PageRank helps to determine the ranking of a publication by taking into account the number of times it has been cited by other highly cited articles.^[24]

In this study, PageRank was employed to determine the most important articles in the co-citation network. Under the statistics tab in Gephi, the PageRank algorithm was used to calculate the PageRank of all the nodes or publications in the network. The nodes were then sized according to their PageRank. The publications with the highest PageRank were determined to be the most important article in a particular cluster.

h-Index

The h-index is a critical indicator of the impact of a scientist's publications. It takes into account both the number of publications as well as citations count of a scientist, group of scientists, country or institutions in order to rank them.^[25] It discusses the productivity as well as the quality of the research carried out. An h-index of X means that X scientific articles have been referenced a minimum of X times.^[26] The h-index can be calculated using the data downloaded from the database and BibExcel. The specific steps involved are available on the homepage of the BibExcel software website².

It should be noted that h-index is a dynamic number and thus varies from database to database. This is because the indexing of journals in various databases differs in numbers and only takes into account the number of citations from the journals indexed in their database.

RESULTS AND DISCUSSION

General Statistics

The total number of publications in the field of hydrochar from 2009 to 2018 was recorded to be 659 articles. Original articles excluding conference paper, proceedings, book chapters, editorial material and reviews accounted for 92.4 %

1. <https://homepage.univie.ac.at/juan.gorraiz/bibexcel/>

2. Website is <https://homepage.univie.ac.at/juan.gorraiz/bibexcel/>

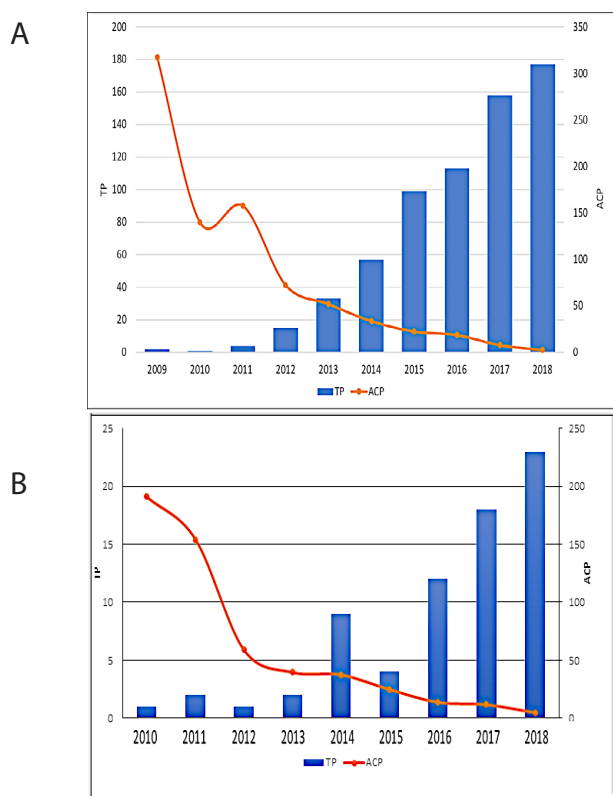


Figure 2: General statistics on the Total Number of publications per year (TP) and Average Citations per year (ACP) for (a) hydrochar and (b) bio-oil.

of the total number of publications. As depicted in Figure 2, the number of publications remained low until 2011 as the field was still developing. Recently, research on hydrochar has become more active since it is currently being considered both an economical and environmentally friendly substitute for fossil fuels. The total number of publications on hydrochar has continuously increased from 2 publications in 2009 to 177 publications in 2018. The highest average citation per year was 180 in 2009 and the lowest average citation per year of 1 occurred in 2018. The average citation per year during 2009 to 2011 has been found to be higher than the average citation per year in the years to follow. This can be attributed to low initial numbers of publications in the field of hydrochar and the time factor where new articles tends to get fewer citations. Figure 2 demonstrates this more clearly.

The first two published articles that appeared online on the Web of Science Core Collection database in the field of hydrochar was in 2009 focused on the production of hydrochar from hydrothermal carbonization using glucose, sucrose and starch.^[27,28] These studies revealed the properties of hydrochar and its potential applications in the field of catalysts, drugs delivery and nanotechnology. And the second study by^[29] focused on the production of hydrochar from corn stover.

The total number of articles published on bio-oil was 94 from 2010 to 2018. Original articles in the field accounted for 75.5%

of the total articles. The total number of publications on bio-oil was low until 2013, after which the number of articles has increased incrementally. The highest average citation per year was recorded to be 18 in the year 2010 and the lowest was found to be 1 in 2018.

Performance of Countries

From 2009 to 2018, 659 publications on hydrochar were published in 56 countries. Additionally, from 2010 to 2018, 71 publications on bio-oil were published in 25 countries. Tables 1a and 1b list the top 10 countries publishing articles along with their h-indexes and their number of citations. China, Germany and the United States of America are currently the top three most productive countries researching the topic of hydrochar. They account for 70 percent of the total number of publications. It is evident from Table 1a that China produces two times more articles than Germany and about 2.3 times more papers than the USA. China, USA and Malaysia are the top three countries producing articles related to bio-oil.

