



Laser pyrolysis in papers and patents

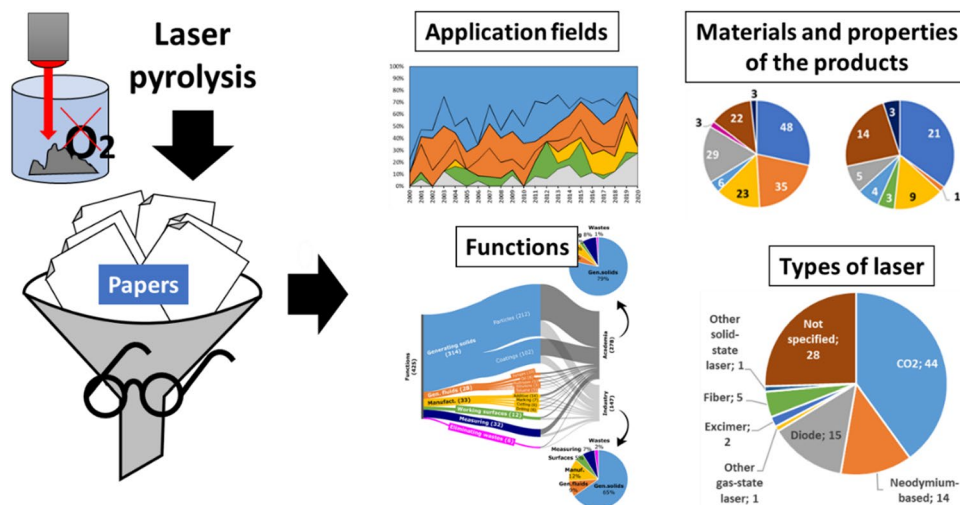
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Abstract

This paper presents a critical review of laser pyrolysis. Although this technology is almost 60 years old, in literature many researchers, both from academia and industry, are still developing and improving it. On the contrary industrial applications are struggling to take off, if not in very restricted areas, although the technology has undoubted advantages that justify future development. The aim of this work consists in analysing a representative pool of scientific papers (230) and patents (121), from the last 20 years, to have an overview about the evolution of the method and try to understand the efforts spent to improve this technology effectively in academia and in industry. This study is important to provide a complete review about the argument, still missing in the literature. The objective is to provide an overview sufficiently broad and representative in the sources and to capture all the main ways in which laser pyrolysis has been used and with what distribution. The main focuses of the study are the analyses of the functions carried out by laser technologies, the application fields, and the types of used laser (i.e. models, power and fluence). Among the main results, the study showed that the main use of laser pyrolysis is to produce nanoparticles and coatings, the main materials worked by laser pyrolysis are silicon and carbon dioxide and the main searched properties in the products of laser pyrolysis are catalysts activity and electrical conductivity. CO₂ lasers are the most used and the have high versatility compared to others. In conclusion, the study showed that laser pyrolysis is a consolidated technology within its main application fields (nanoparticles and coatings) for several years. Within this context, the technology has been developed on very different sizes and processes, obtaining a very wide range of results. Finally, these results may also have stimulated new areas of experimentation that emerged mainly in recent years and which concern biomedical applications, additive manufacturing, and waste disposal.

Graphical abstract



Keywords Pyrolysis · Laser pyrolysis · Bibliometric analysis · Patents

Extended author information available on the last page of the article

Introduction

Laser pyrolysis is a technology known at least since the sixties (Folmer & Azarraga, 1969; Karn et al., 1967), although still today it is considered by several researchers (Gao et al., 2019; Koshida & Nakamura, 2019; Weyermann, 2019) as an emerging technology both in its most well-known fields of application and in the frontier research. Laser pyrolysis exploits a laser beam to provide the energy necessary for the pyrolysis reaction of a solid, liquid, or gaseous reagent inside a reactor in which there is a controlled and oxygen-free atmosphere. The goal is to obtain the cleavage and subsequent recombination of the chemical bonds of the reactants to generate products of different materials. A field where it is particularly known is the generation of nanopowders consisting of silicon and metal oxides or noble metals starting from a gaseous precursor (Kim et al., 2019a, 2019b).

Several parameters can be considered to describe laser pyrolysis plants from a technological point of view. The most important are the type of laser and the setting parameters (i.e. pulse frequency, diameter of the nozzle, distance between the nozzle and the material to be treated by the laser, focal position and length, type and pressure of auxiliary gas) that are necessary to determine the types of processed materials. Some reasons are the different absorption coefficients, which depends by the electromagnetic wavelength of the laser, the power of the plant, the heating rate, the reaction temperatures, the processed flow rate, and the generated products.

If compared with other types of pyrolysis (e.g. plasma, microwave, fixed and fluidized bed, with hot sand), from the point of view of the chemical characterization of the reaction, laser pyrolysis could ideally be considered as an alternative for flash and fast pyrolysis. In fact, the heating rates and the temperatures of reaction are high, the generation of gaseous products is predominant, and the reaction occurs in a few seconds. However, laser pyrolysis is not concurred to these technologies within their typical fields of application, such as waste disposal or electricity generation (Bridgwater, 2012; Lewandowski et al., 2019; Sharuddin et al., 2016).

Given the very high precision of the interaction with the raw material, laser pyrolysis is mainly exploited when a very selective heat transmission is required, such as the treatment of the nano powders and the produce sintered coatings. In this field, laser pyrolysis allows to eliminate some onerous stages of the process, such as the washing and drying steps, which are instead necessary in competing wet-chemical methods. In addition, these last are less performing in terms of heating transfer (Kim et al., 2014). For these reasons, in this field, laser pyrolysis is

progressively stealing the market segment to other methods (Wang et al., 2017 and Tangermann-Gerk et al., 2016). Its main advantages are the high fluence and the continuous heat transfer, allowing a rapid synthesis processes up to 1 kg/h in industrial plants (Leconte et al., 2007). A recent trend, however, is to reduce the vacuum degree and its complication up to the realization of the so-called laser coatings (Simoni et al., 2021).

The laser pyrolysis can also ensure a high purity of the materials produced since by managing to confine the heat source and consequently the reaction zone away from the walls of the reactor, contaminations are reduced. In addition, the heat concentration favours a very high thermal gradient. For this reason, the dissociation and reassociation of the molecules of the reactants are extended to a greater number of different chemical bonds to produce generate a wider range of different products and materials (Wang et al., 2017). Compared to microwaves and plasma pyrolysis, in laser pyrolysis the heat transmission can be better controlled, by ensuring both steeper heating ramps and higher precision (Bridgwater, 2012). Finally, based on pure bibliographic studies and theoretical evolutive models, laser pyrolysis emerged to be more advanced than competing pyrolysis technologies (Russo et al., 2019; Spreafico et al., 2021).

Therefore, by virtue of these advantages, the hypothesis of this study is that laser pyrolysis, thanks to its peculiarities, in the near future, may be exploited in various fields, despite the long period of incubation within the most peculiar ones. For this reason, investigating the current state of development of the technology in the literature can be more strategic than analysing commercial applications, to see the development directions still experimental. However, today, in literature an extensive review about laser pyrolysis do not seem to exist. Only some contributions compare pros and cons of laser pyrolysis with other alternative technologies, also not involving pyrolysis and used in the same application field (e.g. Jamkhande et al., 2019; Ealias and Saravanakumar, 2017). Such studies can be useful to select a technology to be used in a specific application field according to some parameters about the features of the obtained products (e.g. purity, mechanical strength, electrical conductivity) and the production process (e.g. time, flow and required energy). Finally, only one type of laser (e.g. CO₂) and with a determined power is generally considered, while the field of application are few and too specific.

To fill this gap, this article is the first to propose an extensive review on laser pyrolysis, analysing and classifying many documents from the reference literature. Both scientific papers and patent were included to provide the reader with a double perspective related to both the academic and the industrial contexts. The considered parameters of laser pyrolysis are:

- *Application fields* in which the same technology or its products can be used, e.g. electronics, medical, chemistry.
- *Functions*, i.e. the operations that laser pyrolysis can perform, e.g. obtaining particles, depositing a coating, working a surface.
- *Technology*: types of used laser and their performances.

The analysis is based on bibliometric indicators, such as the number of the sources and the time trend of the publications, to provide a quantitative indication. The counting of the documents in the different classes was carried out in a purely manual modality, considering only what is explicitly reported within the analysed documents. This review aims to provide an overview on the real current diffusion of laser pyrolysis, and its future potential both in academia and in industry.

This study introduces some elements of novelty compared to the previous reviews in the literature.

- The number of considered documents passing from few units to hundreds.
- The provided classification by application fields and technologies is not entirely new. However, the studies that have already adopted this classification have not linked the two aspects, while this review provides a new perspective, describing exactly how a technology works to fulfil a purpose typical of an application field.
- In addition, the novel classification by function has been introduced, which has no equivalent in the literature. In this study, the function is used as a linkage between the technology and the application field, as experimented in Russo et al. (2020).
- The analysis at the bibliographic level is a novelty for this topic, since the other reviews propose analysis exclusively focused on the operational parameters.
- Finally, the review about the future emerging application fields is the last element of novelty since previous reviews mainly compare the current and most diffused applications of laser pyrolysis.

This study has a clear practical significance for researchers and professionals involved in laser pyrolysis or interested in all the fields where the technology can be applied. The mapping offered for the operating parameters of the laser according to the objectives (functions and fields of application) is sufficiently broad and complete to serve as a knowledge base for an initial technological assessment. The professional interested in selecting the most suitable type of laser can benefit from the presentation of the technical parameters and the discussion of the main pros and cons of each technology. The detailed presentation of the many alternative methods of use, especially the most innovative

ones, can instead be useful to highlight the new directions of development of the technology. A researcher can take advantage of understanding at what level the research has gone into the various fields as well as learning who is working on the topic and how. An entrepreneur can instead be stimulated to invest in the technology in the most innovative areas, especially by discovering the many presented scientific studies and patents, which are not yet developed.

The knowledge gap that this article aims to fill concerns the lack of an overall broad comparison on the topic of laser pyrolysis, which shows its applications over the years. In the scientific literature, a comparison showing the relative distribution of the uses of this technology is missing, as is that of the different types of exploited lasers, while both these aspects are addressed in this study. The bibliographic analysis conducted on scientific articles brings new evidence, since the few reviews on the subject do not provide a valid overview since they analyse very few contributions. The knowledge emerging from the analysis of the patents is instead completely new in this field, providing an idea about how industry is working in this field, also in comparison with academia.

Research methodology

The documents considered in this review were collected and analysed through a multi-step procedure based on an extensive manual review. Although contributions about laser pyrolysis could be heterogeneously disseminated among scientific articles, conference proceedings, books, technical catalogues, and patents, in this review, only the first and the last ones were considered due to their reliability and completeness. The articles have been considered because they should provide a truthful and non-commercial data presentation perspective and they are usually reviewed through a rigorous peer-review process. For this reason, only those published in international journals, indexed in the main scientific databases, were selected. While patents were considered for their linkage with the industrial field, albeit the revision process is less rigorous than articles from the scientific point of view.

The articles were searched within the SCOPUS database, while the patents in Fampat database developed by Questel, using the same query, unless the software syntax changes, within the title, abstract and keywords of the documents. The query was (*pyrol* AND laser**), where the truncation operator is “*” in SCOPUS and “+” in Fampat. Among the obtained documents, only those published since 2000 (i.e. publication date for papers and priority date for patents) have been collected, using the SCOPUS and Fampat automatic filters. This choice was arbitrarily decided to limit the pool

of documents to be analysed. These queries provide 2168 articles and 234 patents.

