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Review

Non-Thermal Plasma as a Biomass Pretreatment in Biorefining Processes

Carmen Maria Meoli, Giuseppina Iervolino * and Alessandra Procentese

Department of Industrial Engineering, University of Salerno, 84084 Fisciano, Italy
* Correspondence: giiervolino@unisa.it

Abstract: Climatic changes and the growing population call for innovative solutions that are able to produce biochemicals by adopting environmentally sustainable procedures. The biorefinery concept meets this requirement. However, one of the main drawbacks of biorefineries is represented by the feedstocks' pretreatment. Lately, scientific research has focused on non-thermal plasma, which is an innovative and sustainable pretreatment that is able to obtain a high sugar concentration. In the present review, literature related to the use of non-thermal plasma for the production of fermentable sugar have been collected. In particular, its sugar extraction, time, and energy consumption have been compared with those of traditional biomass pretreatments. As reported, on one hand, this emerging technology is characterized by low costs and no waste production; on the other hand, the reactor's configuration must be optimized to reduce time and energy demand.

Keywords: non-thermal plasma; biorefinery; biomass pretreatment

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1. Introduction

According to *World Population Prospects 2019*, the human population will reach 8.5 billion in 2030 and 9.7 billion in 2050 [1]. Because of this trend, an increase in waste production is expected. Wastes are generated from various human activities, and their improper management has a negative impact on the environment. In addition to waste management, the climate is also affected by the use of fossil fuels [2]. Biorefining could fix both issues of the increased waste production and fossil fuel use. Indeed, a biorefinery is defined as an integrated industry that is able to produce biofuels and biochemicals from wastes such as dedicated crops (*Miscanthus*, perennial grass, etc.) [3], agricultural residues (corncobs, wheat straw, sugarcane bagasse, etc.) [4], and industrial wastes (spent brewery grains, coffee silverskin, cheese whey, etc.) [5]. Dedicated crops and agricultural residues are produced in forests as diverse flora and in farmlands as residues of food crops, respectively. Industrial wastes are by products of industrial processes which are produced in localized but smaller quantities [5]. These biomasses are composed of cellulose, hemicellulose, and an external layer of lignin, which must be removed to make the fermentable sugars available [6]. The lignin makes the biopolymeric structure recalcitrant. For this reason, several studies in the literature have focused on pretreatments able to remove the external layer of lignin [7].

Pretreatment methods can be classified into two categories: conventional and non-conventional methods. In the scientific literature, there are many articles about the conventional pretreatments (such as extrusion, milling, steam explosion, acid treatment, alkaline treatment, and others). However, these pretreatments are not environmentally friendly and they lead to the formation of both chemical wastes and inhibitors of fermentation [8]. These negative aspects have encouraged the investigation of non-conventional and eco-friendly pretreatments for lignocellulosic biomass. A non-conventional method recently investigated is plasma technology [9].

Plasma technology is based on a physical principle. When energy is supplied to matter, this changes the state: solids become liquid, and liquids become gaseous. If even more

energy is supplied to a gas, it goes into the plasma state, the fourth state of matter. In particular, the plasma technique can be classified as either non-thermal plasma (NTP) or thermal plasma (TP). This distinction is based on the thermodynamic equilibrium that is established between the species that are generated. In particular, in thermal or hot plasma, the temperatures of all species present are in thermal equilibrium; instead, in non-thermal plasma, the heavy species and electrons are not in thermal equilibrium. Because of this difference, it is also called non-thermal plasma or cold plasma because the gas temperature remains so low that they can even be touched with a finger. In non-thermal or cold plasma, although the electrons absorb energy in the same way as in thermal plasma, they are unable to transfer energy to the heavy species because there are fewer collisions caused by low pressure. Hence, the temperature of the electrons remains higher than the temperature of the other species [9,10].

Because of its peculiar characteristics, non-thermal plasma is applied in various fields from water treatment to the decomposition of volatile organic compounds (VOCs) [11], and to the unconventional pretreatment of biomass [12–15]. Studies in the literature have shown that there is a clear delignification and oxidation of lignocellulose caused by a series of free radical reactions following plasma treatment [16]. The main results in terms of delignification and sugar release after a non-thermal plasma pretreatment have been collected in recent reviews [12,13,17]. However, as reported in the scientific literature, one of the main problems related to non-thermal plasma pretreatment is energy consumption [12–15]. For this reason, in the present review, studies reporting energy consumption data after conventional and non-conventional biomass pretreatment have been collected. The aim was to compare these values to the ones reported after the use of non-thermal plasma technology in order to identify if this emerging technology is valuable to pursue in terms of both delignification and energy consumption.

2. Feedstocks for Biorefining Processes

Biorefining is based on range of technologies that are able to both disassemble the feedstocks into their building blocks (such as proteins, carbohydrates, etc.) and to use them to produce energy or added-value products (such as biofuels and biochemicals). The term "feedstock" refers to the raw materials used in biorefinery. These raw materials can be sugars, dedicated crops, agricultural residues, and/or agro-industrial residues.

Sugars (such as corn sugars) are defined as "first-generation feedstocks". They compete with the food market and, nowadays, they are no longer investigated in the biorefining processes [18]. Dedicated crops, agricultural residues, and agro-industrial residues are "second-generation feedstocks" and their use is not in competition with the food market [19].

The dedicated crops mainly investigated in the scientific literature are *Miscanthus* and switchgrass. On one hand, they are characterized by a high amount of sugars; on the other hand, a long cultivation time and considerable arable area is needed [20].

Agricultural residues (such as rice straw, wheat straw, sugarcane, corn stover, cassava peels, etc.) are produced during the harvest of agricultural products. One of the main problems related to agricultural residues is the collection and transport costs, which can affect the overall process from the economic and environmental point of view [4].

Agro-industrial residues (such as grape pomace, wheat bran, spent coffee grounds, cheese whey, etc.) are by-products from various processes of the food industry (such as beer or cheese production, coffee torrefaction, etc.). However, the use of agro-industrial residues can have limitations such as the low amounts and the collection and transport costs [5].

