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Perspective

Evolution and Prospects of Hydrothermal Carbonization

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Abstract: Hydrothermal carbonization enables the valorization of biomass via thermochemical conversion into various products. Today, this technology is experiencing a situation similar to that experienced in the past by other process technologies. Of these technologies, some have become important industrial realities, such as reverse osmosis, while others have never been able to establish themselves fully. This paper presents a brief overview of this technology's current status, highlighting its strengths and various drawbacks. The primary purpose of the research activity is to identify a possible future scenario toward which this technology is heading. Hydrothermal carbonization has already been established on a laboratory scale for some time, and now it is in a transitional phase between pilot-scale and industrial-scale applications. The interest that HTC has aroused and continues to arouse is evidenced by the growing number of publications and patents published. In particular, the uniform percentage of patents filed in various countries testifies to the worldwide interest. This technology has advantages but also some bottlenecks that have yet to be overcome. Process integration, higher-capacity plants, and the use of Industry 4.0 technologies seem to be the most interesting options to overcome the last limiting factors and make hydrothermal carbonization an established industrial reality.

Keywords: hydrothermal carbonization; hydrochar; waste valorization; thermochemical conversion; upgrading; economies of scale

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1. Hydrothermal Carbonization Technology

Hydrothermal technologies allow for the transformation of biomass into solid, liquid, or gaseous products in an aqueous environment. Based on the physical state of the generated products, three technologies are distinguished: hydrothermal carbonization (HTC) if the product is a carbonaceous substance with characteristics similar to lignin, hydrothermal liquefaction (HTL) if the product is an organic liquid, and hydrothermal gasification (HTG) if the product is a gas. All three technologies are very similar and are mainly characterized by the different operating conditions of temperature and pressure, as reported in Figure 1.

HTC takes place in a batch or a continuous reactor at a temperature range of 180–280 °C and under autogenous pressure (approximately water vapor pressure at the operating temperature) [1]. Usually, the biomass is fed into the reactor with a water–biomass ratio that varies from 5 to 10. This process imitates the natural phenomenon of coalification, i.e., the formation of raw coal. However, it manages to reproduce the phenomenon with the residence times of the biomass in the reactor, which vary in the range of 0.25–2 h according to the feedstock type, unlike the natural process, where much longer times are needed [2,3].

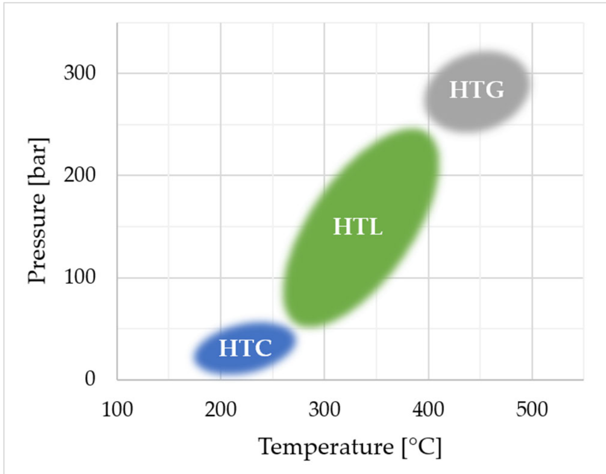

Figure 1. Operating temperatures and pressures of hydrothermal technologies.

Hydrolysis, dehydration, decarboxylation, and aromatization are the principal reactions during HTC processes. Removing carboxyl and -OH groups significantly reduces the O/C and the H/C ratios to make the final product more energy dense. A small quantity of gas, mainly CO_2 (about 1% of the dry organic biomass processed), evolves during the HTC treatment. This gas product is discharged into the atmosphere after purification, giving rise to a carbon-rich hydrochar separated from the process water via filtration or centrifugation. On a dry basis, the overall yield of hydrochar varies in the range of 30–70% depending on the biomass characteristics, preliminary treatments, operating temperature, residence time, reactor type, water–biomass ratio, and pH [4].