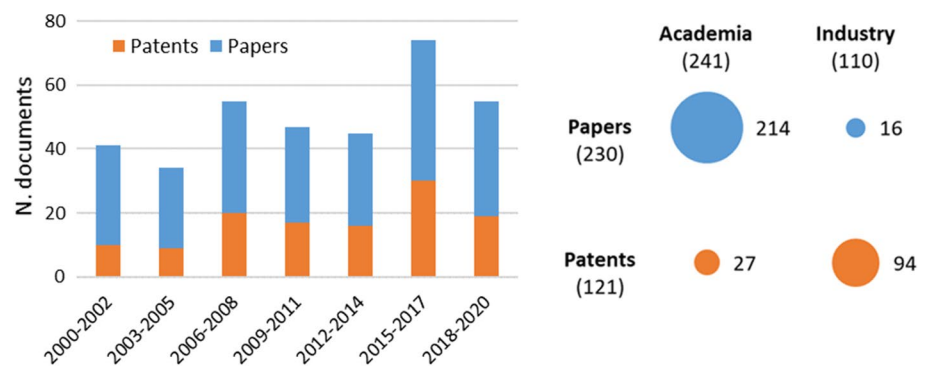
Then, by manually analysing titles and abstracts of all the documents, only those pertinent with the topic were considered for the deeper manual analysis in full text. This manual review phase was very onerous but nevertheless necessary, since the automatic filters of both databases, i.e. proximity operators and truncations for the query keywords, have proved unreliable in various sample tests, mainly as regards recall. Consequently, a drastic reduced the number of documents to be considered in the analysis resulted from the manual review.

The documents excluded from the analysis can be classified into four classes concerning the use of lasers: (i) as an alternative to pyrolysis; (ii) to perform operations (e.g. drying, cutting, surface finishing) on the reagents or on the pyrolysis products, without carrying out the same reaction; (iii) to measure the parameters of the pyrolysis reaction or the characteristics of the reactants and products; (iv) to realize some components of the pyrolysis reactor, e.g. electrodes, thermal vectors, masks/filters. The final pool counts 351 documents: 230 papers (articles) and 121 patents.

Based on the documents bibliographic information the documents were classified according to time distribution and their origin (i.e. academia vs industry). The papers in which all authors have academic affiliations, including research centres, and the patents in which at least an academic institution figures as applicant or co-applicant, were considered “academic”. While the papers including at least one author with an industrial affiliation or co-affiliation and patents having only industries as applicants, were considered “industrial”.

Figure 1 (left) shows the time distribution of the analysed papers and patents, considering the priority date for the latter, within the entire considered time interval. As can be seen, the distribution of the documents is growing, except for the last three years (2018–2020), since patents from first 18 months are not disclosed. Figure 1 (right) shows the distribution of the documents according to type (paper vs patent) and origin (academia vs industry).

Fig. 1 (Left) Time distribution of papers and patents (priority date). (Right) Distribution between papers/patents, and source academia/industry



Results

Application fields

In this section, we introduce the main application fields of the products of laser pyrolysis, considering only those explicitly declared by authors in the considered documents. All the applications fields have been classified according to a two-level hierarchical classification and distributed on a temporal axis to identify potential trends. The first level of the classification includes nine generic classes: (i) “Chemistry”; (ii) “Electronic” and (iii) “Electrochemical” products and components realization; (iv) “Medical” applications of laser pyrolysis or of its products; (v) “Environment” monitoring and preservation; (vi) “Precision manufacturing” operations; (vii) “Energy production” exploiting the reactions outputs; (viii) “Food production” monitoring and preservation; (ix) “Aerospace” products and components realization.

In the following paragraphs a brief description of each class is presented.

- The application of the laser pyrolysis to *chemistry* is linked to the production of catalysts for chemical reactions that have a higher efficacy and a lower manufacturing cost than alternatives produced with other technologies (e.g. Yeon et al., 2019). Furthermore, the use of laser pyrolysis in chemical industry is also confined to the pure production of materials to be successively processed (e.g. Malekzadeh et al., 2020) and for purposes related to the analysis of the properties and compositions of the materials, such as spectrometry (e.g. Prati et al., 2014).
- Laser pyrolysis in the *electronics* industry is used to produce mainly small parts or coatings of many products, such as: special electronic components where standard electrical conductivity or insulation capabilities are required together with miniaturization or flexibility or mechanical strength (e.g. Rahimi et al., 2016); solar cells, where the produced material have certain photo-

electric properties (e.g. Belchi et al., 2019); semiconductors, where laser pyrolysis is generally used both for the realization of silicon components and coatings (e.g. Jeong et al., 2017); superconductors, where the electrical properties are guaranteed by the increased control over the microstructure ensured by laser pyrolysis (e.g. Rijckaert et al., 2020); other electronic components used for the realization of displays, sensors and storage memories (e.g. Martins et al., 2019).

- *Electrochemistry* exploits laser pyrolysis to produce battery components, such as especially coatings for anodes and cathodes (e.g. Kim et al., 2019a, 2019b), supercapacitors (e.g. Bhattacharjya et al., 2018) and fuel cells (e.g. Yeon et al., 2019).
- Different *medical* applications exploit the products of laser pyrolysis. Powders are generally used in this field because thanks to their properties can act as a contrast for magnetic resonance (e.g. Popovici et al., 2007). Another option is to exploit them as ingredient for medications in order to favour a more localized action (e.g. Mejías et al., 2008). Finally, their chemical and biological properties are instead exploited in anticancer radiotherapy (e.g. Kabashin et al., 2019)
- Other fields of application of laser pyrolysis are: the protection and monitoring of the *environment*, e.g. through the production of catalyst nanopowders for air depollution (Barrault et al., 2009) or its direct application for the study of rocks as a measuring instrument (Al Sandouk-Lincke et al., 2013), *precision manufacturing*, by replacing of other less performing technologies (Shin et al., 2020), *energy production*, exploiting the heat generated by the reaction of pyrolysis or producing gas that can be used as fuel (Masyuk et al., 2018), *food production* and conservation through the chemical action especially of nanopowders and coatings produced by laser pyrolysis (Wang et al., 2019) and *aerospace*.

Figure 2 summarizes the proposed classification in classes (in grey) and subclasses (in white) of the applications of the products of the laser pyrolysis.

Table 1 reports the number of documents referring to the various application fields.

Figure 3 depicts the comparison of the identified application fields between academia and industry.

Analysing the results shown in Table 1 and Fig. 3, some considerations can be drawn, in relation to the documents analysed and the proposed classification of the results. Each analysed document claims on average 1.07 different application fields, considering both classes and sub-classes, with a slight prevalence of industry contributions (1.13 applications) compared to those from the academia (1.04 applications). Overall, laser pyrolysis is mostly used in the field of chemistry and electronics, with about 75% of overall cases. Among the chemical applications, the production of catalysts (57% of all chemical products), mainly nanopowder, and materials has been highlighted (35% of all chemical products). In electronics, the production of special components, starting from nanopowders, alone counts for 49% of the cases. In electrochemical applications, the contribution from the production of batteries (69% of the cases) is particularly noticeable, especially coatings. By comparing the distributions of the application fields, academia is strongly interested in chemical applications, with 49% of the total cases. Industry is instead more interested in electronics, although not in a less preponderant way, i.e. with a deviation of 4% respect to chemistry.

To provide an evidence about how the distribution of the application fields changed during time, in Fig. 4, the percentage distribution considering the aggregated data of all the considered documents in the last 20 years has been compared with that resulting by considering only the documents from the last 5 years. This comparison clearly showed that the main percentage variations can be encountered in

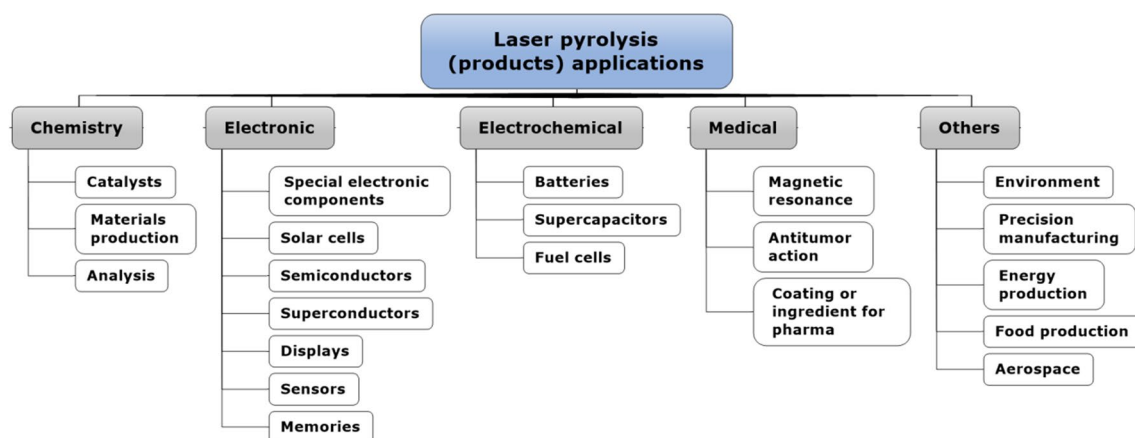


Fig. 2 Proposed classification of the identified applications fields of the products of the laser pyrolysis

Table 1 Number of citations in papers/patents for each application field

Application fields	Number of citations in papers/ patents		
	Academia	Industry	Total
<i>Chemistry</i>			
Catalysts	66	21	87
Materials production	42	15	57
Analysis spectrometry	15	6	21
Sub-total	123	42	165
<i>Electronic</i>			
Special electronic components	34	23	57
Solar cells	20	1	21
Semiconductors	7	12	19
Superconductors	1	4	5
Displays	3	2	5
Sensors	4	1	5
Memories	0	4	4
Sub-total	69	47	116
<i>Electrochemical</i>			
Batteries	12	7	19
Supercapacitors	4	0	4
Fuel cells	1	3	4
Sub-total	17	10	27
<i>Medical</i>	17	13	30
<i>Environment</i>	8	4	12
<i>Precision manufacturing</i>	7	3	10
<i>Energy production</i>	4	4	8
<i>Food production</i>	2	1	3
<i>Aerospace</i>	3	0	3
Total	250	124	374

Bold values are used for the classes

electrochemical field (+13%), other electronic fields (-7%) and chemical analysis (-5%).

Figure 5 shows the results of the analysis of the percentage distribution of publications relating to the different application fields of laser pyrolysis during time. In addition, in the two most common application fields, i.e. chemistry and electronic, the data were divided between academia and industry.

The analysis of the results shown in Fig. 5 provides an important clarification to the results emerged from Fig. 3. Although overall the most widespread applications of laser pyrolysis are those relating to chemistry and electronics, the percentage of the sum of the annual publications referring to them has been decreasing in the last twenty years. The aggregate percentage value of chemical and electronic applications passes from around 90% in the early 2000s to around 60% in the last four years. Furthermore, this decrease is more pronounced in chemistry, which has lost a lot of

interest especially in academia (-13%), compared to electronics, which maintains a substantially stable interest in the academic field (+5%). This decrease is due to the growing spread of laser pyrolysis applications, especially in electrochemistry (27 documents vs 1) and in other fields of applications. On the contrary, the values of medical applications seem rather fluctuating.

Functions

In this section, we introduce the main functions of laser pyrolysis, considering only those explicitly carried out by the same process as declared by authors in the considered documents. As consequence, the proposed analysis excludes all the secondary functions that can be carried out by the products of laser pyrolysis. The functions have been classified according to a hierarchical classification with multiple levels.

The first level of the classification includes six generic functions described in the following paragraphs.

- The laser pyrolysis can be used for *generating solid materials*, typically of micro or nanometric dimensions, exploiting the concentrated heat of the laser beam that crosses a flow of gaseous (typically) reagents, such as silane gas and germane gas, heating them rapidly and in an extremely focused way in the space. As a result, the chemical bonds of the molecules of the reagents, originating a supersaturated vapor from which the nucleation of particles takes place, whose nuclei grow by coagulation until solidification. Solid materials produced in this way are single particles, such as powders (e.g. Kim et al., 2019a, 2019b) and nanotubes (e.g. Bystrzejewski et al., 2009) or coatings (e.g. Tangermann-Gerk et al., 2016).
- The *generation of fluid materials* by laser pyrolysis can lead to the formation of gases such as: syngas (e.g. Patent No. WO2019159088, 2019), mainly comprising carbon monoxide, hydrogen and methane; pure hydrogen (e.g. Baymler et al., 2018), typically generated by processing the same materials used to obtain syngas but by raising the reaction temperature to obtain a greater molecular dissociation; and ethylene. Among the generated liquids we found oils and toluene above all.
- The laser pyrolysis can be used for special *manufacturing* operations on very small components and/or with high precision. This because the atmosphere inside to the reactor, necessary to carry out the pyrolysis reaction, drastically reduce the presence of contaminants that could negatively affect the results. Among the special manufacturing there are: additive manufacturing when particularly fine surface finishes are required (e.g. Vangelatos et al., 2020), marking and cutting with ultra-fine lines (e.g. Aminuzzaman et al., 2010) and drilling.