All previous feedstocks can be described as lignocellulosic biomasses. Lignocellulosic biomass has a complex polymeric structure including cellulose, hemicellulose, and lignin. These components are associated with each other to form a recalcitrant structure. In addition, the lignocellulosic biomass contains small quantities of inorganic components [21]. In general, the cellulose represents 40–60% of the biomass, hemicellulose represents 20–40%,

and lignin represents 10–24% [6]. However, these percentages can change for the different types of biomasses [22].

3. Feedstock Pretreatments

Pretreatments are necessary for breaking the inter- and intra-molecular bonds among lignin, cellulose, and hemicellulose, making the cellulose more accessible to enzymatic attack. Pretreatment can be the most expensive step in processing biomass and may decide the destiny of the process [23]. An ideal pretreatment process should have low energy requirements, low investment capital, insignificant generation of fermentation inhibitors, and no/low waste production [24]. In the next subsections, the main conventional and non-conventional pretreatments reported in the scientific literature are described.

3.1. Conventional Pretreatments

Conventional pretreatments can be mainly classified into four groups:

- Chemical (organosolvents, acid/alkaline solutions, ionic solvents, etc.);
- Physicochemical (steam explosion, ammonia fiber explosion, CO_2 explosion, etc.);
- Physical (extrusion, milling);
- Biological (enzymes or micro-organisms).

These four categories work differently to break the complex structure of lignocellulosic biomasses.

In the organosolv process, lignocellulosic biomasses are pretreated with an organic solvent (such as ethanol, methanol, acetone, organic acid, organic peracid, ethylene glycol, etc.) or their aqueous solutions [25]. Organic solvents and their aqueous solutions break down the internal bonds between lignin and hemicellulose. To improve the delignification of lignocellulosic biomass, a catalyst (such as phosphoric acid, sulfuric acid, etc.) can be used. Unfortunately, the cost of solvents can be high, and the process generates fermentation inhibitors and chemical wastes [25].

Acid pretreatment of lignocellulosic biomass is based on the sensitivity of the glycosidic bond between the hemicellulose and cellulose to acid [26]. Different inorganic acids (such as phosphoric acid, nitric acid, maleic acid, and formic acid) are used. Acid pretreatment can be classified as: (i) concentrated acids (used at low temperatures, below 100 °C) and (ii) dilute acids (used at high temperatures, between 100 and 250 °C). This treatment is simple and is it characterized by its low cost; however, it requires neutralization of the hydrolysate and generates fermentation inhibitors [26].

Ionic solvents are a class of solvents for which the melting point is under 100 °C. They are composed of cations (such as imidazolium, pyridinium, alkylated phosphonium, etc.) and anions [27]. Cations and anions have an important role in the delignification of lignocellulosic biomass. The ionic liquid treatment does not generate toxic inhibitors and it is characterized by the efficient dissolution of cellulose. However, chemical wastes are produced by the process, and the cost of some ionic liquids is high [27].

Milling is one of the most investigated physical pretreatments reported in the literature. Milling reduces the crystallinity and particle size of lignocellulosic biomass to 0.2 mm. This method is chemical-free. However, it is characterized by high energy consumption and non-efficient removal of lignin [28].

Steam explosion treatments combine mechanical and chemical forces. During steam explosion pretreatment, at the beginning, the biomass is subjected to high-pressure saturated steam (0.69–4.83 MPa) at a temperature of 160–260 °C. Water molecules enter into substrate. The pressure is then reduced, which explodes the bulk lignocellulosic biomass into separated fibers. This method is characterized by high glucose yields. However, it is not characterized by high hemicellulose degradation [29].

Biological treatment is an eco-friendly technique of treating lignocellulosic biomass. This method is not characterized by the formation of inhibitors and use of chemicals. Biological treatment is based on lignin-degrading bacteria or fungi (such as enzymes or cells). One of the main issues related to this process is the required time (days), which

affects the overall process's productivity [29]. In Table 1,the main results for each type of traditional pretreatment are collected [30].

Table 1. Conventional pretreatments.

Pretreatment	Energy	Average Time (min)	Wastes	Production of Fermentation Inhibitors	Results	Limitations to Improvement	TRL	Reference
Organosolv treatment	0.02–0.04 kWh/mol of xylan	10–90	Residual solvents	Yes	55% of xylan was obtained, starting from 10 g of a dry agro-fiber crop (*Arundo donax* L.) treated for 30 min	Recovery and reuse of chemicals Develop methods to add value to lignin High capital and operating costs	4–6	[30]
Dilute acid hydrolysis	1.46 kWh/kg of glucose	10–90	Residual acids	Yes	About 220.7 g of glucose kg^{-1} biomass was obtained after 30 min	Developing micro-organisms more tolerant to inhibitors	5–7	[31]
Laccases	-	4320	No	No	About 73.75–76.6% of glucose was produced, starting from 2.5 g of corn stover	Development of robust micro-organisms	3–4	[32]
Steam explosion	12.03 kWh/kg of fermentable carbohydrates	1–3	No	Yes	76% of glucose was obtained, starting from 100 g of cardoon after 10 min.	Development of new catalysts Developing micro-organisms more tolerant of inhibitors	6–8	[33]
Milling	0.50–2.15 kWh/kg of glucose extracted	30	No	No	About 24.45–59.67% of glucose was obtained, starting from 250 g of Douglas fir forestry residues treated for 7–30 min.	Integration of the process, combined with mild chemical treatments	5–6	[34]
Alkaline treatment	0.71 kWh/kg of glucose	10–90	Residual alkaline solution	Yes	440.6 g of glucose kg^{-1} biomass was obtained after 30 min.	Recovery and reuse of chemicals	5–7	[35]

As reported, the highest sugar concentration was obtained after steam explosion, which is the technology with the highest TRL (technological readiness level). Comparable results were obtained after acid/alkaline and organic solvent pretreatment. However, these three procedures are characterized by both the production of chemical waste and the formation of inhibitors. On the contrary, laccases and milling technology do not produce wastes and inhibitors; however, they need to be optimized in terms of the sugars released, the time required, and energy consumption. Indeed, both are still characterized by a low TRL value. As regards the energy consumption, a precise analysis regarding this aspect is difficult to carry out. Most of the studies in the literature do not evaluate this aspect. Moreover, if this value is reported, it is evaluated in different ways by the different research groups, and thus a real comparison among the values reported in Table 1 is still difficult.