Table 1: (a) Top 10 most productive countries publishing articles in Hydrochar.

| Country | Total articles | Total citations | Institutions | Authors | h-index |
|-------------|----------------|-----------------|--------------|---------|---------|
| China | 215 | 3076 | 275 | 778 | 29 |
| Germany | 116 | 2408 | 157 | 339 | 27 |
| USA | 91 | 2455 | 155 | 303 | 25 |
| Spain | 48 | 1669 | 64 | 136 | 18 |
| Italy | 33 | 561 | 77 | 115 | 14 |
| England | 31 | 562 | 51 | 97 | 13 |
| Canada | 22 | 354 | 38 | 85 | 8 |
| Japan | 20 | 130 | 19 | 52 | 7 |
| France | 19 | 370 | 58 | 78 | 8 |
| South Korea | 19 | 371 | 49 | 74 | 7 |

Table 1: (b) Top 10 most productive countries publishing articles in Bio-oil.

| Country | Total articles | Total citations | Institutions | Authors | h-index |
|-----------|----------------|-----------------|--------------|---------|---------|
| China | 37 | 869 | 43 | 144 | 14 |
| USA | 12 | 521 | 28 | 28 | 7 |
| Malaysia | 3 | 29 | 6 | 14 | 2 |
| Singapore | 3 | 80 | 3 | 6 | 3 |
| Turkey | 3 | 13 | 6 | 11 | 2 |
| Australia | 2 | 1 | 3 | 7 | 1 |
| England | 2 | 15 | 2 | 6 | 2 |
| Japan | 2 | 10 | 5 | 11 | 2 |
| Poland | 2 | 88 | 3 | 7 | 1 |
| Slovenia | 2 | 30 | 1 | 8 | 1 |

China and USA are the most prominent countries working on the production of bio-oil from biomass through pyrolysis or hydrothermal carbonization treatment. These two countries account for 69% of total articles in the field of bio-oil.

Journal Distribution

The top ten journals publishing articles in the field of hydrochar and bio-oil are shown in Tables 2.1 and 2.2 respectively. The top ten journals represent approximately 40 and 63 percent, respectively of the total number of articles published. Tables 2a and 2.b display the number of papers, average number of citations and the h-index of the top ten journals in these two fields. The "Bioresource Technology" journal had the highest numbers of publications on hydrochar, followed by "ACS Sustainable Chemistry and Engineering" and "RSC Advances". The h-index of each of the ten journals

varied greatly between 7 and 25. Articles in "Bioresource Technology" often discussed the production and application of hydrochar in green engineering, energy and environmental concerns. However, articles in "ACS Sustainable Chemistry and Engineering" and "RSC Advances" generally dealt with the physico-chemical characterization of hydrochar, such as adsorption of metals or biotic contaminants from the waste, production of carbon nanodots or nanospheres and applications in the field of chemistry. For bio-oil, the top three journals were "Bioresource Technology", "Fuels" and "Energy Fuels". The h-index for these journals varied between 2 and 8. The articles in "Fuels" had more citations than those in "Bioresource Technology" even though it had fewer numbers of publications.

Performance of Authors

The top five authors and their number of citations and h-indexes are shown in Figure 3 (a) and 3 (b) for hydrochar and bio-oil respectively. In hydrochar, the top author is Reza M Toufiq from Ohio State University with 22 total publications and an h-index of 13. Andrea Kruze from the University of Hohenheim in Germany has the second highest number of publications followed by Liu ZhenGang from the Chinese Academy of Sciences and Jianmin Chen from Fudan University in China and finally Jan Mumme from the University of Edinburgh in Scotland. Coincidentally, the top five authors

Table 2: (a) Top ten Journals publishing articles in Hydrochar.

| Journal Name | Total number of publications | Total number of citations | h-index |
|---|------------------------------|---------------------------|---------|
| Bioresource Technology | 90 | 1937 | 25 |
| ACS Sustainable Chemistry and Engineering | 25 | 313 | 11 |
| RSC Advances | 25 | 260 | 10 |
| Journal of Analytical and Applied Pyrolysis | 21 | 322 | 11 |
| Energy Fuels | 18 | 244 | 7 |
| Bioresources | 14 | 78 | 5 |
| Chemosphere | 13 | 201 | 7 |
| Applied Energy | 12 | 526 | 8 |
| Energies | 12 | 75 | 3 |
| Energy | 12 | 229 | 7 |

Table 2: (b) Top ten Journals publishing articles in Bio-oil.

| Journal Name | Total number of publications | Total number of citations | h-index |
|--|------------------------------|---------------------------|---------|
| Bioresource Technology | 16 | 268 | 8 |
| Fuels | 5 | 307 | 4 |
| Energy Fuels | 4 | 141 | 4 |
| ACS Sustainable Chemistry Engineering | 3 | 67 | 2 |
| Energy | 3 | 28 | 2 |
| Environmental Science and Pollution Research | 3 | 19 | 2 |
| Environmental Science Technology | 3 | 76 | 3 |
| RSC Advances | 3 | 38 | 3 |
| Waste Management | 3 | 16 | 2 |
| Bioresources | 2 | 26 | 2 |