Fig. 3 Distribution of the application fields for academia and industry

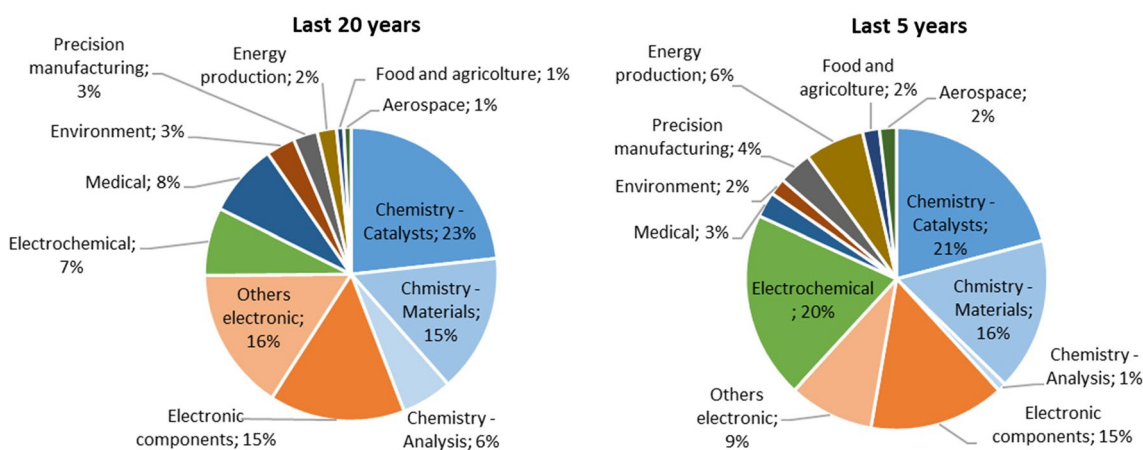
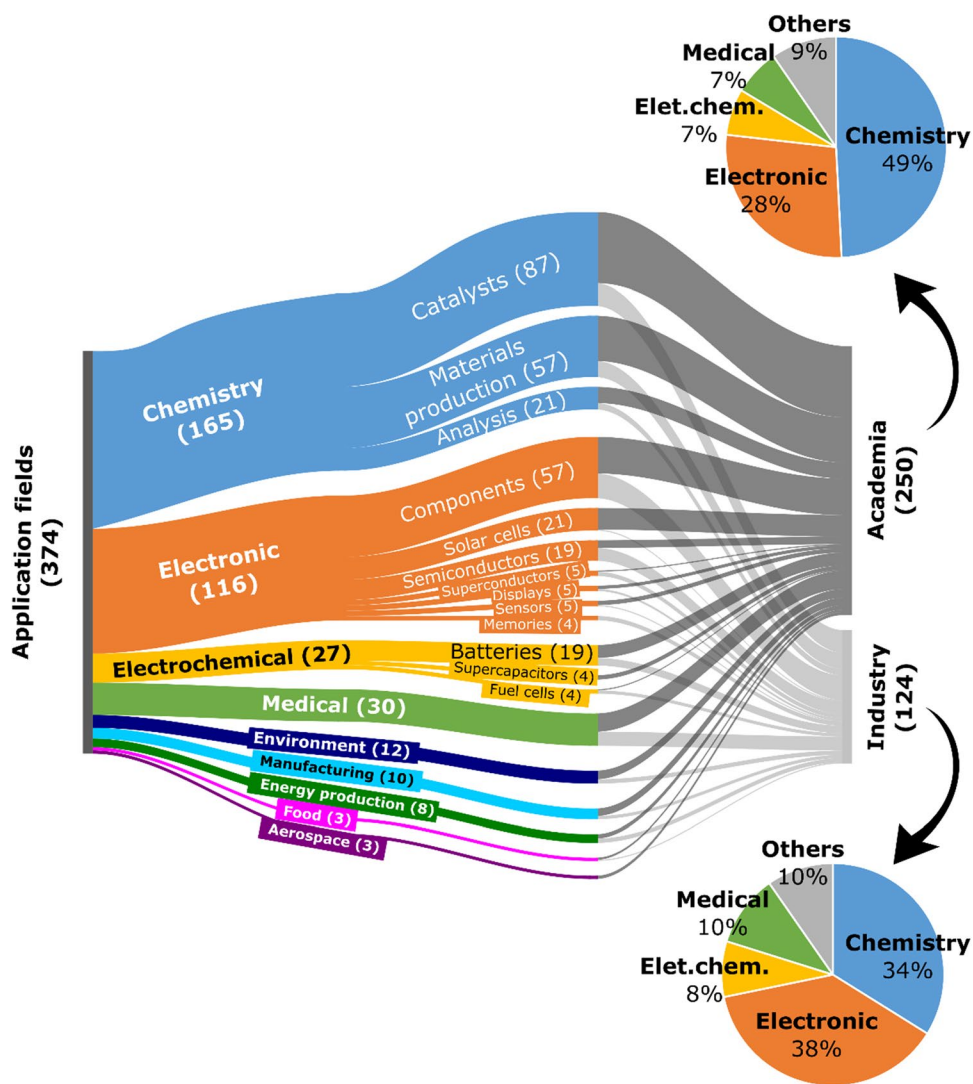
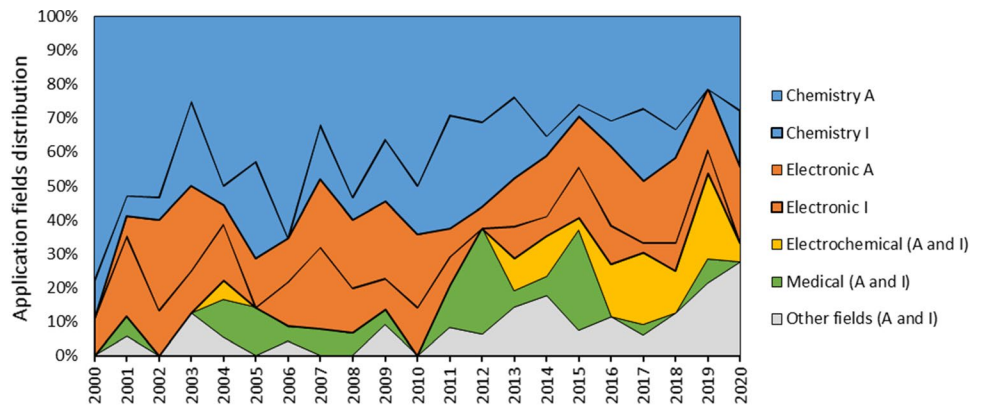


Fig. 4 Comparison of the percentage distribution of the application fields in all documents in the last 20 years and in the last 5 years

Fig. 5 Percentage distribution of the application fields during time (where A = academia and I = industry)



- The *surface treatments* (e.g. D'Amato et al., 2017) obtained with laser pyrolysis, without addition filler material, aim to obtain a certain porosity or to chemically stabilize a surface by removing a layer of material or an oxide and acting on the surface itself by plastic deformation in order to increase its hardness.

Finally, there is the use of laser pyrolysis to directly perform precision *measurements* such as spectroscopy (e.g. Marosfői et al., 2007) and *eliminating wastes*, providing them with the necessary amount of heat to perform pyrolysis (e.g. Patent No. WO2019159088, 2019).

Figure 6 summarizes the proposed classification of the functions of the laser pyrolysis, with the generic functions (in grey) and the subclasses (in white).

Table 2 reports the number of documents referring to the different described functions.

Figure 7 depicts the comparison of the identified functions between academia and industry.

Analysing the results reported in Table 2 and Fig. 7 some considerations can be drawn in relation to the analysed documents. On average, the industry works on slightly more functions than academia. Overall, laser pyrolysis is mostly used to generate materials, with over 97% of the total cases. Among them, solid materials constitute in turn the 91%, where particle production is mentioned in more than twice as many documents as coatings production. Among the other considered functions only marginally, we highlight the uses of laser pyrolysis for special manufacturing (8% of the total), and for additives, and measuring (7% of the total).

Comparing instead the distributions of the functions between academia and industry, we can note that in the first one, the generation of solids is greater than in the second one by as many as 14%. Furthermore, academia is more interested than industry in the production of particles, claimed in

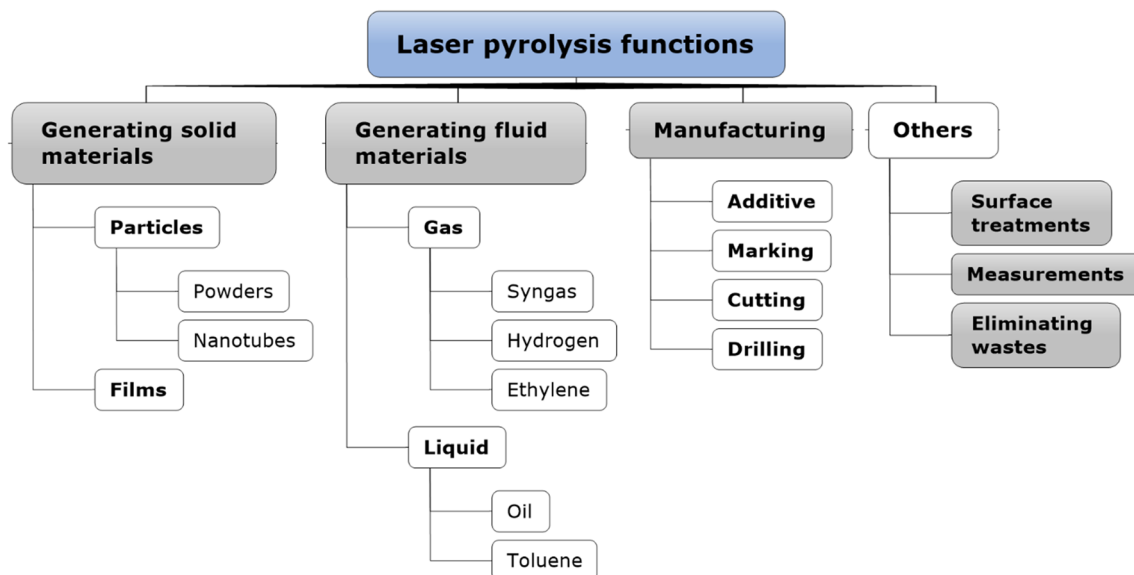


Fig. 6 Proposed classification of the identified functions of the laser pyrolysis

Table 2 Number of citations in papers/patents for each function

Functions	Number of citations in papers/patents		
	Academia	Industry	Total
<i>Generating solid materials</i>			
Particles	149	63	212
Film	69	33	102
Sub-total	218	96	314
<i>Generating fluid materials</i>			
Syngas	6	4	10
Oil	3	5	8
Hydrogen	3	2	5
Ethylene	2	1	3
Toluene	1	1	2
Sub-total	15	13	28
<i>Manufacturing</i>			
Additive	8	6	14
Marking	3	4	7
Cutting	1	5	6
Drilling	3	3	6
Sub-total	15	18	33
<i>Surface treatments</i>	5	7	12
<i>Measurements</i>	22	10	32
<i>Eliminating wastes</i>	3	3	6
Total	278	147	425

Bold values are used for the classes

almost 62% of the documents of the first one against 57% of the second one. While regarding coatings, the gap is reduced to only 2% in favour of the industry, always normalizing the number of functions by the number of documents from academia and industry. For other functions, we note the predilection of industry towards the generation of fluids (+3%) and manufacturing (+7%) compared to academia.