Hydrochar can be used for various purposes depending on its different chemical and physical properties, which are mainly dependent on the characteristics of the fed biomass and the operating conditions of the process. Table 1 summarizes the different applications of hydrochar depending on all these parameters [5,6].

Table 1. Applications and properties of hydrochar from different biomass types.

Biomass Type	Operating Conditions	Higher Heating Value (MJ/kg)	Carbon Content (wt%)	Nitrogen Content (wt%)	Applications	Ref.
Agricultural residues	Temperature: 180–250 °C Pressure: 10–30 bar Residence time: 0.5–2 h	17–30	40–70	0.5–2.5	Fertilizer, solid fuel, pollutant adsorbent	[7,8]
Forest residues	Temperature: 180–240 °C Pressure: 10–30 bar Residence time: 1–3 h	17–30	45–55	0.2–1.5	Solid fuel, activated carbon, pollutant adsorbent	[9,10]
Agro-industrial residues	Temperature: 180–250 °C Pressure: 10–30 bar Residence time: 0.5–10 h	20–30	40–70	0.5–2.5	Solid fuel, pollutant adsorbent, production of bio-oils and biogas	[11,12]

Organic fraction of municipal solid waste	Temperature: 120–280 °C Pressure: 10–20 bar Residence time: 0.5–6 h	20–35	50–75	2–6	Fertilizer, solid fuel, pollutant adsorbent	[13]
Livestock waste (manure, digestate)	Temperature: 180–260 °C Pressure: 10–30 bar Residence time: 0.5–1.5 h	5–15	30–45	2–6	Fertilizer, solid fuel, pollutant adsorbent	[14,15]
Marine biomass (algae)	Temperature: 180–230 °C Pressure: 10–30 bar Residence time: 2–16 h	15–25	45–55	2–6	Production of biogas, solid fuel, fertilizer	[16,17]

HTC is an exothermic process releasing 25–38% of the dry biomass's energy value, resulting in a significant improvement in the energy balance of the whole process. The hydrochar higher heating value (HHV) is around 13–30 MJ/kg, depending on the initial energy content of the feedstock [2,18].

In addition to hydrochar and the CO_2-rich gas phase, HTC produces a large volume of process water. Water acts as a solvent and a reaction medium with the mechanisms described. During the process, the ionic product of water increases, whereas the dielectric constant decreases. Consequently, water acts more as a non-polar solvent [19].

Different types of biowaste can be processed through HTC, which include food and garden waste in mixed municipal solid waste, waste from the food and drink industry, waste from the agricultural sector, and municipal wastewater digestate. HTC does not require a pre-drying stage of the fed biomass, as it can process feedstocks with a high water concentration. All this reduces time, energy, and cost, making the process even more economically and environmentally sustainable.

The conversion of matter to hydrochar has numerous benefits; the most important ones are improved hydrophobicity, the possibility of a more efficient recovery of nutrients and critical substances, the elimination of the energy-intensive pre-drying stage of feeding, an increased dewatering efficiency, and a lower environmental impact compared to high thermochemical processes.

Hydrochar has less moisture and is more hydrophobic than raw feedstock. These characteristics reduce transportation costs and improve storage by preventing wettability and spoilage during storage. Moisture grade management can be carried out through palletizing and briquetting operations, turning it into a real resource used in various energy valorization plants.

Another key aspect to consider concerns the nutrients and critical substances in the hydrochar at the end of the process. Nitrogen (N), phosphorus (P), potassium (K), and carbon (C) are some of the elements of most significant interest in terms of quantity and usability. These substances give hydrochar characteristics suitable for use as a fertilizer. This use is constrained by the material sent to the HTC plant. Depending on the material treated, pollutants hazardous to the environment and human health, such as heavy metals (Ni, Pb, Cr, and Cd), may be found with concentrations above the legal limits [20]. However, several treatments allow for reductions in the concentrations of these substances to those below the legal limits, and for some of them, selective recovery strategies and methods can be introduced. In the case of other pollutants in the feedstock, HTC can degrade microplastics (MPs) [21]; pharmaceutical and personal care products (PPCPs); and other persistent organic pollutants, such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) [22].