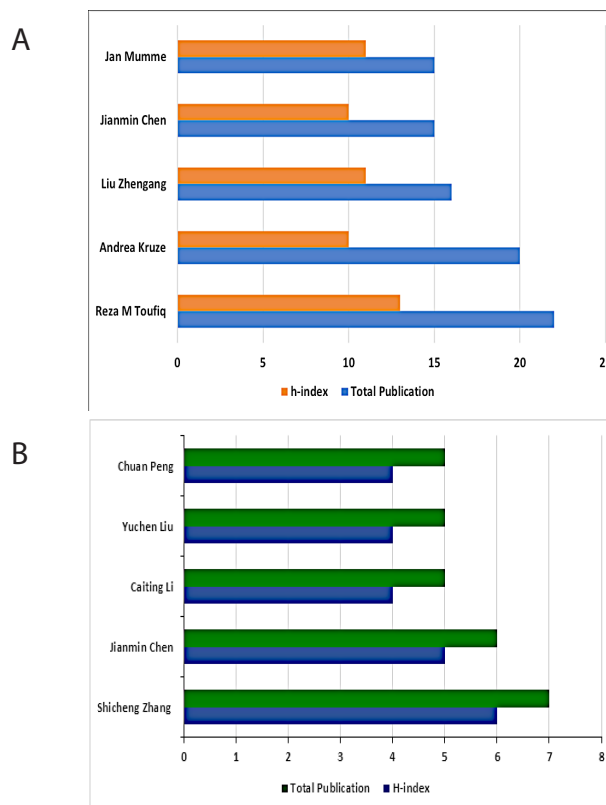


Figure 3: Top five authors in (a) hydrochar and (b) bio-oil.

also belong to top five countries contributing to research on the topic of hydrochar. For bio-oil, Shicheng Zhang from Fudan University is the top author with seven publications and an h-index of six. The second is Jianmen Chen who is also from Fudan University and who has six publications and an h-index of five. The remaining top three authors have same number of publications (five) and same h-index values (four).

The co-author analyses of the various authors publishing articles in the field of hydrochar and bio-oil are shown in Figures 4 (a) and (b). Kyoung S. Ro from USDA has the largest node and he often collaborates with Judy A. Libra from the German Academy of Science, Yong Wang from Zhejiang University and with Liang Li and Joseph RV Flora from the University of South Carolina.^[5] The second largest node belongs to Shicheng Zhang from Fudan University. Shicheng Zhang collaborates frequently with three other authors from Fudan University: Yuchen Liu, Jianmen Chen and Feng Qian. Peng Chuan from the Hunan University has the third largest author collaboration network. Peng Chuan works closely with other authors at the Hunan University. Peng Chuan is often associated with Guangming Zeng, Yun Zhu, Yunbo Zhai and Tengfai Wang. Evidently, most of the authors that collaborate are from the same institutions.

For bio-oil, the author with the highest node was Zhang SC from Fudan University. Zhang SC effectively collaborates

with JM Chen, YC Liu and F Qian. This research group belong solely to Fudan University in China.

Institutional Analysis

The top ten institutions along with their total number of publications, total number of citations and their h-index are shown in Table 3a and 3b for hydrochar and bio-oil, respectively. A total of 623 institutions have contributed to

Table 3: (a) Ten most popular in institutes publishing articles on Hydrochar.

| Institute | Total number of publications | Sum of total number of citations | h-index |
|---|------------------------------|----------------------------------|---------|
| Chinese Academy of Science | 30 | 290 | 11 |
| Leibniz Institute of Agricultural Engineering and Bio-Economy | 30 | 793 | 16 |
| Helmholtz Association | 29 | 380 | 11 |
| Nevada System of Higher Education | 27 | 849 | 16 |
| Spanish National Research Council | 21 | 1211 | 12 |
| University Hohenheim | 21 | 287 | 10 |
| Fudan University | 16 | 464 | 11 |
| South China University of Technology | 16 | 445 | 9 |
| Tokyo Institute of Technology | 15 | 118 | 7 |
| United State Department of Agriculture | 15 | 783 | 11 |

Table 3: (b) Ten most popular in institutes publishing articles on Bio-oil.

| Institute | Total number of publications | Sum of total number of citations | h-index |
|---|------------------------------|----------------------------------|---------|
| Chinese Academy of Science | 13 | 784 | 11 |
| Fudan University | 7 | 213 | 6 |
| Hunan University | 5 | 107 | 4 |
| National University of Singapore | 3 | 80 | 3 |
| South China Agricultural University | 3 | 27 | 3 |
| University of Minnesota | 6 | 520 | 6 |
| University of North Carolina | 3 | 7 | 1 |
| Huazhong University of Science Technology | 2 | 17 | 2 |
| North Caroline at State University | 2 | 7 | 1 |
| Old Dominion University | 2 | 156 | 2 |