Finally, to provide an evidence about how the distribution of the functions changed during time, in Fig. 8, the percentage distribution considering the aggregated data of all the considered documents in the last 20 years has been compared with that resulting by considering only the documents from the last 5 years. This comparison showed that the generation of particles decreased by 8% compared to the average, while the generation of film increased by 5%. While the percentage variations of the other functions are instead more contained.

Generating solid materials

Since the contributions related to the production of particles and coatings are by far the most widespread, we decided to analyse them better, classifying them according to their physical properties and the constituting materials, to provide new data for the discuss of this result. The identified

properties of particles and coatings are: Chemical, exploiting their catalysing effect in various industrial environments as well as the affinity of polluted substances in order to clean the air or to produce water (e.g. Maskrot et al., 2006); Electrical, in terms of conductive, insulation or capacitive (e.g. Govender et al., 2014); Optical, being permeable in different ways to the light or emitting light when subjected to electric fields (e.g. Huisken et al., 2003); Magnetic, both in terms of actuation and catalytic (e.g. Kuncser et al., 2017); Mechanical, in terms of increased breaking strength (e.g. Horcher et al., 2020); Biological, ensuring biocompatibility within the human body for medical or food conservation and production purposes (e.g. Dumitrache et al., 2015); Thermal, mainly due to the high conductivity or insulation to heat transmission (e.g. Kruger et al., 2017). Furthermore, only for the coatings, other properties have also been identified, including resistance to surface corrosion (e.g. Horcher et al., 2020), hydrophobicity (e.g. Dumitrache et al., 2015) and superficial properties, i.e. roughness and hardness.

Figure 9 represents the distribution of the properties of particles and coatings in academia and industry, reporting the value of the number of documents referring to each property.

Analysing Fig. 9, we first notice two rather different distributions of the properties between the particles and the coatings. In the case of particles, chemical and electrical properties, more on an industrial level (corresponding to 59% of the total), and optical properties, especially in the academy (19% of the total), are preferred. While all other properties are claimed in just over the 25% of the total cases. In the case of coatings, the attention to electrical properties, and to the increase in surface electrical conductivity, can be noted above all, both in academia (35% of the total) and industry (40% of the total). In the other cases, the academia also shows a certain interest in surfaces and mechanical properties (19% of the total), while in industry, all the other properties are divided almost equally.

Figure 10 represents instead the distribution of the particles and coatings materials in academia and industry, reporting the value of the exact number of documents that refer to each chemical element. The identified elements can be found in form of oxides (generally) of alone as rare metals or polymers, although in many cases both particles and coatings consist of more elements (e.g. Silicon-Carbon Core-Shell Nanomaterials, Alper, 2017).

As can be seen from the analysis of Fig. 10, in the case of particles production, silicon is the most exploited material (31% of the cases), generally in form of silicon oxide or rarely silicon carbide (e.g. Hofmeister et al., 1999), followed by iron (e.g. Dumitrache et al., 2005) and carbon (15% of the cases), which in turn includes above all graphite, diamond and fullerene, although both iron and carbon have a diffusion mostly in academia. In the case of coatings, the diffusion

Fig. 7 Distribution of the functions for academia and industry

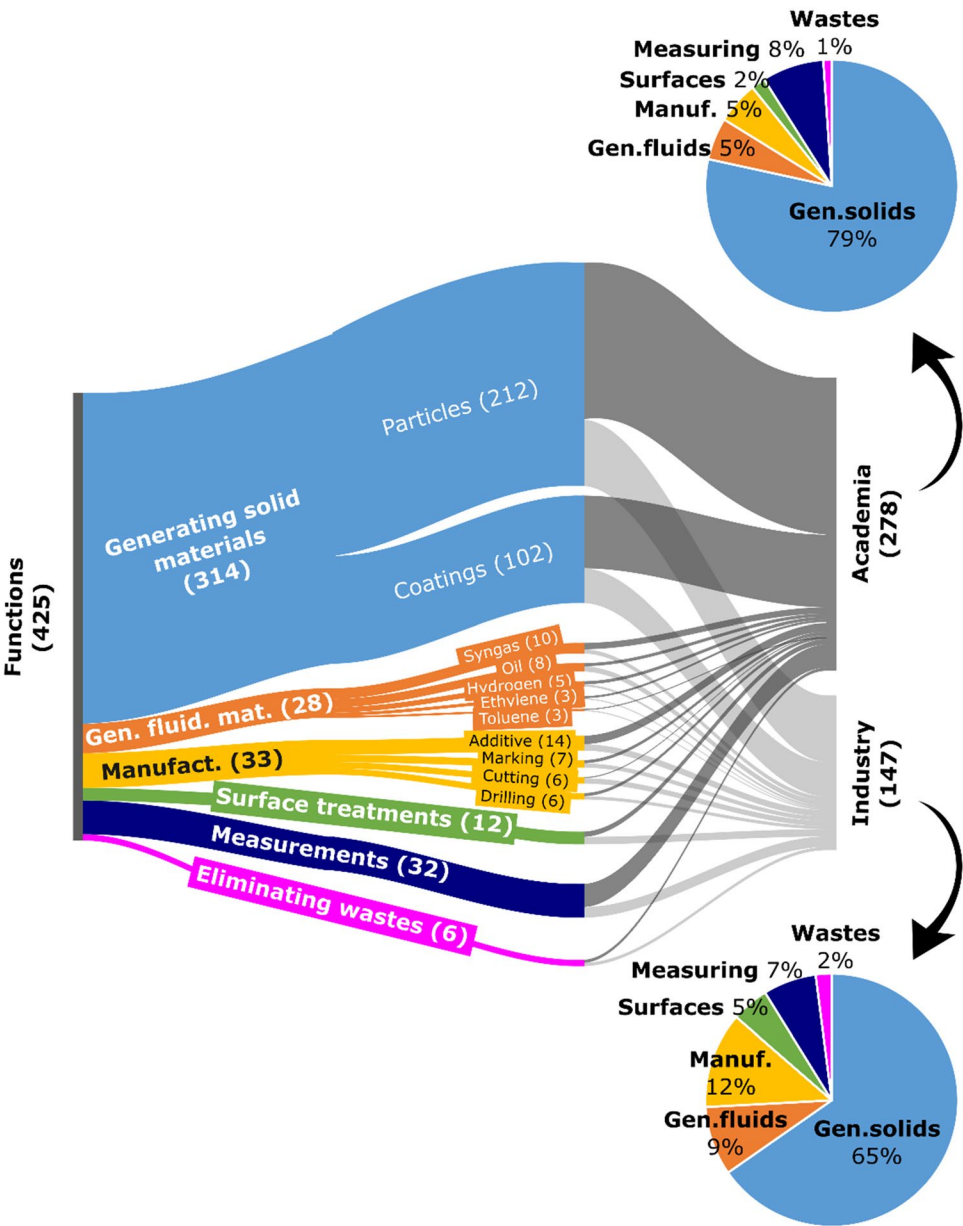


Fig. 8 Comparison of the percentage distribution of the functions in all documents in the last 20 years and in the last 5 years

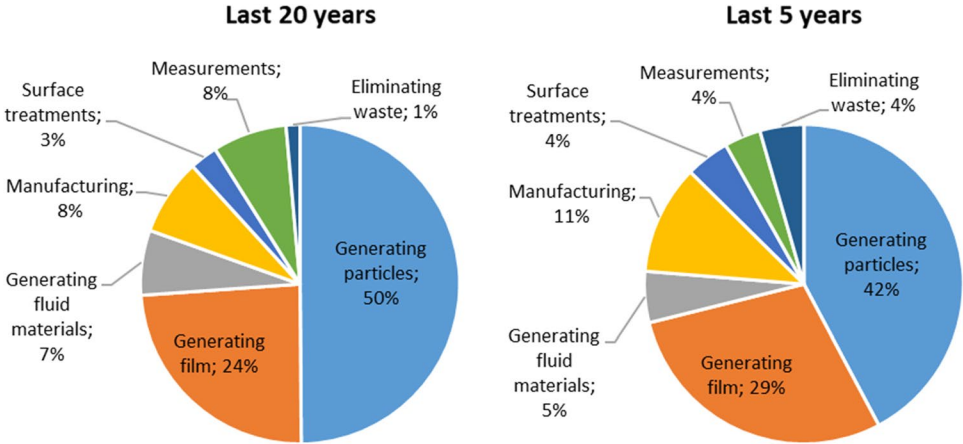


Fig. 9 Distributions of the properties of particles and coatings in academia and industry

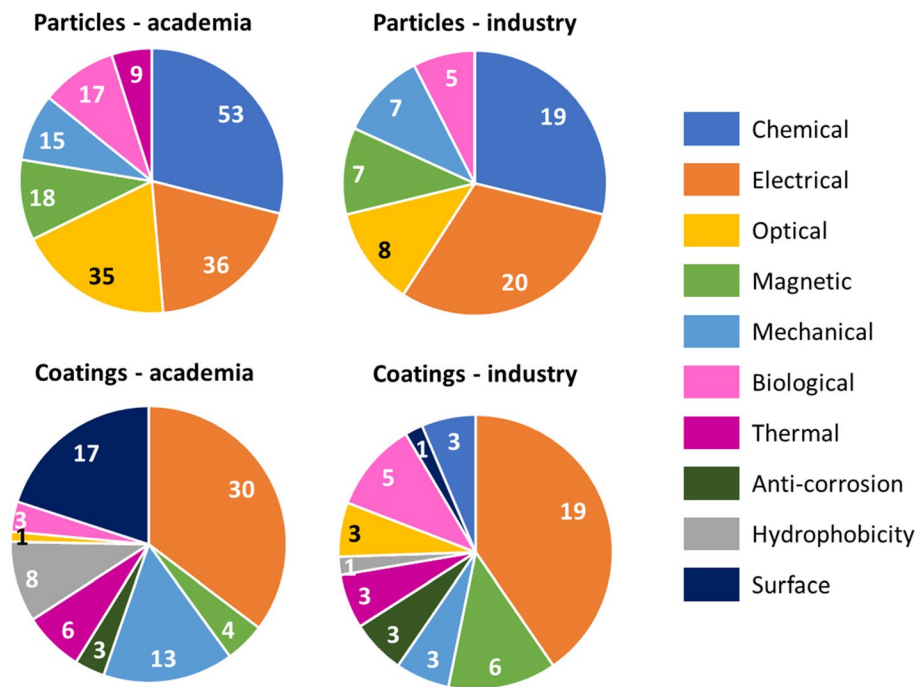
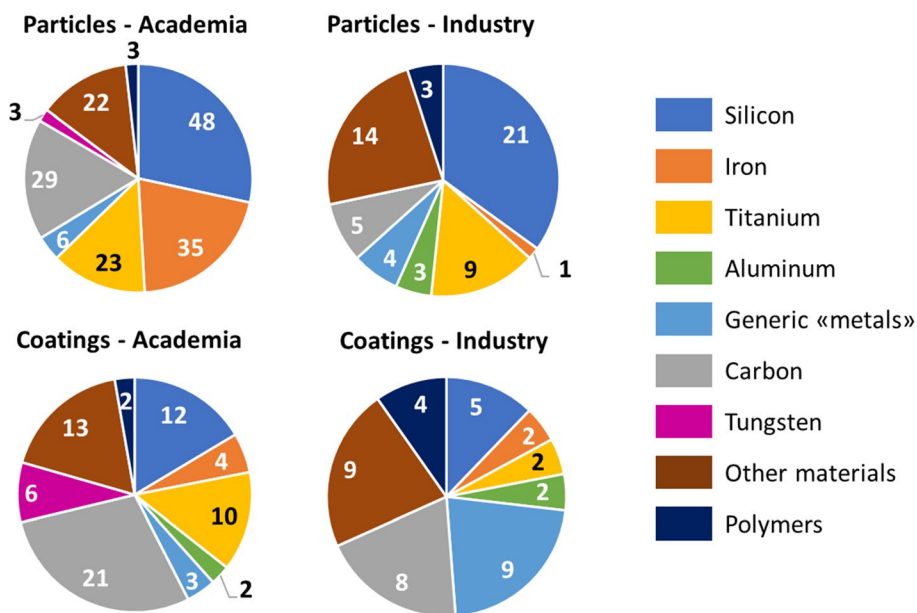