3.2. Non-Conventional Pretreatments

Non-conventional methods for the pretreatment of lignocellulosic biomass are discussed below. Ultrasound pretreatment of biomass is based on cavitation. When ultrasound waves pass through low-pressure areas, this produces gas or vapor bubbles. These bubbles gradually grow until imploding. The consequences of implosion are high temperatures, the formation of oxidative radicals, and the generation of shearing forces. The results of this pretreatment depend on the amplitude, temperature, power, and duration of sonication [36].

Hydrodynamic cavitation (HC) is based on the same principle as ultrasound pretreatment. The process is based on the creation, expansion, and collapse of bubbles in a short period of time [37]. Energy is released, thus causing the formation of free radicals. With these free radicals, the structure of the biomass changes. Cavitation can be induced by using an orifice plate, curved channel, or Venturi tube [38]. Sometimes, hydrodynamic cavitation is used with conventional pretreatments (such as alkali treatment) to obtain a

major release of sugar. The treatment cost depends on the type of the biomass substrate. Woody biomasses require more energy than grassy biomasses [23].

High hydrostatic pressure (HHP) is characterized by a range of pressure from 100 to 800 MPa. This treatment is based on two main principles:

- Le Chatelier's principle: if the pressure changes, the volume also changes;
- The isostatic principle: pressure is transmitted throughout the biomass [39].

There are few articles in the literature about this treatment, so is not possible to define its cost and its energy requirements with precision. However, it is known that this treatment is not mass- or time-dependent, so it requires a shorter period to obtain the same results as other methods [40].

Microwave pretreatment is based on the treatment of lignocellulosic biomasses by the application of an electromagnetic field. Molecular collisions and thermal energy are generated by dielectric polarization and cause the disruption of the structure of the lignocellulosic biomass [40]. This treatment has several advantages, such as the minimal formation of inhibitors, its high capacity in a short period of time, and its easy operation [41].

Gamma irradiation involves electromagnetic waves generated when cobalt 60 and cesium 137 isotopes are subjected to radioactive decay. Gamma rays pass through the lignocellulosic biomass and transfer their energy to the atoms. Thus, the formation of free radicals occurs. This pretreatment requires a short period of time and low operating costs; however, exposure to gamma irradiation is harmful [42].

Table 2 shows the main results reported in the literature regarding the non-conventional pretreatments.

Table 2. Non-conventional pretreatments.

Pretreatment	Energy	Average Time (min)	Wastes	Production of Fermentation Inhibitors	Results	Limitations to Improvement	TRL	Reference
Non-thermal plasma	60 kWh/kg of biomass	60–420	No	No	51.3% of glucose was obtained from 10 g of dry raw sugarcane bagasse after 120 min	Homogeneous and heterogeneous catalysts should be used to reduce the process the time. The reactor's configurations should be optimized to achieve high pretreatment efficiency	2–4	[43]
Ultrasound	75 kW/kg of biomass 12.5 kHz/g of biomass	10–80	No	No	Around 59.56% of reducing sugar was released from 2 g of dry garden biomass after 60 min of treatment	Reducing the energy loss by using a proper configuration	2–4	[44]
Hydrodynamic cavitation	55 kW/kg of biomass	10–50	No	No	67.61% of glucose was released from 20 g of dry sugarcane bagasse after 10 min of treatment	Optimizing the operating conditions such as the liquid's flow rate, the inlet pressure, and the number of recirculation passes across the cavitation zone	2–4	[45]
Microwave irradiation	58.47 kW/kg of biomass	5–30	No	Yes	Around 75.4% of reducing sugars was obtained from 5.13 g of maize stillage after 10 min of treatment	Reducing high-capital investments through the use of an optimal system to generate microwaves	2-4	[46]
Gamma irradiation	200 kGy/mg of biomass	10–80	No	No	75.4% of reducing sugars was released from 5 mg of poplar bark.	The dosage of gamma rays should be optimized to achieve high pretreatment efficiency	2–4	[47]

As reported in Table 2, on one hand, all these innovative procedures are characterized by no production of chemical waste or formation of inhibitors; on the other hand, more energy is required with respect to the conventional pretreatments (Table 1). However, the concentration of sugars obtained is comparable with the results obtained by the conventional techniques. For this reason, further studies are needed to improve the efficiency of these emerging technologies to make them scalable to industrial level.

4. Plasma Technology

In 1928, Irving Langmuir proposed the term "plasma" to describe a region containing charges of ions and electrons. Plasma, in fact, is a partially or fully ionized gas based on electrons, atoms, ions, and metastable and excited molecules [48]. It is generated by electric or electromagnetic fields. Temperature can be used to describe plasma technology. In thermal plasma (TP), electrons and heavy particles (such as ions, atoms, molecules, and radicals) have a similar temperature and they are at the thermodynamic equilibrium. Instead, in non-thermal plasma (NTP), the electrons' temperature (10^4–10^5 k) is higher than the heavy particles' temperature (300–1000 k) because of their different masses. Indeed, in non-thermal plasma, the electrons' mass is less than the mass of the ions, atoms, molecules, and radicals, so all the species are not in thermodynamic equilibrium. Non-thermal plasma is a partial electrical discharge initiated at a sufficient voltage. In non-thermal plasma, lightweight electrons are accelerated in an electrical field and reach a temperature of 10,000 k to 250,000 k. When these electrons bombard the heavy particles, these become metastable or excited. The metastable and excited molecules collide among themselves or are bombarded again by the electrons; therefore, processes such as ionization and dissociation occur. These processes entail the formation of highly reactive species (such as ozone, hydronium ions, and radicals). This method has been extensively studied in recent years because of its excellent potential in various areas [49] such as the treatment of water contaminated by pharmaceutical compounds [50], by dyes [51], or by p-nitrophenol [52]; in the treatment of mammalian cells [53] or of biofilms [54]; and the treatment of lignocellulosic waste [11,17]. In particular, as regards the pretreatment of lignocellulosic matrices, the use of plasma allows researchers to improve the phase of access to the enzymatic complex of the lignocellulosic matrix. The interest in this pretreatment technique is based on the fact that it is possible to carry it out at atmospheric pressure, thus avoiding the presence of a vacuum chamber and the use of air as an ionizing gas. In this way, it is possible to significantly reduce the operating and maintenance costs [11]. For this reason, NTP can be considered an interesting alternative to conventional biomass pretreatment techniques, which are certainly more aggressive.