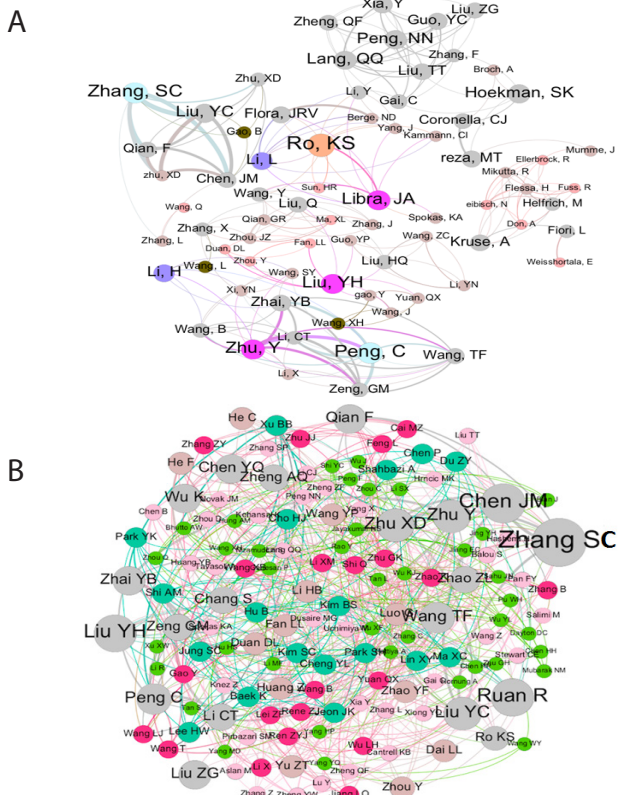


Figure 4: Author collaboration network for (a) hydrochar and (b) bio-oil.

the research related to hydrochar, out of which 79 different institutions have published at least 7 articles in the domain. The top three institutions publishing in the field of hydrochar are the Chinese Academy of Science, the Leibniz Institute of Agricultural Engineering and Bio-Economy (ATB) and the Helmholtz Association of German Research Centers. The Chinese Academy of Science published 30 articles and has an h-index of 11. The ATB published 30 articles and has an h-index of 16 while the Helmholtz Association has published 29 articles and an h-index of 11. Even though the number of articles for the Chinese Academy of Science and ATB are the same, the citational impact of the latter is more than the Chinese Academy of Science.

The total number of institutes publishing on bio-oil was 102, however within this value, some institutions appeared more than once. For example, the University of Minnesota and the University of Minnesota Twin Cities are the same institute. The total number of publications, h-index and the sum of total citations were presented in Table 3.2. The top three institutes with the highest number of publications in the field of bio-oil are the Chinese Academy of Science, Fudan University and

the University of Minnesota. The Chinese Academy of Science published 13 articles and has an h-index of 11, while Fudan University published 7 articles and has an h-index of 6. Finally, the University of Minnesota published 6 articles and has an h-index of 6.

Citation Analysis

For hydrochar, there were 11,434 citations from 659 publications, while for bio-oil, there were 1,570 citations from 71 publications. The top 10 cited papers for hydrochar and bio-oil are presented in Tables 4.1 and 4.2.

The “Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides” by^[27] was the article with the highest citation for hydrochar. This article discusses the proprieties of hydrochar made up of microspheres produced from saccharides.^[27] state that hydrochar produced from saccharides can potentially be used as nanocomposites or in various vivo applications. The most cited paper on bio-oil was the “Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment” by.^[30] Hydrothermal char and

Table 4: (a) The top ten most cited papers in Hydrochar.

| Article | Number of Citations | Journal name | Year | Reference |
|---|---------------------|---|------|--|
| Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides | 610 | CHEMISTRY A European Journal | 2009 | [27,28] |
| Hydrothermal Carbonization of municipal waste streams | 230 | Environmental Science and Technology | 2011 | Berge <i>et al.</i> ^[4] |
| Characterization of hydrochars produced by hydrothermal carbonization of lignin, cellulose, D-xylose and wood meal | 216 | Industrial and Engineering Chemistry Research | 2012 | Kang, Li, Fan and Chang ^[5] |
| Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior | 204 | Applied Energy | 2013 | [11] |
| Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests | 189 | Chemical Engineering Journal | 2012 | Xue <i>et al.</i> |
| Impact of biochar and hydrochar addition on water retention and water repellency of sandy soil | 179 | Geoderma | 2013 | Abel <i>et al.</i> |
| Effect of feedstock type, production method and pyrolysis temperature on biochar and hydrochar properties | 170 | Chemical Engineering Journal | 2014 | Sun <i>et al.</i> |
| Hydrothermal carbonization of biomass as a route for the sequestration of CO ₂ : Chemical and structural properties of the carbonized products | 159 | Biomass and Energy | 2011 | [29] |
| Chemical, structural and combustion characteristics of carbonaceous products obtained by hydrothermal carbonization of palm empty fruit bunches | 145 | Bioresource Technology | 2013 | [7] |
| Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonization of corn stover. | 140 | Australian Journal of Soil Research | 2010 | [29] |

Table 4: (b) The top ten most cited papers in bio-oil.

| Article | Number of Citations | Journal name | Year | Reference |
|--|---------------------|---|------|-------------------------------|
| Qualitative analysis of volatile organic compound on biochar | 194 | Chemosphere | 2011 | Novak <i>et al.</i> |
| Characterization and application of chars produced from pyrolysis and hydrothermal treatment | 191 | Fuels | 2011 | [30] |
| Chemical structures of swine-manure chars produced under different carbonization conditions investigated by advanced solid state C12-nuclear magnetic resonance (NMR) spectroscopy | 115 | Energy and Fuels | 2012 | Cao <i>et al.</i> |
| A novel porous carbon derived from hydrothermal carbon for efficient adsorption of tetracycline | 88 | Carbon | 2013 | Zhu <i>et al.</i> |
| Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon | 87 | Chemical Engineering Journal | 2012 | Kolodynska, Krukowska, Thomas |
| Production of char from sewage sludge employing hydrothermal carbonization: Char properties, combustion behavior and thermal characteristics | 66 | Fuel | 2013 | Peng <i>et al.</i> [12] |
| High-yield harvest of nanofibers/mesoporous carbon composite by pyrolysis of waste biomass and its application for high durability electrochemical energy storage | 65 | Environmental Science and Technology | 2014 | Liu <i>et al.</i> |
| Novel and high-performance magnetic carbon composite prepared from waste hydrochar for dye-removal | 59 | ACS Sustainable Chemistry and Engineering | 2011 | Zhu <i>et al.</i> |
| Cultivation of a microalga <i>Chlorella vulgaris</i> using recycled aqueous phase nutrients from hydrothermal carbonization process | 59 | Bioresource Technology | 2013 | Du <i>et al.</i> |
| Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor | 58 | Bioresource Technology | 2010 | Chang <i>et al.</i> |

pyrolytic char were characterized and used as absorbent for the copper removal from aqueous solution.