Fig. 10 Distributions of the materials of particles and coatings in academia and industry



of carbon is noted above all, linked more to the academia (17% of the cases), and mainly due to the development of graphene (e.g. Qian et al., 2011) which accounts for most of the cases in this class, as emerged by analysing the documents. Other materials of both particles and coatings are: silver, quartz, tungsten, zirconium, vanadium, zinc, boron, barium, manganese, germanium, selenium, lithium, and tin. These materials are distributed in a homogeneous way both in particles and coatings, both in academy and in industry, without any significant preference. Finally, polymers are

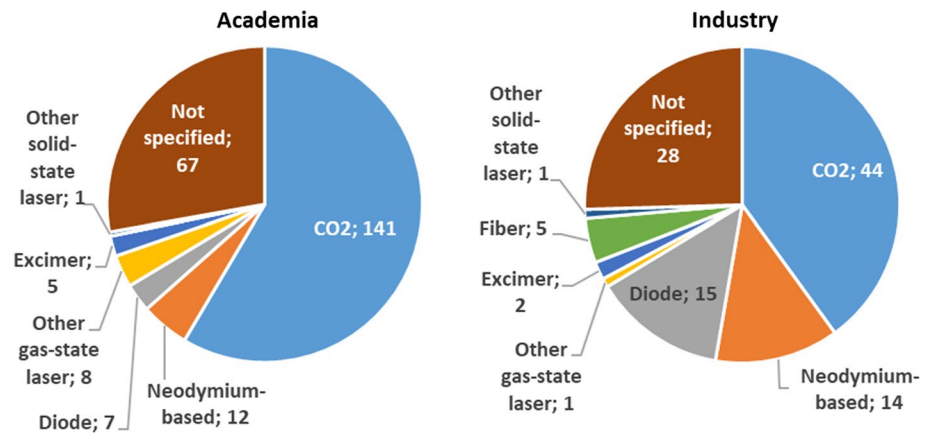
alternative to oxides and pure metals even if in very limited percentages both in particles and in coatings.

Adopted laser technologies

Types of laser

In this section, we introduce the adopted laser technologies for realizing the pyrolysis, considering only those source models and parameters explicitly declared by authors in the considered documents. Figure 11 shows

Fig. 11 Distribution of the types of laser for realizing the pyrolysis in academia and industry



the distribution of the types of lasers used for pyrolysis, respectively claimed in the contributions of the academy and industry.

As can be seen from the analysis of Fig. 11, the CO₂ laser is widely the most widespread, followed by the neodymium-based, mainly Nd:YAG, and by diode lasers. In the case of the academy, the predominance of CO₂ lasers is even more marked, in industry, solid-state laser and diodes are also used in a fair percentage of the total cases, while in more than a quarter of the total cases, the type of laser is not specified.

In general, the CO₂ lasers, which have an emission wavelength around 9–10 μm , are ones of the most widespread and well-known in the world, and ones of the first power lasers. Like other gas-state lasers, their equipment is quite voluminous, consisting of a tube for the cavity with a length at least equal to 50 cm, or more commonly to one meter. Finally, the powers are significative, and the selling price are decent.

Solid state lasers, and in particular Nd families, which emit a wavelength around 1 μm , are the most accurate. Their powers are equal or higher than CO₂ lasers, even if with a higher cost. These lasers are more easily controlled, even directly via PC, and have spectral purity and quality of the

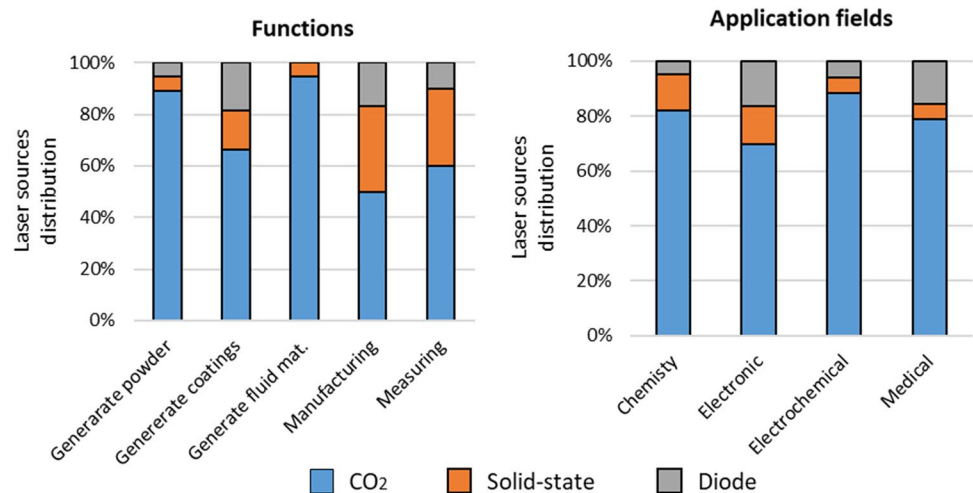
optical beam far superior to CO₂, but these characteristics are not always worth the price differences, although decreasing in the last period.

Diode lasers have emission wavelength of 600–800 nm, powers comparable to solid-state lasers, ease integration and management and a small size. Usually, their cost is lower than solid-state lasers, while the wall plug efficiency, i.e. the ratio between the optical power emitted and the electrical power necessary for their operation, is always greater than 50%. On the other hand, their optical beam is limited and much worse than solid-state lasers. For this reason, their use is generally excluded when high precision is required. High temperature stability can also be controlled, although solid-state laser is generally more reliable for this purpose.

Figure 12 shows the distribution of the main types of lasers used for pyrolysis according to the most diffused functions and application fields.

Analysing Fig. 12, the overall distribution of laser types is substantially reflected also within the single functions and application fields. The cases that differ most from the general distribution are, in the case of functions, the generation of powders and fluids, where there is a more marked

Fig. 12 Comparison between most diffused types of laser sources, functions, and application fields in laser pyrolysis



use of CO₂ lasers, manufacturing and measuring, where instead CO₂ lasers are only just over half of the total cases, and instead there is a greater use of the neodymium-based laser. In the case of application fields, on the other hand, the distributions between the different categories are more like each other and the CO₂ lasers is the more considered.

Laser performances

In this section, the performances of the types of used lasers are analysed according to their powers and fluences for

realising the pyrolysis, only in documents where such values were explicitly stated. Table 3 reports the results, by specifying the source, the types of laser and the achieved functions. Its compilation required some attention since we had to discriminate, where possible and especially in patents, the values indicated as "preferable" from those that are simply claimed. In fact, in patents there is a tendency to declare a range of values for a given sensitive parameter rather than its precise value, to obtain greater legal protection, and eventually to suggest a narrower range or a value, contained in the first range, to ensure the better performances.

Table 3 Identified values of power and fluence of the used types of lasers for realizing the main functions (where * indicates values claimed but not described as preferable)

Lasers	Functions	Document	Power (W)	Fluence (W/cm ²)
CO ₂	Generating particles	Laguna-Marco et al. (2014)	82	652
		Dumitrache et al. (2005)	55–75	1100–1500
		Govender et al. (2014)	n.a	51.2
		Réau et al. (2012)	1000–5000	150–2050
		Gavrila-Florescu et al. (2017)	130	1680
		Kim et al. (2015)	57	n.a
		Jäger et al. (2009)	n.a	850–6400
		Galvez et al. (2002)	250–800	n.a
		Leconte et al. (2007)	2400	n.a
		RO131729	100	n.a
		DE10296273	n.a	7–108
		US10023813	1200	1200 (1000*-10,000*)
		CN108465814	50–400	n.a
		CN107043259	9 (5*-55*)	n.a
		WO2017/039477	n.a	10
		WO2008/118865	104 (30*-300*)	n.a
		WO2006/051233	5000	750 (up to 25,000*)
		US7601321	58.5	2000
		US10199177	640	n.a
		FR2984867	5000 (up to)	n.a
KR101841558	200–700	n.a		
EP3395437	500	n.a		
CO ₂	Generating coatings	Tiliakos et al. (2020)	n.a	0.26
		CN111403691	40 (5*-500*)	n.a
	Generating fluid materials	BR102013031976	60 (20*-100*)	n.a
		Measurements	RU145336	n.a
Solid-state	Generating particles	Wilden and Fischer (2007)	900	n.a
	Generating coatings	CN108281490	1000	1–500
		JP5066686	n.a	0.001–0.1
		RO132432	4.8–6	n.a
		JP4799459	n.a	0.015–0.4
Diode	Generating particles	Lin et al. (2014)	106	n.a
		US20100308286	600	2000
	Generating coatings	Qiao et al. (2018)	350–800	n.a
		CN109402615	300	n.a
		JP2002274950	n.a	0.03–0.1
		CN105821400	500 (300*-800*)	n.a

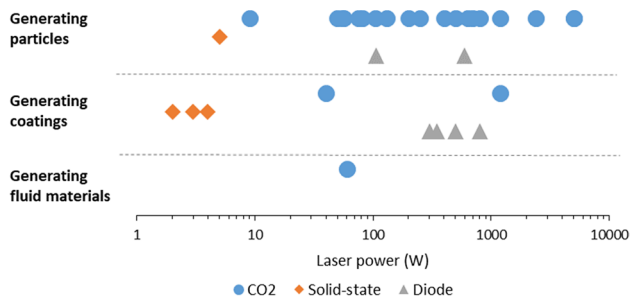


Fig. 13 Comparisons between types of laser, power, and main functions from the analysed documents

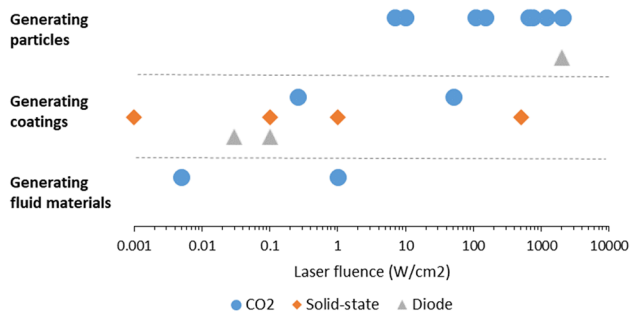


Fig. 14 Comparisons between types of laser, fluence, and main functions from the analysed documents

Figure 13 graphically represents the results about the powers of the laser (see Table 3), by considering only those explicitly declared preferable values.

Figure 14 graphically represents the results about the fluences of the laser (see Table 3), by considering only those explicitly declared preferable values.

Analysing the results shown in Figs. 13 and Fig. 14 emerges that for CO₂ lasers, the ranges of powers and fluence are much wider than in other types of lasers. While comparing the performances of the lasers for the different functions, generating particles emerged to be the one requiring the highest power and fluence and widest ranges of power, although, this is more evident for CO₂ lasers.

Discussion of the results

The obtained results communicate that laser pyrolysis technology, for some years, has been having an academic and industrial interest due to its versatility towards several different uses and applications. Although our study does not compare laser pyrolysis with competing technologies, we nevertheless believe that the detailed discussion of the obtained results, proposed in this section, may highlight some of its more unique advantages. Within this aim, in the following paragraphs, the results are discussed, by comparing functions, application fields and types of laser.

Table 4 summarizes the main advantages that have been identified for the different applications of laser pyrolysis in relation to any most suitable types of lasers.

Generating solid materials (particles and coatings)

This study clearly demonstrated that, apart from rare exceptions, laser pyrolysis is a technology mainly dedicated to the production of solids (particles and coatings), mostly nanometric in size, starting from gaseous precursors. In this field, the process has been refined over the last twenty years, significantly improving the quality of the generated solid products and allowing them to be exploited in an increasing number of different application fields (see Fig. 4). This is mainly due to the improvement of the exploited technologies and the optimization of the process parameters that have made it possible to generate particles and coatings with many different properties and materials (see Fig. 9 and Fig. 10).