4.1. Chemical Effects of Non-Thermal Plasma

If the possible reactions that can be carried out with non-thermal plasma are considered, then it is possible to consider all reactions to have high activation energy. This is because in NTP, the electrons are characterized by a high temperature of 10^4–10^5 K (about 1–10 eV mean energy). This implies that with non-thermal plasma, almost all chemical processes are feasible, including processes of synthesis. Moreover, since only the electrons are characterized by high temperatures but all the gas surrounding them is at a relatively low temperature, no thermal dissociation phenomena of the reaction products are observed, and no cooling will be necessary. This aspect is very important because it allows us to say that the walls of the reactor will not have to undergo any thermal stress. The importance of this aspect is obvious, especially regarding non-thermal plasma's applications, such as microelectronics, or future applications such as plasma medicine. NTP processes occur under conditions of high disequilibrium for all species. This makes the modeling of this phenomenon very complicated, since it would be necessary to know the energy distribution function of the electron gas in the active zone of the reactor. In general, the solution to this complex problem is a challenge for computational physics. However, it is imperative to begin studying NTP with a thorough understanding of the plasma source. This is essential to optimize the process. To achieve this, it is important to know the operating parameters of the discharge (absorbed power, pressure, flow, gas mixture, etc.) and its interconnection with the most important parameters of plasma (gas temperature, electronic density, electronic energy, electronic distribution, etc.) and the plasma itself in terms of particle density, mass balance or surface properties [55].

4.2. Configuration of the Non-Thermal Plasma Reactor

In order to understand the effectiveness of NTP, it is interesting to note that it can be generated by reactors with different configurations, such as corona plasma and dielectric barrier discharge. Corona discharge can be classified as pulsed corona discharge and pulseless corona discharge. A non-thermal plasma reactor with pulsed corona discharge can be used in different industrial applications (surface treatments, cleaning of liquids, etc.). It is based on an electric circuit, where the electrical particles moving from one electrode to another electrode [41]. This configuration produces radicals and atoms under ambient conditions. A pulseless corona discharge reactor, unlike a pulsed dielectric discharge reactor, works continuously [41]. On the one hand, the productivity of the process is high; on the other hand, it consumes high amounts of energy. Dielectric barrier discharge reactors are generally based on two electrodes. One electrode is exposed to the air and the other electrode is covered by dielectric material. The insulating dielectric material can be quartz, Plexiglas, alumina, or ceramic. Quartz is the most widely used material because of its moderate price and its commercial availability. The two electrodes are supplied with alternating current voltage. The consequences of the high level of alternating current voltage are the ionization of the area above covered electrode. The ionized air is called plasma. Dielectric barrier reactors have different advantages [43]:

- Their geometrical configuration is simple;
- They can be easily used for industrial applications;
- The plasma conditions are stable and reproducible;
- They can work at atmospheric pressure.

For these reasons, dielectric barrier discharge (DBD) is the configuration most widely used in the literature.

A schematic representation of a DBD reactor is shown below. In particular, in the literature, it is possible to find both a cylindrical DBD configuration [49,56] (Figure 1a) and a configuration that involves the use of two plates as electrodes (Figure 1b) [57].

Furthermore, data from the literature have reported that specifically for the pretreatment of biomass, the NTP reactor can have two different main configurations: it can be electrode-based or electrodeless; however, it is not always possible to make a clear distinction, as hybrid configurations are also often proposed [58].

This distinction found in the literature is quite interesting since, for each one, it is possible to distinguish specific conditions which can lead to a more or less thorough pretreatment of the biomass, with greater or lesser energy efficiency. In electrode-based configurations, the discharge is initially ignited between two metal electrodes, one of which has a high voltage (HV), while the other is grounded. In this configuration, depending on the gas flow, two types of plasma can be obtained. In particular, if the flow of gas is high, the plasma shoots outward as a plume, typically known as a "jet" or "torch" [58]. This same type of plasma plume can be a non-transferred or transferred plasma jet. In non-transferred plasma jets, the electrodes are housed in the main body of the reactor where the plasma jet is started. In the transferred plasma jets, only one electrode (preferably the HV electrode) is housed in the main body of the reactor, while the ground electrode is placed outside, allowing the plume to stretch over a long distance. This distinction allows us to observe that the non-transferred plasma jets operate at lower gas flow rates and voltages than the transferred ones [58]. Furthermore, the non-transferred plasma jets can be used for any raw material, regardless of its characteristics, unlike the transferred ones. However, if energy efficiency is considered, the non-transferred plasma jets can achieve a relatively lower energy efficiency of 40–50%. In contrast, an energy efficiency of 70–80% can be achieved by the transferred plasma jets, which could be further increased. Dielectric barrier discharges (DBD) constitute a special configuration of electrode-based plasma reactors, which (as seen before) mainly operate at low temperatures (and hence are used for delignification and hydrolysis) and at atmospheric pressure [58]. In electrodeless plasma reactors, the plasma is obtained by applying an external electromagnetic field in radio frequencies or microwaves. In particular, injectors of the nozzle type are used, through which the gas is

introduced into the reactor's interior. The plasma is ignited at the edge (tip) of the nozzle, where the field is enhanced. Electrodeless plasma reactors have longer operating times and require less maintenance because of the absence of electrodes. Moreover, with this type of reactor, the forced removal of humidity from the starting biomass is not required. Furthermore, less heat is dissipated into the surrounding environment by radiation and conduction, and plasmas with high energy and a high density of active species are ignited, which is why they are a type of plasma typically used for the treatment of biomass at high temperatures [58].