Using the co-citation network, the citing references were examined for hydrochar and for bio-oil. For proper visualization of the complex citational network, a full graph and zoomed out version of each cluster were stored in the Figure share repository at <https://doi.org/10.6084/m9.figshare.7966634.v2> for hydrochar and at <https://doi.org/10.6084/m9.figshare.8161646.v1> for bio-oil.

Four hundred and fifty cited references were studied in the co-citation network of hydrochar. This analysis resulted in a total of 7 clusters, depicted by 7 different colors. Four hundred and seventy-eight references were analyzed to determine the co-citation network for bio-oil. This resulted in five separate and unique colored clusters for bio-oil. Moreover, the modularity class separates each cluster. The nodes vary in size according to their PageRank. Information related to

each cluster and their area of study is shown in Tables 5.1 and 5.2. Major research areas that are currently being studied in the field of hydrochar are; various types of biomass and its treatment through pyrolysis or hydrothermal carbonization, a comparison between conventional processes and assisted processes through microwaves, properties of hydrochar and biochar, biochars adsorption capability of various elements or pollutants, waste management and sewage sludge treatment systems as well as its production of lithium ion batteries with the help of biomass derived carbon are being analyzed. The application of hydrochar as an alternative energy source and as a soil amendments or fertilizers is being investigated. For bio-oil, hot topics of research are production of bio oil through different processes including HTC or hydrothermal liquefaction or gasification or catalytic co-pyrolysis, adsorption potential of hydrochar, hydrothermal techniques and pyrolysis.

Table 5: (a) Co-citation analysis clusters along with top five paper and area of study for hydrochar.

| Cluster | Top five articles title | PageRank | Area of study |
|---------|--|----------|---|
| 0 | Comparison of the effect of wet and dry torrefaction on chemical structure and pyrolysis behavior of corncobs | 0.024667 | Pyrolysis characteristics of various biomass, hydrothermal carbonization, Combustion properties of various hydrochar and biochar. |
| | Microwave-assisted preparation of hollow porous carbon spheres and as anode of lithium-ion batteries | 0.014658 | |
| | Comparison Study on Pyrolysis Characteristics and Kinetics of Corn Stover and Its Digestate by TG-FTIR | 0.013335 | |
| | Investigation of thermodynamic parameters in the pyrolysis conversion of biomass and manure to biochars using thermogravimetric analysis | 0.01217 | |
| | Characteristics of co-hydrothermal carbonization on polyvinyl chloride wastes with bamboo | 0.011548 | |
| 1 | Controllable synthesis of magnetic carbon composites with high porosity and strong acid resistance from hydrochar for efficient removal of organic pollutants: An overlooked influence | 0.013882 | Biochar and its various properties, adsorption capacity of biochars. |
| | Characterization of biochar derived from rice husks and its potential in chlorobenzene degradation | 0.01006 | |
| | Biochars with excellent Pb (II) adsorption property produced from fresh and dehydrated banana peels via hydrothermal carbonization | 0.007505 | |
| | Degradation of <i>p</i> -Nitrophenol on Biochars: Role of Persistent Free Radicals | 0.005439 | |
| | Effect of pyrolysis temperature on char structure and chemical speciation of alkali and alkaline earth metallic species in biochar | 0.005267 | |
| 2 | Carbon-Based Supercapacitors Produced by Activation of Graphene Cation- π Interaction: A Key Force for Sorption of Fluoroquinolone Antibiotics on Pyrogenic Carbonaceous Materials | 0.026491 | Adsorption capability of carbon, carbon nanotubes or carbon-based super capacitor. |
| | Response surface methodology approach for optimization of ciprofloxacin adsorption using activated carbon derived from the residue of desiccated rice husk | 0.010048 | |
| | Adsorption removal of ciprofloxacin by multi-walled carbon nanotubes with different oxygen contents from aqueous solutions | 0.00783 | |
| | Adsorptive removal of antibiotics from aqueous solution using carbon materials | 0.006458 | |
| | | | |
| 3 | Biomass waste inspired highly porous carbon for high performance lithium/sulphur batteries | 0.024487 | Lithium ion batteries production from biomass hydrothermal carbonization |
| | <i>Eucalyptus</i> sawdust derived biochar generated by combining the hydrothermal carbonization and low concentration KOH modification for hexavalent chromium removal | 0.013363 | |
| | Magnetic PSA-Fe ₃ O ₄ @C 3D mesoporous microsphere as anode for lithium ion batteries | 0.00921 | |
| | Biomass carbon derived from sisal fiber as anode material for lithium-ion batteries | 0.007177 | |
| | Encapsulating Co ₂ P@C Core-Shell Nanoparticles in a Porous Carbon Sandwich as Dual-Doped Electrocatalyst for Hydrogen Evolution | 0.00592 | |
| 4 | Phytotoxins during the stabilization of organic matter | 0.012466 | Hydrothermal carbonized carbon for energy use and soil amendment. |
| | Carbon markets investment criteria for biochar projects | 0.00674 | |
| | Thermochemical Transformation of Agro-biomass into Biochar: Simultaneous Carbon Sequestration and Soil Amendment | 0.00473 | |
| | Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage | 0.00434 | |
| | A Direct Synthesis of Mesoporous Carbons with Bicontinuous Pore Morphology from Crude Plant Material by Hydrothermal Carbonization | 0.003298 | |