Over the past 50 years, several process engineering technologies have found themselves in the same situation in which HTC finds itself today. Many of these technologies have had good luck in application on an industrial scale, and still, it took 20 to 30 years after their discovery to witness this final scale-up. These technologies include membrane technologies, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (RO). Another important example is gas permeation, which can separate two or more gases, as in the case of separating methane from carbon dioxide in anaerobic digestion processes of biomass. Sterilization with pressure rather than temperature has also been very successful on an industrial scale, as has extraction with supercritical carbon dioxide (SCD). For some of these technologies, it seemed impossible to achieve a degree of application on an industrial scale; however, not only have they become a viable alternative to the related earlier technologies, but, in some cases, they have become the predominant technologies for specific applications (RO for desalination).

However, numerous process technologies have not been successful. One of these is SCD for sterilization. Numerous studies have been conducted, with many books and articles about it. However, the real commercialization of this technology has yet to be achieved.

A thorough literature review showed that HTC has been studied from many different perspectives. Numerous papers have been published where only one or a few aspects of this technology emerge, leaving out a more general and complete description of its evolution and prospects.

This paper aims to give a brief overview of the progress made in this field and to try to understand in which direction HTC development is heading. The research was designed with the following criteria: a brief analysis of the history of HTC and a more in-depth analysis of the situation in the last three years. In particular, we want to show the state of the art of HTC and its recent developments with its pros and cons by giving our opinion on the challenges, opportunities, and perspectives of HTC. In other words, we want to answer the following such questions: How widespread is this technology? At what level is it? Who is investing in HTC? How sustainable is it economically?

Section 2 shows the evolution of HTC in recent years, followed by Section 3 with its prospects. Finally, there is a brief conclusion of the work carried out.

2. Evolution

The history of HTC is relatively short; it was theorized for the first time by Friedrich Bergius in 1913 [23], and it has gained increased attention in recent years due to its potential as a sustainable solution for managing organic waste and reducing greenhouse gas emissions. This technology is already well-established worldwide, with more than 200 companies and organizations conducting research and professional activities on this topic. In recent years, the number of HTC-related patents worldwide has increased exponentially [24], as can be seen in Figure 2. As evidence of the worldwide research that is taking place on this technology, the percentages of patent registrations for different countries are shown. The monotonous increase in registered patents on hydrothermal carbonization since 1996 shows that, over the last 25 years, there has been a continuous investment in this technology. Thirty-nine percent of the patent applications involved several countries, filed with the European Patent Office and the World Intellectual Property Organization. Most patent applications on hydrothermal carbonization were filed in China at 27%, the USA at 14%, and Germany at 10% [25]. All this testifies to the strong industrial interest in this technology. The mental and economic efforts mean that the organizations and industries working with HTC believe in its technological future.

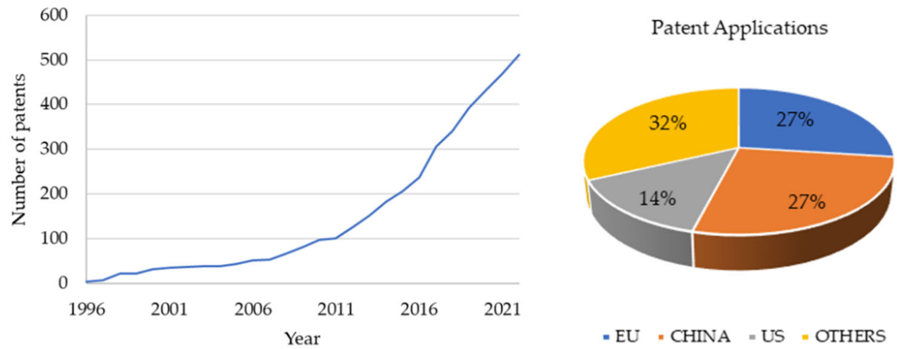

Figure 2. Number of patents over the past few years and percentages of patent registrations in different countries.