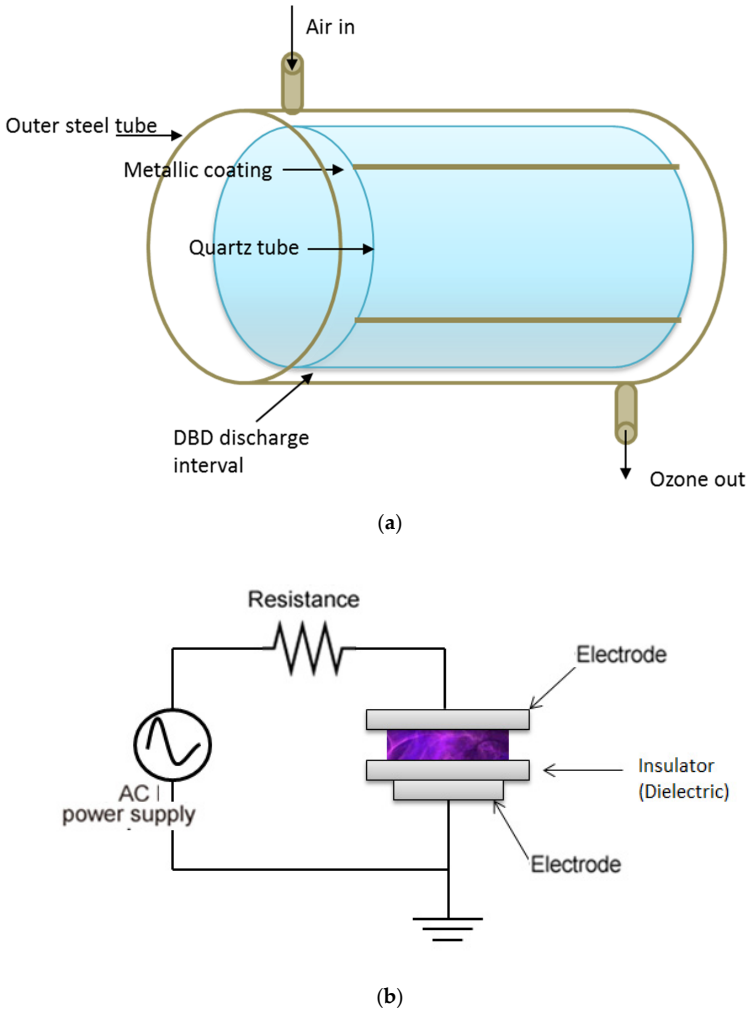


Figure 1. Typical configuration of a DBD reactor: (**a**) cylindrical configuration and (**b**) plate electrode configuration.

In addition to the reactor's configuration, the operating conditions in which the plasma is applied also become important for obtaining the best results in all the fields of applications for plasma, including biomass pretreatment. In particular, the type of plasma gas, the treatment time, the gas flow rate, and the applied voltage can influence the operating efficiency. The type of gas used for the process can affect the chemical reactions of the ionized atoms with the exposed surfaces. Studies in the literature have reported that variations in the composition of the gas can generate different ionized species and oxidants which interact with the substrate [59]. Typically, the processing gases used to generate the plasma are air, oxygen, nitrogen, carbon dioxide, argon, and helium, but the ones most commonly used on an industrial level because of their low cost are air, nitrogen, and CO_2. The type of gas influences the types of oxidizing species, and the treatment time also has a significant impact, especially when it comes to the removal of

lignin [60,61]. Therefore, according to the data from the literature, it is possible to state that the modification of cellulosic biomass at the expense of non-thermal plasma seems to be a powerful and important means to improve enzymatic hydrolysis.

4.3. Application of Non-Thermal Plasma in Biorefineries

Although, as is now known from the literature, NTP has interesting applications in different types of fields, lately, some studies have also focused on pretreatment of lignocellulosic biomass using NTP. Figure 2 shows the results obtained using Scopus as a search engine for the period from 2000 to February 2023 for several pretreatments using different keywords. In particular, when a broad search was carried out using the keywords "pretreatment and acid hydrolysis" and "pretreatment and non-thermal plasma", 6173 and 118 results were obtained, respectively (Figure 2A). However, pretreatment can be applied to different kinds of biomasses. Indeed, when a search was carried out using the keywords "lignocellulosic biomass and acid hydrolysis" and "lignocellulosic biomass and non-thermal plasma", 2724 and 11 results were obtained, respectively (Figure 2B). Moreover, pretreatment of lignocellulosic biomass can have different aims (such as extraction of antioxidants, lignin removal, recovery of fermentable sugars, etc.). When a more accurate search was carried out using the keywords "biorefinery and acid hydrolysis" and "biorefinery and non-thermal plasma", 1374 and 4 results were obtained, respectively (Figure 2C). As expected, the more accurate the keywords used, the fewer the results that were obtained. However, it is worth highlighting that for all three different searches (Figure 2A–C), the proportions of the different kinds of pretreatment were constant. In particular, acid hydrolysis pretreatment was characterized by the highest number of scientific papers, followed by steam explosion. Innovative pretreatments such as deep eutectic solvents and non-thermal plasma had the lowest number of articles.