The analysis of the technologies proposed in “Adopted laser technologies” section, is a possible starting point for discussing these aspects. From it, CO₂ lasers were found to be the most suitable for generating particles (see Fig. 12). A possible justification for this aspect may be due to their wide range of regulation of power and fluence during the particles production (see Fig. 13 and Fig. 14). This fact, according to Sublemontier et al. (2009), is the main advantage of this technology that allows its better adaption to the different geometric, mechanical, and magnetic properties of the nanopowders, as well as to obtain many different materials (Veintemillas-Verdaguer et al., 2003). Similar considerations can be made for the coating production, although in relation to a smaller number of results and applications fields and with a more homogeneous distribution among the types of lasers. While more detailed considerations can be made in relation to the different application fields, while also investigating the specific technological aspects.

In chemical applications, for the realization of particles and coatings with catalyst functions, where the control of the microstructural aggregation and chemical properties is required, pulsed lasers are preferable being able to generate a series of continuous heating and cooling favouring these properties (Ishikawa et al., 2016). When the goal is to maximize the production of nanoparticles and nanocoatings, continuous CO₂ lasers are particularly suitable, allowing to balance the exposure through continuous power flow (Jamkhande et al., 2019). Instead, only through the precise spatial control of the energy supplied to the gaseous precursor, which the CO₂ laser pyrolysis can ensure, a deposition of bimetallic coatings starting from the same precursor can be obtained. In this way, according to Martinez et al. (2018), the catalytic properties of the coating are improved.

In electronic applications, for the production of semiconductors, the Nd:YAG laser allows to obtain nanopowders of silicon oxides averagely having a greater purity, and therefore

Table 4 Main advantages of laser pyrolysis in relation to the application fields and the eventual most suitable laser technologies

Application fields	Laser pyrolysis advantages	Preferred types of laser
Chemistry	Producing catalytic particles and coatings with microstructural and chemical properties optimization	Pulsed CO ₂
	Maximize the production of nanostructures	Continuous CO ₂
	Realizing bimetallic coatings to increase the catalytic properties	CO ₂
	Increasing the mass production of ethylene	IR
	Reducing the energy consumption during the production of light olefins	CO ₂
Electronics	Increasing the electrical and magnetic properties of silicon oxides nanopowders used for semiconductors	Nd:YAG
	Increasing the control over the thickness of coatings/deposition layers in integrated circuits	Nd:YAG
	Improving the insulating properties of ceramic coatings	Nd:YAG
	Improving the photoelectric properties of particles and coatings used for solar cells	CO ₂
Electrochemistry	Increasing the life of the carbon nanoparticles that make up the membranes of fuel cells, and consequently their durations	CO ₂
Biomedical	Producing drug coatings with greater and more controlled biodegradability	
	Making nanopowders to treat cancer in a more localized way	Pulsed CO ₂
	Optimizing the surface finish of prostheses to reduce the time for the welding with the bone	
Waste treatment	Improving the properties of the syngas produced by the waste pyrolysis	Pulsed diode
	Improving the efficiency and reducing the process times	

better electrical and magnetic properties, than those prepared with other technologies (Liu et al., 2017). As for the realization of integrated circuits, where it is essential to guarantee a very precise control of the thickness of the deposited coating and at the same time to realize net discontinuities of the thicknesses, even in very close areas, the laser pyrolysis based on Nd:YAG preferable option, allowing to adjust the depth of penetration of the focus point very precisely (Shamardin et al., 2019). To create electrical and thermal insulators in the form of coatings, typically consisting of ceramic materials, laser pyrolysis (with Nd:YAG) has proved to be one of the most reliable options. In fact, its pulsation can be optimized to increase the microstructural quality and reducing bubbles (Tangermann-Gerk et al., 2016). Furthermore, the possibility of creating, especially with CO₂ lasers, powders and coatings with strong photoelectric properties is the basis of the recent use of laser pyrolysis in the production of solar cells (Belchi et al., 2019).

In electrochemistry, the use of CO₂ laser has instead allowed to generate various types of carbon nanoparticles used for the proton exchange membranes of fuel cells, which have a superior durability and electrical conductivity, and which therefore also allow to improve the durability of the same cells (Yeon et al., 2018).

In medical applications, the fine control on the microstructural properties of powders and coatings, which can be ensured by laser pyrolysis, can guarantee their natural and controlled degradation within the human body, thus making them particularly useful for realizing capsules for drug delivery. (Kabashin et al., 2019). The ability of laser pyrolysis to create increasingly smaller nanopowders, using CO₂ pulsed lasers, synthesizing biocompatible materials at the same time,

is the basis of their application for the treatment of cancer. This because in this field, a focused action on diseased cells, ensured by the laser, is crucial to not damage the healthy surrounding tissues (Gavrila-Florescu et al., 2017). While the control on the surface finish allows to optimize the roughness and porosity of implantable prostheses, e.g. bone scaffolds and joint replacements, to promote better surface interaction and then welding with the bone, by reducing the patient recovery times (Patent No. WO2015121369A1, 2015).

Generating fluid materials

Although laser pyrolysis has been exploited only marginally for producing fluids, this technology can guarantee two main advantages if compared to concurrent technologies, according to what we learned from the considered documents. During the production of ethylene, which is widely used in chemical industry to produce various rubbers, and synthetics plastics, IR laser can increase the production rate up to 25% compared to the conventional steam cracking method (Stadnichenko et al., 2014). While during the production of light olefins starting from hydrocarbons, CO₂ laser induced pyrolysis can instead save energy compared to other pyrolysis methods used for this purpose, which reactors also have high wall temperature and producing large amounts of undesired carbonaceous side-products (Masyuk et al., 2018).

Eliminating wastes

The development of laser pyrolysis in the field of waste elimination could open important growth prospects for this technology,

which can compete with other pyrolysis technologies. The advantages of laser pyrolysis compared to these latter, such as fixed bed, fluidized bed and hot sands, concern both the simplification of the systems, with the elimination of voluminous heating and recirculation systems of the thermal carrier, the ensured portability, and the increased heating efficiency, since mechanical energy-intensive heating mediums can be substituted by heat source directed into the raw material. Laser pyrolysis could also be better than the most modern and radiation-based pyrolysis technologies such as microwave and plasma, both by raising the reaction temperature compared to the first one and increasing the efficiency and heating rate compared to the latter, being able to focus more the transmission of heat on the raw material (i.e. waste). The experiments of Zaitsev et al. (2018) on laser pyrolysis, with pulsed diode laser, and waste gasification showed reduced processing times and good properties of the generated syngas. This latter can be considered a valid fuel because of its calorific value and the high percentage of hydrogen. Finally, Patent No. WO2019159088 (2019) proposes a particularly significant system for this application field, proposing laser pyrolysis for eliminating different types of wastes, including rubber, bitumen and tires, and the production of syngas. In this invention, the waste transits on a conveyor belt and is hit by a beam of lasers arranged in parallel that point from above. The syngas is sucked from the top of the reactor, while the ashes remain on the conveyor belt.

Other functions

Laser pyrolysis has been proposed in various sectors of manufacturing and surface cleaning, allowing some advantages, albeit with few contributions relating mostly to niche applications and which remain confined to academic research. As part of the measurement, laser pyrolysis has been an option for chromatography since the late sixties. Compared to its first applications limited to the characterization of very small portions of coal and polymers, the most recent proposals enlarged the number of analysed materials and compared to traditional gas chromatography and the chromatography based on pyrolysis (without laser), ensure the possibility to perform non-destructive tests by significantly reducing the execution times. Despite these advantages, the publication trend on the subject has been declining over the past 15 years. Among the documents identified in this context, Patent No. US10054577B2 (2015) proposes a spectroscopy method for determining chemical characteristics of geological samples, rocks and which can also be extended to stone materials for construction and concrete.

Conclusions

In this paper, a survey about the last twenty years of more than 350 publications about laser pyrolysis has been proposed to identify and compare main functions, application fields and

technological aspects. The main novelty concerns the use of both papers and patents, to provide comparative perspective on how academia and industry are moving on the subject. Each document has been manually analysed and the main outputs of this work were accurately presented and discussed. In addition, the conjunct analysis of functions, application fields and technological aspects allowed to highlight some interesting intersections particularly interesting for professionals dealing with technology transfer.

The analysis of the application fields showed the predominant use of laser pyrolysis in chemistry and electronics, where academia is more oriented towards the first field, while industry in the second. In chemistry the focus is mainly on the production of catalysts and materials, while in electronics on micro-components and solar cells. While the study of the time trend showed that these fields have been declining in the last twenty years and new opportunities are being investigated, such as the production of batteries, components for the medical sector and for environmental protection.

For what concerns the functions carried out with laser pyrolysis, academia resulted more interested in the production of nanoparticles, while industry in coatings characterized by a greater variety of physical and chemical properties. Among them, chemical, electronic (e.g. super or semi conduction), optical (e.g. photoconduction) and magnetic properties are the most searched both by academia and industry.

The analysis of the types of lasers highlighted the predominant use of CO₂ lasers, followed at a distance by neodymium-based and diode ones. The analysis of the laser power and fluence ranges also showed the versatility of the CO₂ laser compared to others, although this data should be read mainly in function of the large number of CO₂ laser applications identified among the analysed documents. According to the analysis of the power and fluence of lasers, patents tend to be less reliable, providing ranges and values that are sometimes even imaginative, without considering the real industrial realization.

Finally, the intersection between the three aspects of the analysis allowed to highlight some common advantages of laser pyrolysis, and to hypothesize, by virtue of these characteristics, possible future expansions. Among them there are the production of bi-material nanoparticles and coatings with different properties, especially useful in medicine for the cure of cancer, and the waste (tyres) processing, where laser pyrolysis can be more efficient than traditional pyrolysis, by reducing the process energy consumption, increasing the cycle time, and obtaining syngas.

The planned future developments of this study concern an expansion towards the technological aspects, in terms of the types of lasers and systems, as well as on their current state of development, which can be used to obtain the different functions in the different application fields. In addition, the most innovative and strategic fields of application, even

purely theoretic, which have been highlighted in this study, could be monitored, updating this analysis periodically with new documents, to intercept new opportunities as soon as their development could take off.

Appendix

See Table 5.

Table 5 Classification of all the considered sources divided between papers and patents

Sources	Academia (A) or Industry (I)	Fields	Functions	Lasers
<i>Papers</i>				
Abd Elrahman and Mansour (2019)	A	Medical	Particles	n.a
Ahlhelm et al. (2013)	A	Precision manufacturing	Additive	n.a
Al Sandouk-Lincke et al. (2013)	A	Environment	Measurements, Drilling	n.a
Alexandrescu et al. (2010a)	A	Materials production	Particles	CO ₂
Alexandrescu et al. (2010b)	A	Electronic components	Particles	CO ₂
Alexandrescu et al. (2009)	A	Electronic components	Particles	CO ₂
Alexandrescu et al. (2004)	A	Catalysts	Particles	CO ₂
Allen and Russell (2004)	A	Analysis	Measurements	CO ₂
Allen and Russell (2002)	A	Catalysts	Particles	CO ₂
Aminuzzaman et al. (2010)	A	Materials production	Particles, Marking	Ion
Aminuzzaman et al. (2009)	A	Electronic components	Film	CO ₂
Aminuzzaman et al. (2008)	A	Solar cells	Film	CO ₂
Bachmatiuk et al. (2009)	A	Electronic components	Particles	CO ₂
Badoi et al. (2016)	A	Materials production	Particles	n.a
Bădoi et al. (2015)	A	Medical	Particles	n.a
Bahgat (2006)	A	Materials production	Particles	n.a
Baia et al. (2011)	A	Catalysts	Particles	CO ₂
Balas et al. (2018)	A	Electronic components	Film	CO ₂
Barrault et al. (2009)	A	Environment	Particles	CO ₂
Baskakov et al. (2018)	A	Catalysts	Particles	Excimer
Belchi et al. (2019)	A	Solar cells	Particles, Film	n.a
Bhattacharjya et al. (2018)	A	Supercapacitors	Film	CO ₂
Bodzay et al. (2009)	A	Analysis	Measurements	CO ₂
Bomatí-Miguel et al. (2008)	A	Catalysts	Particles	CO ₂
Bomatí-Miguel et al. (2006)	A	Materials production	Particles	CO ₂
Bomatí-Miguel et al. (2005)	A	Medical	Particles	CO ₂
Botti et al. (2001)	A	Catalysts	Particles	CO ₂
Bouclé et al. (2005)	A	Catalysts	Particles	Ion, He_Ne
Bouhadoun et al. (2017)	A	Catalysts	Particles	CO ₂
Bouhadoun et al. (2015)	A	Catalysts	Particles	CO ₂
Bourrioux et al. (2017)	A	Batteries	Particles	CO ₂
Bystrzejewski et al. (2009)	A	Materials production	Particles	CO ₂
Bystrzejewski et al. (2008)	A	Catalysts	Particles	CO ₂
Chen et al. (2020)	A	Catalysts	Particles	CO ₂ , excimer
Chen et al. (2013)	I	Electronic components	Film	Diode
Chen and Mao (2006)	A	Semiconductors	Film	CO ₂
Chizhik et al. (2009)	A	Solar cells	Particles	CO ₂
Choi et al. (2017)	A	Catalysts	Particles, Film	n.a
Chou et al. (2007)	A	Electronic components	Film	CO ₂
Colder et al. (2004)	A	Electronic components	Particles	CO ₂
Combemale et al. (2009)	A	Electronic components	Particles	CO ₂