| | | | |
|---|---|----------|--|
| 5 | The transformation pathways of nitrogen in sewage sludge during hydrothermal treatment | 0.020737 | Sewage sludge treatment, Biomass processing for syngas production. |
| | Effect of the hydrothermal pretreatment for the reduction of NO emission from sewage sludge combustion | 0.012624 | |
| | Effect of Hydrothermal Pretreatment on Convective Drying Characteristics of Paper Sludge | 0.004854 | |
| | Hydrophobic precipitation of carbonaceous spheres from fructose by a hydrothermal process | 0.003997 | |
| | Model-based downdraft biomass gasifier operation and design for synthetic gas production | 0.00307 | |
| 6 | Impact of pretreatment on solid state anaerobic digestion of yard waste for biogas production | 0.010499 | Anaerobic digestion for disposing of waste, biochar and combustion properties. |
| | Co-combustion characteristics and blending optimization of tobacco stem and high-sulfur bituminous coal based on thermogravimetric and mass spectrometry analyses | 0.005677 | |
| | Challenges and strategies for solid-state anaerobic digestion of lignocellulosic biomass | 0.003984 | |
| | Energy and exergy analyses of solar-assisted fluidized bed drying integrated with biomass furnace | 0.003105 | |
| | Comparative study of thermal properties of bio-coal from aromatic spent with low rank sub-bituminous coals | 0.002561 | |

Table 5: (b) Co-citation analysis clusters along with top five paper and area of study for hydrochar.

| Cluster | Top five articles title | PageRank | Area of study |
|---------|--|----------|--|
| 0 | Analysis of product distribution and characteristics in hydrothermal liquefaction of barley straw in subcritical and supercritical water | 0.01907 | Hydrothermal liquefaction of biomass (such as barley straw, corn stalk or rice straw) and production of biocrude or bio oil through liquefaction. |
| | Hydrothermal liquefaction of barley straw to bio-crude oil: Effects of reaction temperature and aqueous phase recirculation | 0.011609 | |
| | Elemental migration and characterization of products during hydrothermal liquefaction of cornstalk | 0.008993 | |
| | Hydrothermal liquefaction of biomass: A review of subcritical water technologies | 0.007952 | |
| | Catalytic hydrothermal liquefaction of rice straw in water/ethanol mixtures for high yields of monomeric phenols using reductive Cu Zn Al catalyst | 0.006311 | |
| 1 | Effects of reaction time and catalyst on gasification of glucose in supercritical water: Detailed reaction pathway and mechanisms | 0.024736 | Super critical water gasification for production of hydrogen rich gas, bio-oil and hydrochar from sewage waste, effect of pre-treatments on biomass for the production of the bio oil. |
| | An overview of characteristics of municipal solid waste fuel in China: Physical, chemical composition and heating value | 0.019546 | |
| | Clean solid biofuel production from high moisture content waste biomass employing hydrothermal treatment | 0.018603 | |
| | Hydrothermal carbonisation of sewage sludge for char production with different waste biomass: Effects of reaction temperature and energy recycling | 0.014182 | |
| | Effect of torrefaction on structure and fast pyrolysis behavior of corncobs | 0.013057 | |

| | | | |
|---|---|----------|---|
| 2 | Production of aromatic hydrocarbons from catalytic co-pyrolysis of biomass and high-density polyethylene: Analytical Py-GC/MS study | 0.01724 | Aromatic hydrocarbon production through catalytic co-pyrolysis from biomass, combination of liquefaction and hydrotreating for production of oil. |
| | Catalytic Conversion of <i>Chlamydomonas</i> to Hydrocarbons via the Ethanol-Assisted Liquefaction and Hydrotreating Processes | 0.009319 | |
| | Integration of biomass catalytic pyrolysis and methane aromatization over Mo/HZSM-5 catalysts | 0.004204 | |
| | Catalytic co-pyrolysis of biomass and polyethylene in a tandem micro-pyrolyzer | 0.003593 | |
| | Activated carbons from waste biomass and low rank coals as catalyst supports for hydrogen production by methanol decomposition | 0.003148 | |
| 3 | Adsorption removal of cadmium and copper from aqueous solution by areca—A food waste | 0.014789 | Removal of heavy metals or harmful elements from the waste water with the help of food waste or biochar through adsorption technique. |
| | Assessment of toxic copper (II) biosorption from aqueous solution by chemically-treated tomato waste | 0.007995 | |
| | Evaluation of adsorption potential of bamboo biochar for metal-complex dye: equilibrium, kinetics and artificial neural network modeling | 0.005611 | |
| | Adsorption removal of reactive dyes from aqueous solution by modified basic oxygen furnace slag: Isotherm and kinetic study | 0.004373 | |
| | Adsorption of Cu (II) by biochar's generated from three crop straws | 0.003607 | |
| 4 | Polycyclic aromatic hydrocarbons (PAH) formation from the pyrolysis of different municipal solid waste fractions | 0.023855 | Production of aromatic hydrocarbons through pyrolysis, hydrothermal treatment or microwave assisted pyrolysis or microwave assisted hydrothermal treatment of waste or biomass. |
| | Insights into pyrolysis and catalytic co-pyrolysis upgrading of biomass and waste rubber seed oil to promote the formation of aromatics hydrocarbon | 0.012892 | |
| | Recovery of reducing sugars and volatile fatty acids from cornstalk at different hydrothermal treatment severity | 0.01926 | |
| | Fast microwave-assisted ex-catalytic co-pyrolysis of bamboo and polypropylene for bio-oil production | 0.009047 | |
| | Effect of pyrolysis temperature, heating rate and residence time on rapeseed stem derived biochar | 0.00705 | |