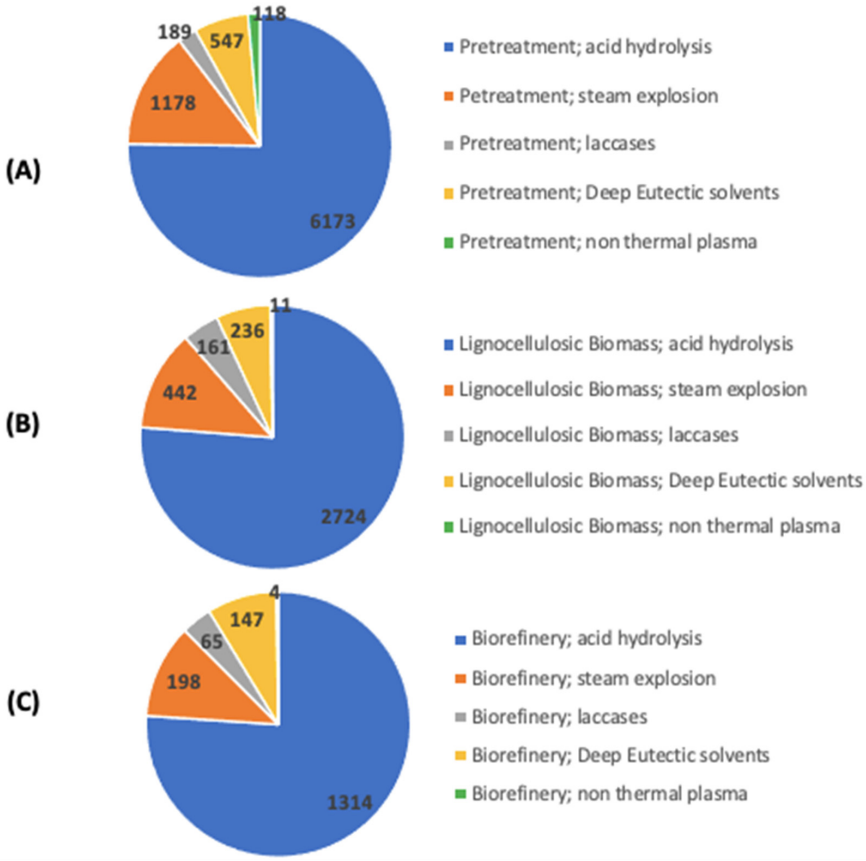


Figure 2. The number of studies in the literature on several biomass pretreatments using different keywords: (**A**) pretreatment; (**B**) lignocellulosic biomass; (**C**) biorefinery.

This result underline the emerging interest in NTP as a pretreatment in biorefining processes [58]. This is because it has the following advantages: easy management, the low cost of treatment, and no waste production [17,47,62]. However, the optimal reactor configuration and the combination of non-thermal plasma with heterogeneous catalysis must be selected to increase the extraction of sugars and to reduce the time and the energy required [63].

4.4. Chemistry of Non-Thermal Plasma Pretreatment

Ozone is highly reactive with compounds that are characterized by conjugated double bonds and functional groups with high electron densities [64]. Lignin contains many carbon–carbon double bounds (C=C), so ozone can oxidize it. In particular, after the oxidation step, hemicellulose and cellulose are released and lignin is degraded in a direct reaction [65,66]. These are defined as "direct reactions", and they are prevalent in ambient conditions with a low pH [67]. As an alternative to direct treatment with ozone, it is possible to exploit the oxidizing potential of hydroxyl radicals and oxygen.

$$O_2 + e^- \rightarrow 2O$$

$$O + O_2 \rightarrow O_3$$

In fact, if water is added to the discharge environment together with the processing gas, the formation of $OH^\bullet$ and $H^\bullet$ radicals is promoted according to the reactions below:

$$H_2O + e^- \rightarrow OH^\circ + H^\circ + e^-$$

$OH^\bullet$ can react with ozone, because of the instability of O_3.

$$O_3 + OH^\circ \rightarrow O_2 + HO_2{}^\circ \; HO_2{}^\circ + HO_2{}^\circ \rightarrow O_2 + H_2O_2$$

Hydrogen peroxide increases the oxidative power of the plasma. In the presence of H_2O_2, more $OH^\bullet$ radicals can be generated by indirect reactions.

$$H_2O_2 + H_2O \leftrightarrow H_3O^- + HO_{2^-} \; O_3 + HO_{2^-} \rightarrow O_{2^-} + OH^\circ + O_2{}^\circ$$

These are "non-direct" reactions and are prevalent in a basic environment (with a high pH value). In particular, hydroxyl groups lead to the breaking of the bonds between the subunits of phenylpropane of which the lignin is composed, leading to the gradual degradation of this in the lignocellulosic biomass [68].

When air (or an oxygen–air mixture) is used as the processing gas for non-thermal plasma, reactive oxygen species and reactive nitrogen species are formed according to the following equation:

$$N_2 + e^- \rightarrow N^\circ + N^\circ \; N_2 + O \rightarrow NO^\circ + N^\circ$$

$$NO^\circ + O^\circ \rightarrow NO_2$$

In the presence of water, $NO_2{}^-$, $OH^\bullet$, and $H^\bullet$ are generated, as reported below [69]:

$$H_2O + e^- \rightarrow H^\circ + OH^\circ + e^-$$

$$2NO_2 + H_2O \leftrightarrow 2NO_{2^-} + NO_{3^-} + 2H^+$$

From the secondary nitrogen and oxygen species, other species are produced [69]:

$$NO_{2^-} + H_3O^+ + H_2O_2 \rightarrow ONOOH + H_2O_2$$

$$ONOOH + H_2O \leftrightarrow ONOO^- + H_3O^+$$

$$ONOOH \rightarrow HNO_3$$

A schematic of the possible degradation mechanism that considers the previous equations and the described phenomena is given in Figure 3.