HTC is still in an evolutionary stage, although many pilot plants and some full-scale plants have been built and operated in Europe. A few years ago in China, a full-scale plant was built with German technology and is now operational for the final disposal of municipal sewage sludge (MSS) with commercial material recovery. HTC technology is emerging for the management of MSS itself, with several favorable implications. Primary and excess sludge, well-thickened or slightly dewatered, can be hydrothermally carbonized directly in situ, i.e., within the wastewater treatment plants, due to the favorable water-to-organic matter ratio.

As mentioned above, the main regions interested in the industrial application of HTC are certainly China, the US and the European Union. The list of plants in the world that use HTC is very long. Moreover, it is often hard to find such data, as companies tend not to disclose internal information. However, we tried to identify some more important data to help understand the industrial development of this technology in different parts of the world.

For example, in China, HTC has already been used on an industrial level for sludge treatment since 2016. The largest HTC sludge treatment plant is located in Jining, Shandong Province. Beijing Aquatic Park Co (Beijing, China), the nation's largest wastewater treatment plant operator, collaborated with TerraNova to test HTC as a promising new sludge treatment solution. The HTC plant in Jining processes 500,000 ae of sludge into approximately 7000 tons of easily dewaterable biochar (14,000 tons/year) [26,27].

In 2022, the same TerraNova company started up another plant in Mexico City capable of processing about 23,000 tons/year of organic waste [28].

HTC development in the United States is still in the early stages. However, there is a growing interest in the potential of HTC as a sustainable alternative for waste management and energy production. Several research institutions and universities in the US are actively investigating HTC and its potential applications. In addition, there are several startups and companies in the US that are working on developing and commercializing HTC technology. The first municipality in North America to adopt HTC technology was Phoenixville, Pennsylvania. Following an accident, the Phoenixville New Energy Optimization (PXVNEO) Project was initiated to convert the old wastewater treatment plant from anaerobic digestion to HTC [29].

In Europe, the situation is certainly more complex and fragmented. The first European hydrothermal carbonization plant with an annual capacity of 8400 tons was commissioned in 2010 in Karlsruhe, Germany, by a Swiss company, AVA-CO2 [30]. It is claimed that it can handle many inorganics in the industrial-scale processing of industrial and municipal solid waste. With the start-up of the world's largest hydrothermal carbonization plant, AVA-CO_2 now establishes itself as the first company to cross the boundary between research and the industrial use of this technology, with a total capacity of 14,400 liters and 8400 tons of biomass processed per year.

In 2010, in Relzow (Germany), the company HTCycleAG became the first to launch an industrial-scale HTC factory. The success led to the opening of a second production plant in 2017 based on the same HTC technology [31].

In July 2010, Ingelia started up the first biomass hydrothermal carbonization plant in Naquera near Valencia (Spain). This plant is probably the world's first industrial plant capable of continuously carbonizing biomass by applying the HTC process. The plant, designed and built by the company Ingelia, can process any organic waste. Now, it is fed with both plant remains (gardening and pruning) provided by the surrounding area in which the plant is located and organic waste from the surrounding municipalities. Regardless of the biomass input, the bio-coal obtained is a solid biofuel with a higher heating value (HHV) of approximately 24 MJ/kg. With its two reactors, this plant can process up to 14,000 tons/year and produce 750 tons of fertilizer concentrate and 3500 tons of bio-coal [32].

The pilot plant in Immingham [33], United Kingdom, was completed in 2018 and is now operational for treating the organic fraction of municipal solid waste. Currently, it consists of a single reactor, and there are plans to expand this plant to four reactors.