Table 5 (continued)

Sources	Academia (A) or Industry (I)	Fields	Functions	Lasers
Costo et al. (2015)	A	Medical	Particles	n.a
Costo et al. (2012)	A	Medical	Particles	CO ₂
Coupé et al. (2012)	I	Catalysts	Particles	CO ₂
Crisan et al. (2020)	A	Sensors	Particles	CO ₂
D'Amato et al. (2017)	A	Environment	Surface treatments	CO ₂
D'Amato et al. (2007)	A	Catalysts	Particles	CO ₂
Das et al. (2017)	A	Materials production	Particles, Measurements	n.a
David et al. (2006)	A	Materials production	Film	Diode
David and Gaume (2015)	A	Materials production	Particles	CO ₂
de Araujo et al. (2017)	A	Batteries	Film	CO ₂
De Castro et al. (2011)	A	Catalysts	Particles, Film	CO ₂
De Castro et al. (2008)	A	Materials production	Particles	CO ₂
Depero et al. (2000)	A	Catalysts	Particles	n.a
Dez et al. (2004)	A	Materials production	Particles, Film	CO ₂
Di Nunzio and Martelli (2006)	A	Materials production	Particles	CO ₂
Dinetz et al. (2002)	A	Catalysts	Syngas	Ion
Dohčević-Mitrović et al. (2006)	A	Semiconductors	Particles	Nd
Dumitrache et al. (2019)	A	Electronic components	Particles	n.a
Dumitrache et al. (2005)	A	Catalysts	Particles, Film	CO ₂
Dumitrache et al. (2004)	A	Materials production	Film	CO ₂
Duty et al. (2003)	A	Precision manufacturing	Film, surface treatments	n.a
Erogbogbo et al. (2011)	A	Solar cells	Particles	n.a
Escamilla-Pérez et al. (2019)	I	Batteries	Film	n.a
Fa et al. (2006)	A	Semiconductors	Particles	CO ₂
Falconieri et al. (2009)	A	Solar cells	Particles	n.a
Figgemeier et al. (2007)	A	Solar cells	Film	CO ₂
Fleaca et al. (2016)	A	Catalysts	Particles	n.a
Fleaca et al. (2015a)	A	Materials production	Particles	CO ₂
Fleaca et al. (2015b)	A	Catalysts	Particles	n.a
Fleaca et al. (2014)	A	Supercapacitors	Particles	n.a
Fleaca et al. (2013)	A	Catalysts	Particles	CO ₂
Florescu et al. (2007)	A	Medicine	Particles	CO ₂
Gadallah et al. (2013)	A	Aerospace	Particles	n.a
Galvez et al. (2002)	A	Analysis	Particles, measurements	CO ₂
Gavrila-Florescu et al. (2017)	A	Medical	Particles	CO ₂
Gavrila-Florescu et al. (2007)	A	Materials production	Particles	CO ₂
Gilmour et al. (2016)	A	Materials production	Measurements	n.a
Govender et al. (2014)	A	Electronic components	Film	CO ₂
Govender et al. (2011)	A	Catalysts	Film	CO ₂
Greenwood (2011)	A	Catalysts	Particles	Neodymium
Greenwood et al. (2002)	A	Analysis	Measurements	Neodymium
Grimes et al. (2000)	A	Catalysts	Particles	CO ₂
Guerrero et al. (2015)	A	Materials production	Surface treatments	Neodymium, CO ₂
Gueunier-Farret et al. (2006)	A	Semiconductors	Film	CO ₂
Han and Zettl (2002)	A	Analysis	Measurements	diode
Herlin-Boime et al. (2004)	A	Catalysts	Particles	CO ₂
Herring et al. (2003)	A	Catalysts	Particles	CO ₂
Horcher et al. (2020)	I	Precision manufacturing	Film	Neodymium

Table 5 (continued)

Sources	Academia (A) or Industry (I)	Fields	Functions	Lasers
Huisken et al. (2003)	A	Displays	Particles	CO ₂
Huisken et al. (2002)	A	Displays	Particles	CO ₂
Huminic et al. (2020)	A	Catalysts	Syngas	CO ₂
Huminic et al. (2017)	A	Materials production	Particles	n.a
Huminic et al. (2016)	A	Materials production	Measurements	CO ₂
Huminic et al. (2015)	A	Materials production	Particles	CO ₂
Ilie et al. (2018)	A	Catalysts	Ethylene	CO ₂
Ilie et al. (2017)	A	Analysis	Measurements	CO ₂
Ivan et al. (2019)	A	Catalysts	Particles, Film	n.a
Jäger et al. (2009)	A	Environment	Particles, Drilling	CO ₂
Jäger et al. (2006)	A	Materials production	Particles	CO ₂
Jang et al. (2020)	A	Semiconductors	Particles	CO ₂
Jeong et al. (2017)	A	Superconductors	Film	n.a
Kabashin et al. (2019)	A	Medical	Particles	Diode
Kassiba et al. (2002)	A	Analysis	Measurements	CO ₂
Kawada et al. (2019)	I	Sensors	Particles, Drilling	n.a
Khan et al. (2015)	I	Medical	Particles	n.a
Kim et al. (2019a)	I	Batteries	Particles	n.a
Kim et al. (2019b)	A	Batteries	Film	n.a
Kim et al. (2017)	A	Batteries	Particles	n.a
Kim et al. (2015)	A	Electronic components	Film	CO ₂
Kim et al. (2014)	A	Environment	Particles	CO ₂
Kim et al. (2014)	A	Batteries	Particles	CO ₂
Kintz et al. (2015)	A	Solar cells	Film	CO ₂
Kobayashi et al. (2011)	A	Precision manufacturing	Film	Ion
Kobayashi et al. (2010)	A	Electronic components	Particles	Ion
Kostecki et al. (2002)	A	Electronic components	Particles, Marking	n.a
Krauss and Motz (2002)	A	Electronic components	Film	n.a
Kruger et al. (2017)	A	Catalysts	Particles	CO ₂
Kushnir and Sandén (2008)	A	Solar cells, Electronic components	Particles	CO ₂
Kuzuya et al. (2002)	A	Analysis	Measurements	Neodymium
Kwok and Chiu (2003)	A	Catalysts	Film	CO ₂
Laguna-Marco et al. (2014)	A	Electronic components	Particles	CO ₂
Leconte et al. (2007)	A	Medical	Particles	CO ₂
Leconte et al. (2006)	A	Materials production	Particles	CO ₂
Ledoux et al. (2009)	A	Electronic components	Film	CO ₂
Ledoux et al. (2002)	A	Catalysts	Particles	CO ₂
Ledoux et al. (2001)	A	Catalysts	Particles	CO ₂
Ledoux et al. (2000)	A	Catalysts	Particles	n.a
Lee et al. (2013)	A	Solar cells, Medical	Particles	CO ₂
Lee et al. (2008)	A	Catalysts	Film	CO ₂
Li et al. (2004)	A	Materials production	Film	CO ₂
Li et al. (2003)	A	Semiconductors	Particles	CO ₂
Lin et al. (2014)	A	Electronic components	Particles	diode
Liu et al. (2018)	A	Electronic components	Film	n.a
Liu et al. (2017)	A	Materials production	Particles, Film	n.a
Liu et al. (2000)	A	Analysis	Measurements	Neodymium
Lomello et al. (2012)	A	Catalysts	Particles	No

Table 5 (continued)

Sources	Academia (A) or Industry (I)	Fields	Functions	Lasers
Ma et al. (2009)	A	Solar cells	Particles	CO ₂
Malekzadeh et al. (2020)	I	Materials production	Particles	n.a
Malumbres et al. (2015)	A	Catalysts	Particles	n.a
Malumbres et al. (2013)	A	Materials production	Particles	n.a
Marosfői et al. (2007)	A	Analysis	Measurements	CO ₂
Martelli et al. (2000)	A	Materials production	Particles	CO ₂
Martin et al. (2008)	A	Electronic components	Particles	CO ₂
Martins et al. (2019)	A	Sensors, Food production	Surface treatments, Measurements	CO ₂
Martinez et al. (2018)	A	Catalysts	Particles	Ion
Martínez et al. (2012)	A	Materials production	Particles	CO ₂
Mas et al. (2020)	A	Materials production, Catalysts	Particles	CO ₂
Maskrot et al. (2006)	A	Catalysts	Particles	CO ₂
Masyuk et al. (2018)	A	Energy production	Syngas	CO ₂
Mathews et al. (2011)	A	Precision manufacturing	Film	Neodymium
Mejías et al. (2008)	A	Medical	Particles	n.a
Melhem et al. (2013)	A	Solar cells	Film	n.a
Melhem et al. (2011)	A	Solar cells	Particles	n.a
Meruva et al. (2004)	I	Analysis	Measurements	Neodymium
Metz et al. (2004)	I	Analysis	Measurements	Neodymium
Minnekhanov et al. (2017)	A	Catalysts	Particles	CO ₂
Morjan et al. (2012)	A	Medical	Particles	n.a
Morjan et al. (2010)	A	Materials production	Particles, Film	CO ₂
Morjan et al. (2009)	A	Materials production	Particles	CO ₂
Morjan et al. (2003)	I	Catalysts	Particles	CO ₂
Murakami et al. (2003)	A	Analysis	Measurements	Neodymium
Mwakikunga et al. (2008a)	A	Analysis	Particles, Film, Measurements	CO ₂
Mwakikunga et al. (2008b)	A	Catalysts	Particles	CO ₂
Ning et al. (2019)	A	Electronic components	Film	n.a
Nurk et al. (2015)	A	Batteries	Film	n.a
Orlanducci et al. (2004)	A	Catalysts	Particles	CO ₂
Park et al. (2012)	A	Solar cells	Particles	CO ₂
Petcu et al. (2000)	A	Catalysts	Toluene	CO ₂
Pignon et al. (2008)	A	Catalysts	Particles	CO ₂
Pokorná et al. (2004)	A	Materials production	Film	CO ₂
Popovici et al. (2007)	A	Sensors, Catalysts, Medical	Particles	CO ₂
Pourchez et al. (2012)	I	Medical	Particles	CO ₂
Pozio et al. (2014)	A	Batteries	Film	CO ₂
Prati et al. (2014)	A	Analysis	Measurements	n.a
Qi-Chen et al. (2017)	A	Electronic components	Film	n.a
Qiao et al. (2018)	A	Electronic components	Film	Diode
Rahimi et al. (2016)	A	Sensors	Film	CO ₂
Réau et al. (2012)	A	Catalysts	Particles	CO ₂
Reynaud et al. (2001)	A	Environment	Measurements	CO ₂
Roberts et al. (2013)	A	Electronic components	Film	Solid state
Rohani (2018)	A	Supercapacitors	Particles	n.a
Rohani and Bae (2017)	A	Catalysts	Particles	CO ₂
Rufino et al. (2011)	A	Materials production	Particles	CO ₂