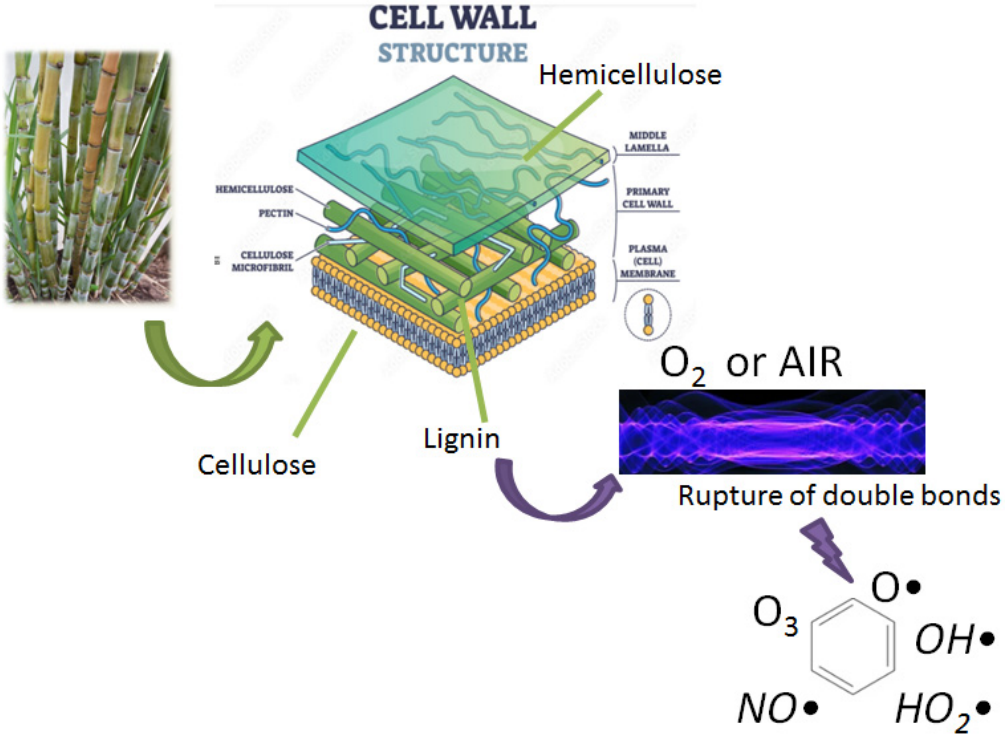


Figure 3. A possible degradation mechanism of lignocellulosic biomass using NTP.

However, some studies have indicated that an environment with a low pH leads to reduced plasma-induced lignin efficiency. This is attributed to the formation and accumulation of strong acids, such as nitric acids, nitrous acid, and other carboxylic acids [70] In any case, what types of biomass can be pretreated with non-thermal plasma? In the literature, the biomasses explored for the non-thermal plasma technique include wheat straw [61], spent coffee waste [71], sugarcane bagasse [43], waste grain from breweries [72], and *Miscanthus* grass [73]. It is interesting to consider that after the NTP pretreatment, acid or enzymatic hydrolysis was applied for the release of sugars. In the following, the main results in terms of lignin degradation and sugar release are described (Table 3).

Schultz-Jensen and co-workers [61] studied the potential of wheat straw for bioethanol production after non-thermal plasma pretreatment. Non-thermal plasma was produced by a barrier discharge reactor. In total, 20 g of glucose/100g of biomass and 76 g of glucose/100 g of biomass were obtained after subsequent enzymatic and acid hydrolysis, respectively. Ravindran et al. [71,72] evaluated the application of a non-thermal plasma treatment to spent coffee waste. In this study, a dielectric barrier discharge reactor was used to produce non-thermal plasma. A reducing sugar yield of 268.8 mg g^{-1} of pretreated spent coffee waste was obtained after enzymatic hydrolysis. Miranda and co-workers [43] obtained a sugar extraction yield of about 26% when sugarcane bagasse was treated with NTP technology followed by enzymatic hydrolysis, carried out with Accellerase 1500 from Genencor. As reported in Table 3, similar results were achieved by Wright et al. [73] when *Miscanthus* grass was treated with NTP, followed by enzymatic hydrolysis using CellicCTec2. When brewery waste grain was pretreated by submerged dielectric barrier discharge (DBD), followed by enzymatic hydrolysis, a 2.14-fold increase in sugar yield was obtained by Ravindran et al. [72]. Other studied concerning the pretreatment of lignocellulosic biomass are present in the literature. These articles have not been mentioned specifically in the table, as the results highlighted in Table 3 were not present in all of them.

However, in order to give a more complete overview of the literature concerning NTP as a pretreatment, the results reported in the more recent works have been indicated below.

Table 3. Non-thermal plasma as a biomass pretreatment in a biorefinery plant.

Substrate	Non-Thermal Plasma	Sequential Pretreatments		Main Results	References
		Acid Hydrolysis	Enzymatic Hydrolysis		
Wheat straw	The dielectric barrier discharge was driven by an alternating current (AC) power supply (adjustable between 10 and 40 kHz). The frequency was set to 18.4 kHz	-	The enzymatic activity of Celluclast was 108 filter paper units (FPU) per cubic centimeter Enzymatic conversion of plasma-pretreated solids (not washed and washed) was performed	The amount of glucose that was released was between 20 g/100 g (6 h of enzymatic hydrolysis of samples that had been pretreated for 1 h) and 30 g/100 g (48 h of enzymatic hydrolysis of samples that had been pretreated for 7 h).	[61]
Wheat straw	The dielectric barrier discharge was driven by an alternating current (AC) power supply (adjustable between 10 and 40 kHz). The frequency was set to 18.4 kHz	Dried and milled samples (160 mg) were treated with 72% (*w*/*w*) H_2SO_4 (1.5 mL) at 30 °C	-	Dried and milled samples (160 mg) were treated with 72% (*w*/*w*) H_2SO_4 (1.5 mL) at 30 °C	[61]
Spent coffee waste	Pre-treatment was performed in a dielectric barrier discharge plasma reactor. The coffee waste samples were subjected to non-thermal plasma in triplicate for 2 min, 4 min, and 6 min at three discrete voltages of 60 kV, 70 kV, and 80 kV	-	Cellulose enzymes with an enzyme activity of 77 FPU/mL were used	268.68 mg of reducing sugar/g of spent coffee waste were obtained after 80 kV and 4 min of NTP pre-treatment	[71]
Sugarcane bagasse	The reactor consisted of a glass container and a Teflon cover supporting four electrodes. The reactor was powered by an alternating high-voltage power supply (14 kV), with frequency of 60 Hz and current of 30 mA	-	The enzymatic cocktail used in the experiments was a commercial cellulolytic enzyme complex (Accelerase 1500, Genencor, CA, USA)	Sugar extraction yields were around 13%.	[43]
Wasted grain brewer	Pretreatment was performed in a submerged dielectric barrier discharge (DBD) plasma reactor. Three voltages (22 kV, 25 kV, and 28 kV) were tested for different durations (5, 10, and 15 min)	-	Cellulose and hemicellulose enzymes with an enzyme activity of 77.08 FPU/mL and 72.23 U/mL. respectively, were used.	162.9 mg of reducing sugars/g of biomass were obtained after NTP pre-treatment at 28 kV for 10 min	[72]
Miscanthus grass	The reactor incorporated a DBD plasma module which consisted of two electrodes. The electrical discharge was driven by a custom-built full-bridge resonant power supply that delivered a sinusoidal voltage of 16.4 kVRMS at 21.2 kHz	-	7.5–30 filter paper units (FPU)/g glucan of Cellic CTec2 cellulase and 100 U/g of SEB xylanase (Advanced Enzymes technology LTD) were used	26% of sugar was released after 3 h	[73]
Ball-milled wooden lignin (MWL) derived from corncobs and poplar	Atmospheric dielectric barrier discharge (DBD) plasma (air was the feed gas), 4.5 kW				[16]