In January 2020, a plant in Heinola, Finland, capable of processing 20,000 tons/year of biological sludge, also went into operation. C-Green's patented solution for efficient chemical heat generation eliminates the need for costly external heat generation. It is so efficient that, once started up, it requires no external heat [30].

As can be seen from the above, many facilities have already been established, while others are in the process of being approved or realized; examples of this are the Piombino and Chiusi facilities in Italy. The Piombino project received a positive assessment from the Environmental Impact Assessment Commission by the Tuscany Region. The company Ingelia Italia is now dealing with the final authorization procedure. The plant will have 10 reactors with a capacity of 60,000 tons/year and will be able to produce 15,000 tons of biocarbon and 2000 tons of fertilizer concentrate [34].

The final project in Chiusi has been handed over to ACEA Ambiente, the plant's owner. The SIA and all the documentation necessary to start the single authorization process were presented to the evaluation commission of the Tuscany Region in November 2018. In this production hub, there will be 8 reactors, and it will be able to treat 80,000 tons/year of biological sludge. It will be able to produce 8000 tons of biocarbon and 6000 tons of biofertilizer with a high phosphorous and potassium content [35].

3. Prospects

It is now common thought in the scientific world that the main advantage of HTC is its flexibility in handling a wide range of wastes. In addition, it has been pointed out that the main product of this technology, hydrochar, can be used in a wide range of applications. The proposed process is feasible from a technological point of view, with many companies worldwide having invested and continuing to invest heavily in developing this technology on an industrial scale.

From an economic point of view, several factorials are to be considered. Several studies have shown that producing hydrochar profitably at a price competitive with that of conventional coal is quite complicated. Figure 3 shows the average selling prices of hydrochar for different types of processed materials [36–40].

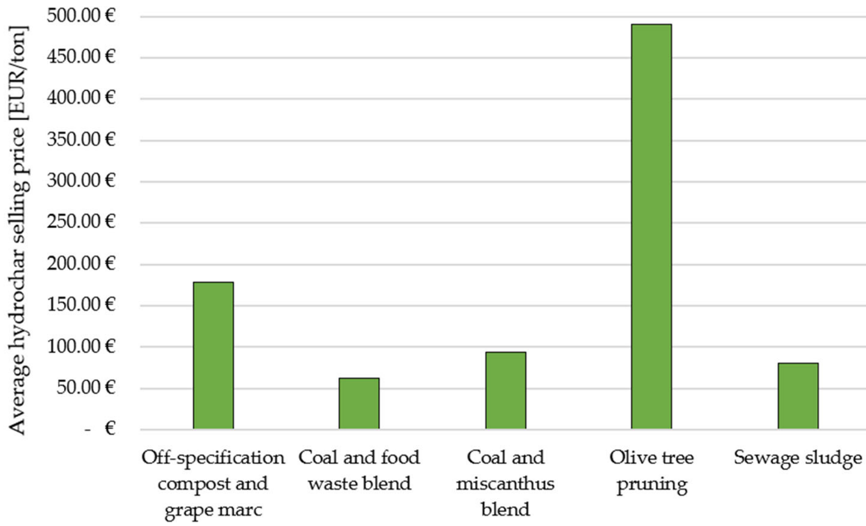

Figure 3. Average hydrochar selling price for different feedstocks.

The size of the plant strongly influences economic feasibility. The importance of this aspect has been studied recently in several papers by González-Arias et al. published in 2021 [39,41–43]. Their study analyzed a case related to using HTC for olive tree pruning. The breakeven selling price was calculated for plants with different capacities. It was found that, for the worst-case scenario (lowest capacity plant with 2500 tons/a of feedstock), the price needs to reach 590 EUR/ton. For the best-case scenario (highest capacity plant with 9900 tons/a of feedstock), the breakeven selling price is about 390 EUR/ton. It is possible to compare the latter figure with the trend in the price of traditional coal, shown in Figure 4. In recent years, due in part to the recent energy crisis, there has been a highly significant increase in the price of coal [44]. Although the profitable production of hydrochar at a price competitive with that of coal was not feasible in the past, as of today, it is a reality.