Subject Distribution

Journals indexed by the Web of Science have one or more subject category, such as arts, humanities, life sciences, biomedicine and physical science. All the articles in Web of Science automatically incorporate the subject categories of the source or the Journal in which it is published. If the article is from a multidisciplinary journal, the subject category is decided based on its cited references. Furthermore, the categories in the Web of Science are not mutually exclusive meaning that one article can be found in many categories. However, it should also be noted here that categories presented in this paper are categorized solely on their journal subject.

Figures 5(a) and (b) represent the percentage of different subject categories related to the hydrochar and bio-oil. The dominant subject categories related to hydrochar were Energy Fuels (41.3%), Chemical Engineering (25.9%) and Environmental Sciences (18.8%). Engineering, chemistry

and environmental sciences account for the majority of the top ten subject categories. For bio-oil the most important categories were Bioresource Engineering (22.2%), Fuels (6.9%) and Energy Fuels (5.6%). Thus, the top ten categories can be portrayed by topics related to bioresource, energy and environment sciences.

Research Hotspots

In a network analysis, the co-occurrence of keywords was examined for hydrochar and bio-oil and the results are shown in Figures 6(a) and (b), respectively. The nodes correspond to the keywords while edges are the lines that link two keywords. The thickness of the edge's correlate to the relationship that each keyword has with one another. A positive correlation exists between the thickness of the edge and the co-occurrence of two nodes or keywords.

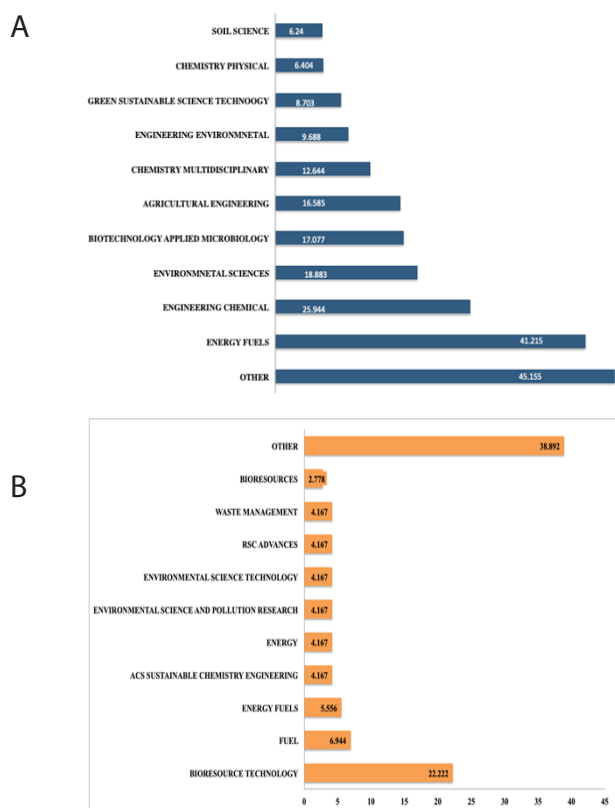


Figure 5: Percentage of research papers in conformance to their subject distribution in (a) hydrochar and (b) bio-oil.

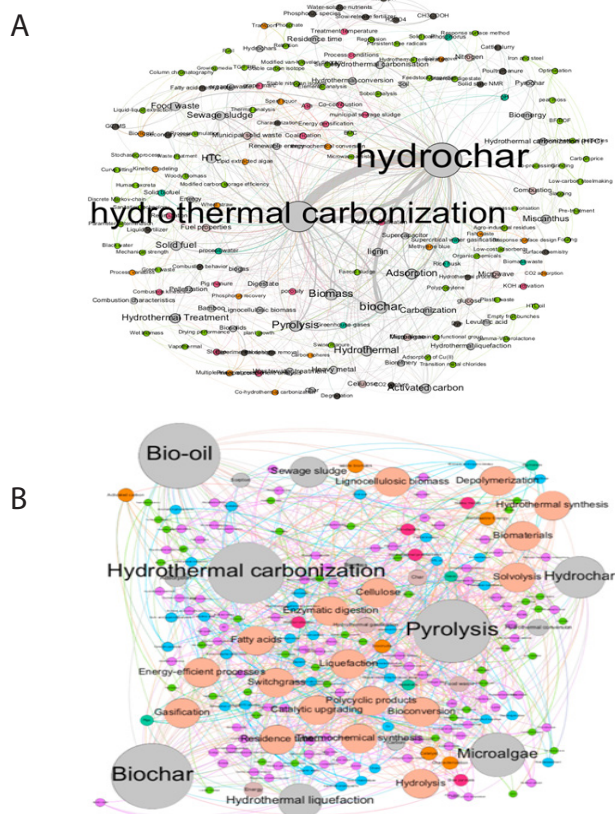


Figure 6: Co-word collaboration network of author supplied keywords for (a) hydrochar and (b) bio-oil.