Cao et al. reported the use of a plasma pretreatment for ball-milled wooden lignin (MWL) derived from corncobs and poplar. In particular, they used a DBD reactor in which air was the feed gas. The parameters of the plasma process applied were adjusted to 4.5 kW and 8 m·min^{-1}. The width of the plasma generator was 20 cm, and the plasma treatment was administered for 1.5 s. The plasma treatment led to evident oxidation of lignin, which may have improved the wettability of lignocellulose and the subsequent efficiency of enzymatic hydrolysis. In this work, the authors also performed a DFT analysis which showed that the oxygen atoms in the aliphatic substructures of lignin were the most likely potential reaction sites [16].

Gao et al. studied plasma electrolysis as pretreatment method for water hyacinth (WH). The biomass samples were added to 100 mL of the electrolyte solutions, and the conductivity of the electrolyte solutions was controlled by the concentration of the electrolytes. DC voltage was applied across the electrodes. Enzymatic hydrolysis was routinely performed using 20 mg of the biomass samples in 30 mL of a 50 mM acetate buffer (pH = 4.8), a Celluclast coating, and b-glucosidase at 50 °C, with shaking at 160 rpm. The effects of the pretreatment conditions, including the electrolyte, conductivity, voltage, and discharge time, on the sugar yield of pretreated WH were investigated. Considering the disruption of Cl^- for the inter- and intra-molecular hydrogen bonds in cellulose, the electrolytes used were HCl, NaCl, KCl, $FeCl_2$, and $FeCl_3$. In fact, the electrolyte influenced the yield of sugars produced after the pretreatment. In particular, the electrolyte solutions containing Fe^{2+} or Fe^{3+} resulted in a Fenton oxidation process that utilized the reaction of Fe^{2+}/Fe^{3+} and H_2O_2 to generate more $OH^{\bullet}$. Thus, the maximum sugar yield was obtained from $FeCl_3$, the second-best electrolyte was $FeCl_2$, and the lowest sugar yield was observed when NaCl or KCl was used [12].

Lusi et al. presented a simple method of producing a high yield of levoglucosan from cellulose without using catalysts, chemicals, solvents, or a vacuum, but using a plasma treatment to control the mechanism of cellulose depolymerization. The cellulose was first pretreated in a dielectric barrier discharge reactor (the AC power conditions during the pretreatments were f = 2 kHz and V = 17.5 kV) operating in air or argon for 10–60 s, followed by pyrolysis at 350–450 °C to yield up to 78.6% levoglucosan. Without the plasma pretreatment, the maximum yield of levoglucosan achieved by pyrolysis of cellulose was 58.2%. In detail, the plasma pretreatment led to homolytic cleavage of the glycosidic bonds [13].

As shown in Table 3 and in the other cited studies, when NTP technology was used to extract fermentable sugars from lignocellulosic biomasses, results comparable with the one obtained by traditional pretreatments were obtained. On one hand, the collected studies reported promising results; on the other hand, only a few studies have investigated the use of NTP to extract fermentable sugars. NTP technology presents the advantage of being non-toxic and non-polluting compared with other traditional methods of pretreatment [17], and it is also an effective method for the extraction of lignin.

More studies are needed to optimize the NTP technology and make it a sustainable alternative for pretreating biomass in a biorefining process.

5. Conclusions

After non-thermal plasma pretreatment of lignocellulosic biomass, the values of lignin degradation and sugar release are comparable with the results reported for traditional pretreatments. Moreover, this emerging technology is characterized by several advantages such as a short processing time, mild processing conditions, no chemical waste production, and no generation of fermentation inhibitors.

6. Challenges and Future Perspectives

Currently, when we talk about the treatment of biomass with plasma systems, only those processes involving the use of thermal plasma have been considered on an industrial scale. Non-thermal plasma reactors are still under development, with laboratory or pilot scale installations available at present. Therefore, data on the biomass using non-thermal plasma are relatively scarce in the literature. Unraveling the critical aspects of the process is challenging. Future studies are needed to better understand and evaluate the technology. In particular, working on model compounds could be crucial to first understand the functioning mechanisms and the role of the oxidizing species, which is very complex to interpret in the case of real biomass samples. This is because the composition of the biomass itself can be highly variable. For the low-temperature conversion of lignocellulosic biomass, plasma technology at atmospheric pressure has been mainly proposed as a pretreatment method to enable delignification and promote subsequent acid-catalyzed or enzymatic

hydrolysis towards increased sugar production [58]. From the results reported in this review and the data in the literature, it has emerged that DBD reactors are the most popular plasma pretreatment reactors. In these reactors, the reactive species mechanism involves the degradation of lignin and disruption of the crystalline structure of cellulose, thus improving the accessibility to catalysts and enzymes, and cleaving the ether bonds in all biopolymers, leading to processable products with a lower molecular weight [58]. In air plasma treatments, the interaction of nitrogen oxides with water leads to acidification, which, in turn, intensifies the acid-catalyzed hydrolysis. In any case, through an evaluation of what is reported in the scientific literature, it emerges that more theoretical/modeling studies are certainly needed, but technical insights are also needed to integrate NTP reactors into modern biorefineries. In particular, the challenges that need to be faced to ensure the scale-up of NTP reactors certainly concern the energy efficiency of this process. This means that we need to consider various aspects ranging from the ability to estimate the energy losses to the ability to regulate the production of oxidizing species in order to regulate the energy demand needed to treat a specific type of biomass. Furthermore, it would be advisable to integrate the experimental data with detailed models of the reactors, which would allow researchers to predict and optimize the heat transport and gas–liquid flow. Therefore, the challenge for the future is to make NTP pre-treatment scalable to an industrial level. For this reason, further studies focusing on this emerging technology are awaited.

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