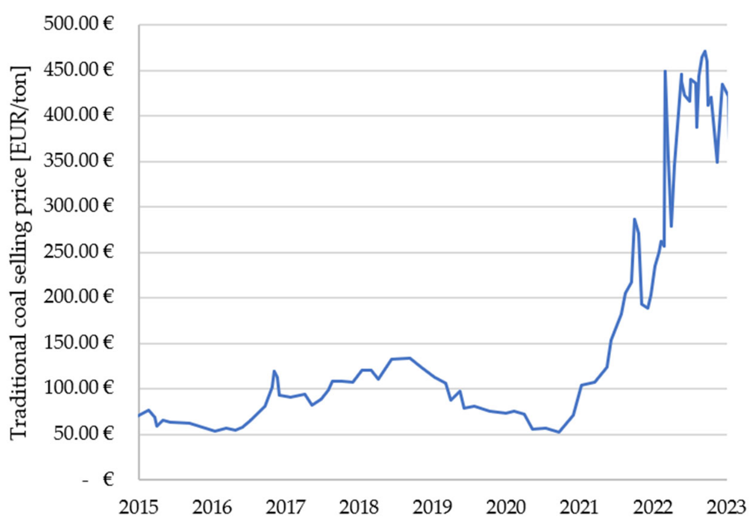

Figure 4. Trend of traditional coal selling price since 2015.

In addition, plants of this type generate a product and valorize waste by avoiding the expenses associated with its management and disposal. Other factors to consider are valorization and the utilization of all by-products of the process. If one analyzes a plant that meets these last two criteria from an economic point of view, the breakeven selling price is significantly reduced. For example, Ciceri et al. analyzed the costs and profits of an HTC plant with a capacity of 78,000 tons/y of biowaste with an annual production of about 15,400 tons of hydrochar and about 48,000 m^3 of liquid fertilizer [45]. The study considered a price for the hydrochar of 180 EUR/ton and a 50 EUR/ton tipping fee. With these data, it was found that, for an investment of about EUR 27 M and operating costs of about EUR 1.5 M, an earnings before interests, taxes, depreciation, and amortization (EBITDA) of about EUR 5 M, a payback time (PBT) of almost 5 years, and an internal rate of return (IRR) of 18.7% are achieved.

However, the scenario that is the most interesting to date involves the integrated use of HTC with other unit operations to process complex raw materials, aiming to recover as much energy as possible and all materials of interest. A primary example of this solution is the integrated use of HTC with anaerobic digestion (AD), which has already been described extensively in the literature [46–49].

The aqueous fraction resulting from the HTC process represents a high COD secondary waste; anaerobic digestion is a possible solution to reduce COD by producing methane-rich biogas. All this contributes to improved energy recovery. The integration of these two technologies results in an overall energy recovery ranging from about 50% to more than 90% [46]. The energy balance shows that the whole system is self-sustainable from a thermal point of view. Moreover, some techno-economic studies and life-cycle assessments only confirm that this solution is up-and-coming.

A second example of process integration concerns the possibility of combining HTC with aqueous-phase reforming (APR) for sewage sludge management and energy recovery. In the HTC process, biomass is first heated and pressurized in the presence of water to create a slurry. The slurry is then maintained at a high temperature and pressure for a specific time. This HTC step produces hydrochar and a liquid phase consisting of water and various organic compounds. The APR process involves further liquid-phase processing to produce additional fuel products. In this step, the liquid phase is mixed with a catalyst and heated to high temperatures, typically above 250 °C. This step causes the organic compounds in the liquid phase to undergo reforming reactions, which break down the larger molecules into smaller ones and produce other gases, such as methane and hydrogen. This system achieves an energy recovery of about 95% and reduces the organic load of the generated process water [50].