Keywords in an article describe its content and thus, can be used to study the hotspots of the research currently being emphasized by various researchers.^[31]

In the case of hydrochar, the top keywords are “hydrothermal carbonization”, “hydrochar”, “biochar”, “biomass”, “pyrolysis”, “adsorption”, “sewage sludge”, “activated carbon”, “solid fuel”, “food waste” and “lignin”. Other important keywords are “miscanthus”, “bio energy”, “heavy metals”, “residence time”, “wastewater treatment”, “digestate”, “combustion” and “microalgae”, etc. The top key words are linked to different kinds of inputs (biomass, lignin, sewage waste, food waste), thermochemical processes (pyrolysis and hydrothermal carbonization), products (hydrochar, biochar) and potential uses of the solid product (fuel, adsorption of heavy metals and/or activated carbon). Other important keywords follow a similar trend suggesting different types of feedstock that can be used. These keywords also suggest that various results can be obtained depending on hydrochar operating conditions.

The top keywords for bio-oil are “bio-oil”, “pyrolysis”, “microalgae”, “hydrochar”, “biochar”, “hydrothermal liquefaction”, “sewage sludge” and “hydrothermal carbonization”. Other important keywords are “fatty acids”, “hydrolysis”, “bioconversion”, “biomaterials”, “hydrothermal synthesis”, “depolymerization”, “solvolysis”, “lignocellulosic biomass”, cellulose”, “enzymatic digestion”, “liquefaction”, “energy-efficient processes”, “gasification”, “residence time”, “catalytic upgrading”, “polycyclic products”, “switchgrass” and “thermochemical synthesis”.

It is important to note that the top keywords for bio-oil correlate to the extraction process. For example, bio-oil is made at the same time as hydrochar by hydrothermal carbonization. Thus, “hydrothermal carbonization” and “hydrochar” are part of the top keywords found in Figure. Similarly, the process of gasification is another keyword. The types of biomass that can be used to create bio-oil as well as the pre-treatments that may be used to create bio-oil as well as the pre-treatments that may be used for processing the biomass in an energy efficient matter by HTC are also discussed here.

DISCUSSION AND CONCLUSION

Limitations in bibliometric analyses do exist. Three limitations have been identified here. Firstly, articles in any database may not always be 100% correct. For example, some articles related to hydrochar and bio-oil may have been left out when using specific keywords, while others may have been included in the search even though they are not directly linked to hydrochar or bio-oil. Secondly, only articles from journals indexed in the Web of Science Core Collection were included in this analysis. The citation count used as a quality parameter has some disadvantages. For example, it is dependent on time. Therefore, newer articles tend to get fewer citations even though they are robust. Moreover, the h-index

is a dynamic number as it is dependent on the database and number of journals indexed under it. Yet, not all the citations from the journals are indexed under Web of Science Core Collection. Consequently, the h-index varies. Thirdly, articles are categorized on the basis of their source but sometimes the original content of the article can be different therefore creating potential errors.

In conclusion, a bibliometric analysis and the scientific study of hydrochar and bio-oil was performed for the period of 2009-2018 and 2010-2018, respectively. During this time a total of 659 articles were published on hydrochar and 71 articles were published on bio-oil. Interest in hydrochar and bio-oil gradually increased in popularity over the years, reflecting in the increase in the annual number of publications in these subject areas. This bibliometric analysis on hydrochar and bio-oil has cast light on the current state of the research. A research trend depicts the multidisciplinary applications of the hydrochar in different fields from energy to waste management and chemistry. Many studies focused on the potential use of hydrochar in applications as a viable energy source, soil amendments and as a low-cost absorbent material for pollutants, among others. Many researchers have shown that bio-oil could be a potential liquid fuel and fertilizer.

Multiple keywords are associated with the terms hydrochar and bio-oil. The implications of the keywords identify the current areas of interests while describing the subject. The top keywords associated with the term hydrochar are linked to various inputs, thermochemical processes, by-products of the reaction and its applications in various sectors. The top keywords associated with the term bio-oil describe different extraction processes. Together, these key words (hydrochar and bio-oil) are increasingly being used by scholars, journals and in industries around the world.

The fields of hydrochar and bio-oil are still developing with numerous scholars scrutinizing the use of different and unique types of biomass such as human bio-waste, sewage sludge, food waste and seafood waste. Further research and cost analyses will help with the commercial acceptance of using this technology for processing and managing bio-wastes.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

ABBREVIATIONS

HTC: Hydrothermal carbonization; ATB: Agricultural Engineering and Bio-Economy; MAPAQ: Ministry of Agriculture, Fisheries and Food of Quebec; NSERC: Natural Sciences and Engineering Research Council of Canada.

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