Table 5 (continued)

Sources	Academia (A) or Industry (I)	Fields	Functions	Lasers
Russell and Yee (2005)	A	Analysis	Measurements	Neodymium
Rybalovskii et al. (2012)	A	Catalysts	Particles	n.a
Sandu et al. (2004)	A	Precision manufacturing	Film	n.a
Scarisoreanu et al. (2020)	A	environment	Particles	n.a
Scarisoreanu et al. (2019)	A	Catalysts	Particles	n.a
Scarisoreanu et al. (2017)	A	Electronic components	Film	CO ₂
Scarisoreanu et al. (2007)	A	Catalysts	Film	CO ₂
Schinteie et al. (2013)	A	Materials production	Particles	n.a
Shimoda (2018)	A	Catalysts	Particles, Film	n.a
Shin et al. (2020)	A	Precision manufacturing	Additive	CO ₂ , excimer
Simakin et al. (2000a)	A	Materials production	Film	Ion
Simakin et al. (2000b)	A	Materials production	Film	Ion
Simon et al. (2010)	A	Solar cells	Particles	CO ₂
Sourice et al. (2016)	A	Batteries	Particles	n.a
Sourice et al. (2015)	A	batteries	Particles	CO ₂
Steglich et al. (2012)	A	Environment	Measurements	Neodymium
Sublemontier et al. (2011)	A	Solar cells, Medical	Particles	CO ₂
Sublemontier et al. (2009)	A	Solar cells, Medical	Particles	CO ₂
Tangermann-Gerk et al. 2016	I	Electronic components	Film	Neodymium
Ténégal et al. (2001)	A	Catalysts	Particles	CO ₂
Ténégal et al. (2000)	A	Catalysts	Particles	CO ₂
Tiliakos et al. (2020)	A	n.a	Film	n.a
Tiliakos et al. (2018)	A	Supercapacitors	Film	n.a
Tiliakos et al. (2016)	A	Electronic components	Particles, Film	CO ₂
Tóth and Piglmayer (2004)	A	Batteries	Film, Drilling	n.a
Vangelatos et al. (2020)	A	Precision manufacturing	Additive	Excimer
van't Zand, (2012)	A	Medical	Particles	Diode
Veintemillas-Verdaguer et al. (2003)	A	Medical	Particles	CO ₂
Veintemillas-Verdaguer et al. (2002)	A	Materials production	Particles	CO ₂
Veintemillas-Verdaguer et al. (2001)	A	Catalysts	Particles	CO ₂
Vladimirov et al. (2014)	A	Catalysts	Particles	CO ₂
Vladimirov et al. (2011)	A	Catalysts	Particles	CO ₂
Wang et al. (2019)	A	Food production	Particles	n.a
Wang et al. (2017)	A	Batteries	Particles	n.a
Wang et al. (2015)	A	Solar cells	Particles	n.a
Watanabe et al. (2005)	A	Catalysts	Film	n.a
Watanabe et al. (2003)	I	Materials production	Film	Neodymium
Watanabe et al. (2002)	A	Catalysts	Film	CO ₂
Wei and Xu (2012)	I	Materials production	Measurements	n.a
Wilden and Fischer (2007)	A	Catalysts	Particles	Neodymium
Xu and Hu (2017)	I	Catalysts	Particles	Yb, fiber, diode
Xue et al. (2016)	A	Materials production	Film	n.a
Yeon et al. (2019)	A	Fuel cells	Particles, Film	CO ₂
Yoshioka and Ishiwatari (2002)	A	Analysis	Measurements	CO ₂
Zhao et al. (2017)	A	Materials production	Film	n.a
Zhao et al. (2001)	A	Electronic components	Particles	CO ₂

Table 5 (continued)

Sources	Academia (A) or Industry (I)	Fields	Functions	Lasers
<i>Patents</i>				
AT544513	I	Electronic components	Particles	n.a
BR102013031976	A	Catalysts	Syngas, Hydrogen	CO ₂
CN101215161	I	Electronic components	Particles	Neodimium
CN101318657	I	Electronic components	Particles	Neodymium
CN102676197	I	Environment, Energy production	Oil, Measurements	n.a
CN103630669	I	Catalysts, Environment	Oil, Syngas, Measurements	n.a
CN104198381	A	Catalysts	Oil	n.a
CN105288621	A	Medical	Film	CO ₂
CN105821400	I	Catalysts	Film	Diode
CN106083059	A	Aerospace, Electronic components	Particles, Additive	n.a
CN106644722	I	n.a	Particles, Drilling	n.a
CN107043259	I	Catalysts	Particles, Additive	CO ₂
CN107838172	I	Energy production	Syngas, Generating electricity, Eliminating waste	Neodymium
CN108281490	A	Electronic components	Particles, Film	Neodymium
CN108414035	A	Electronic components	Film, Cutting	Neodymium
CN108465814	I	Materials production	Particles, Additive	CO ₂
CN109052889	I	Waste	Eliminating waste	n.a
CN109128163	A	Materials production, aerospace	Particles, Additive	n.a
CN109402615	I	Semiconductors, Electronic components	Film	Diode
CN110372390	A	Semiconductors	Film, Additive	n.a
CN110451755	I	Energy production	Eliminating waste	n.a
CN110512193	I	Energy production	Particles, Additive	Neodymium
CN110518256	A	Materials production	Film, Marking, Surface treatments	Neodymium
CN110520381	A	Waste	Film	Excimer
CN110548174	A	Energy production	Eliminating waste	n.a
CN110632165	A	Energy production	Eliminating waste	n.a
CN111018537	A	Materials production	Particles, Additive	n.a
CN111283334	I	Materials production, Precision manufacturing	Film, Cutting	n.a
CN111403691	I	batteries	Film, Cutting	CO ₂
CN1428193	A	Catalysts	Particles, Ethylene, Propene	CO ₂
CN201735397	A	Catalysts	Syngas, Hydrogen	CO ₂
CN204086108	A	Solar cells	Oil	n.a
DE10296273	I	Electronic components	Particles	CO ₂
DE60144572	I	Electronic components, Memories	Marking	Excimer
EP1697257	I	Catalysts	Particles	CO ₂
EP2040772	I	Medical	Film	CO ₂
EP2183058	I	Catalysts	Particles	CO ₂
EP2889271	I	Fuel cells, Materials production	Particles, Oil	CO ₂
EP2889272	I	Fuel cells, Materials production	Particles, Oil	CO ₂
EP2922626	I	Biomedical	Particles	n.a

Table 5 (continued)

Sources	Academia (A) or Industry (I)	Fields	Functions	Lasers
EP3246436	I	Batteries, Fuel cells, Electronic components	Film	CO ₂
EP3395437	I	Electronic components	Particles	CO ₂
US10023813	A	Catalysts	Particles	CO ₂
FR2920965	I	Catalysts	Particles, Syngas	n.a
FR2937419	I	Semiconductors	Particles	CO ₂
FR2984758	I	Catalysts, Materials production	Particles	Fiber
FR2984766	I	Materials production	Particles	Fiber
FR2984867	I	Materials production	Particles	CO ₂
FR3082768	I	Batteries	Particles	CO ₂
JP2002255525	I	Superconductors	Film	n.a
JP2002274950	I	Superconductors	Film, Drilling	Diode
JP2002313147	I	Semiconductors	Film	Excimer
JP2003342013	I	Electronic components	Film	CO ₂
JP2006256294	I	Memories	Film	Diode
JP2013021251	I	Semiconductors	Film, Marking	CO ₂
JP2019079659	I	Batteries	Film	CO ₂ , fiber, neodymium, diode
JP3962283	I	Semiconductors	Film	Diode, krypton
JP4344629	I	Electronic components	Particles, Film, Surface treatments	Diode
JP4629663	I	Catalysts, Precision manufacturing	Particles, Cutting, Measurements	n.a
JP4799459	I	n.a	Film, Marking	Neodymium
JP4833082	I	Food production	Particles	CO ₂
JP4963062	I	Memories	Film	Neodymium
JP5066686	I	Superconductors	Film	Neodymium
JP6257682	I	Displays, Solar cells	Particles	CO ₂
KR100893183	I	Catalysts	Particles	CO ₂
KR101839212	A	Displays	Film	CO ₂
KR101841558	I	Catalysts	Particles	CO ₂
KR10-1918935	A	Catalysts	Particles	CO ₂
KR10-2002853	A	Batteries	Particles	n.a
KR10-2020-0010739	A	Electronic components	Particles	CO ₂
KR10-2118865	I	Catalysts	Particles	CO ₂
KR20120084193	A	Electronic components	Film	n.a
KR20170121985	I	Electronic components	Particles	n.a
WO2006/051233	I	Electronic components	Particles	CO ₂
PL1963004	I	Materials production	Particles	CO ₂
RO126660	I	Electronic components, Medical	Particles	n.a
RO129669	I		Particles	CO ₂
RO130505	I	Electronic components	Particles	n.a
RO131386	I	Electronic components, Medical	Particles	CO ₂ , diode
RO131387	I	Electronic components, Medical	Particles	n.a
RO131388	I	Electronic components, Medical	Particles	n.a
RO131389	I	Electronic components	Particles	n.a
RO131436	I	Medical	Particles	CO ₂ , neodymium

Table 5 (continued)

Sources	Academia (A) or Industry (I)	Fields	Functions	Lasers
RO131631	I	Analysis	Particles	CO ₂ , diode
RO131728	I	Analysis	Particles	CO ₂
RO131729	I	Analysis	Particles	CO ₂ , diode
RO132432	A	Catalysts	Film	Neodymium
RO133164	I	Materials production, Catalysts	Film	Neodymium
RO133406	I	Materials production	Particles, Film, Additive	CO ₂
RU145336	I	Analysis	Measurements	CO ₂
RU2252280	I	Catalysts	Film, Marking, Surface treatments	n.a
RU2326994	I	Semiconductors	Particles	Diode
RU2403499	I	Catalysts	Syngas, Oil	n.a
RU2414420	I	Materials production	Particles	Neodymium
RU2472870	I	Electronic components	Film	n.a
RU2478398	I	Medical	Film, Additive	n.a
RU2602568	I	n.a	Particles	n.a
TW201802868	I	Semiconductors	Particles	Neodymium
UA26961	A	Materials production	Particles, Film, Additive	CO ₂
US10054577	I	Environment	Measurements	n.a
US10160650	I	Electronic components, medical	Particles, Additive	n.a
US10199177	A	Electronic components, solar cells	Particles	CO ₂
US10598012	I	Environment	Cutting, Measurements	Fiber
US10673062	I	Electronic components, batteries	Particles	CO ₂
US20060225534	I	Medical, Electronic components	Particles, Film, Toluene	CO ₂
US20070023038	I	Medical	Particles, Film	n.a
US20080008216	I	Semiconductors	Film	Diode
US20100006187	I	Materials production	Surface finishing, Plastic deforming, Measurements	n.a
US20100308286	A	Electronic components, Solar cells	Particles	Diode
US20120128542	I	Semiconductors	Particles	CO ₂
US20190388865	I	Catalysts	Particles	CO ₂
US20200227884	I	Electronic components	Film, cutting	Diode
US7601321	I	Semiconductors	Particles, surface treatments	CO ₂
US8054558	I	Displays	n.a	n.a
US9096440	I	Superconductors, memories	Film	Neodymium
WO2008/118865	I	Semiconductors	Particles	CO ₂
WO2008/143716	I	Semiconductors	Particles	CO ₂
WO2012/175462	I	Catalysts	Particles	CO ₂
WO2015/183122	I	Catalysts	Olefins, Hydrogen	CO ₂
WO2017/039477	I	Catalysts	Particles, Ethylene, Hydrogen,	CO ₂
WO2019/159088	A	Energy production	Syngas, Hydrogen, Oil, Eliminating waste	CO ₂

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