A third example of process integration involves the combination of HTC with a hydrometallurgy section. In this case, the purpose of the hydrometallurgy section is to recover the critical substances contained in hydrochar. Among the most interesting elements in terms of quantity and strategic interest is certainly phosphorus [51]. For example, in the case of HTC for municipal wastewater (MWW) treatment, the amount of phosphorus remaining in the hydrochar at the end of the process may exceed typical concentrations of the same element in phosphate rock (containing 11–15% of P) [52]. In this case, hydrochar is a valuable secondary source of supply.

However, each of these processes is still the subject of numerous studies aimed at optimizing all the various stages of treatment. A significant result in optimizing the hydrothermal carbonization step has been achieved by introducing catalysts inside the reactor. This is referred to as co-hydrothermal carbonization (Co-HTC) in this case. The presence of catalysts during the hydrothermal carbonization process can increase the efficiency of the process, reduce the time required for coal formation, and improve the properties of the coal produced. Catalysts can consist of materials such as acetic acid, chloridric acid, phosphoric acid, zinc chloride, and iron chloride [53].

However, for a complete and exhaustive analysis of the topic, one must take into account what are the bottlenecks of this technology at present. Among the most significant bottlenecks are the management of the processed water and the produced gases, which still need to be more frequently utilized. Proper disposal of the liquid phase often presents challenges due to the presence of toxic substances (such as polycyclic aromatic hydrocarbons or heavy metals). This aspect limits the applications of these residues, inevitably affecting production costs.

In addition, when using HTC technology alone, significant up-front investments are required for the production capacity to be sufficient to ensure a competitive process in the market [54]. This requires flexible plants capable of handling a wide variety of raw materials. These are industrial initiatives that only some entities can pursue. Unquestionably, intervention by government organizations could help overcome this problem with incentives or support.

4. Conclusions

This perspective presents a brief overview of the development of HTC, analyzing and discussing the evolution of this technology over the past few years and giving insight into its future possibilities. In many papers, HTC is an emerging technology; however, from a more profound analysis, it can be discerned that it is an actual manufacturing reality.

A literature review suggests that HTC has been studied scientifically and is still being studied today. The chemical–physical phenomena that characterize this process have been extensively described and optimized on a laboratory scale.

The last decade has witnessed a scale-up of HTC on a pilot scale, as evidenced by the numerous plants built worldwide. In addition, the number of patents related to this technology has increased exponentially since the move to an increasingly industrial scale. All this testifies to the great interest of public and private entities in this technology. The very uniform percentage of patents filed in different countries shows that everyone recognizes the potential of HTC and its economic implications.

At present, plant capacity is the parameter that most influences the economic viability of this technology: as production capacity increases, there is an increase in economic prospects. All these project this technology directly to an industrial-type scale. There are already many HTC-plant-building companies making large-scale plants. These are undoubtedly full-bodied investment costs, but the profit prospects are more than attractive, with high-profit margins and relatively short payback times for the investment.

Numerous advantages are highlighted throughout this paper; however, some bottlenecks remain to be overcome. Among the most significant, we find the issue of the management and the disposal of the various by-products of the process, especially process water, often home to pollutants. The complete consecration of HTC among the many established process technologies coincides precisely with overcoming these latter limiting factors. In this regard, integrated processes are being studied to process complex raw materials, recover all elements of interest, and optimize energy aspects. Using enabling technologies, the pillars of Industry 4.0, will also contribute to minimizing costs and processing times, increasing plant performance and safety. These aims will be made possible by intelligent controllers; model predictive control (MPC) techniques, rather than adaptive and optimal control (AOP), make it possible to train controllers and make them capable of precisely predicting what will happen in the plant and having the time to carry out actions or adapt the controller to changes in plant parameters over time.

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